THE PROCESSING OF DOUBLE REFRACTORY GOLD ORE:
TREATMENT OF ALKALINE POX FEED AND ALKALINE POX
DISCHARGE

By

Sugyeong Lee

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Abstract

This study examined a refractory gold ore containing carbonaceous matter (C-matter) and sulfide minerals from Barrick’s Goldstrike plant; gold is recovered from the ore using pressure oxidation (POX) followed by thiosulfate gold leaching. However, gold recovery is insufficient using the current process, leading to the investigation of poor recovery and possible solutions. Part I and Part II aimed to solve the problem of low gold recovery by taking a divergent approach: Part I determined that the low gold recovery from the alkaline POX discharge was mainly attributed to finely locked gold in the ore. For improved gold liberation and higher gold recovery, treatments were performed: 1) mechanical activation (MA) improved the gold recovery from 59% to 72% as P80 size decreased from 56.5 to 8.54 μm, 2) acid dissolution resulted in an improvement of gold recovery from 59% up to 66% using H2SO4. Part I concluded that the complexity of the ore cannot be fully overcome by the treatments, which motivated the study of pre-treating the ore using flotation to separate C-matter. Part II investigated flotation before POX to produce a C-matter concentrate and a tailings: the C-matter concentrate could be processed in Goldstrike’s roaster, while the tailings could be sent to the alkaline autoclave. Improved gold liberation and higher gold recovery were expected due to the higher efficiency of the roasting process in the treatment of carbonaceous material. Multi-stage flotation using kerosene and MIBC (Methyl isobutyl carbino) resulted in 70% C-matter recovery and C-matter concentrate grade of 4% using a rougher-scavenger-cleaner flotation circuit. A reagent study demonstrated that 1) higher doses of MIBC increased the flotation rate and reduced the entrainment of gangue minerals, and 2) a kerosene emulsion resulted in higher recovery and faster flotation kinetics than normal kerosene and showed better performance than transformer oil, a novel collector. With the flotation, the overall gold recovery increased from 44% to 60% based on Barrick’s geo-estimation models. Ultimately, this work demonstrated that the main cause of poor performance in thiosulfate gold leaching and flotation was the highly complex nature of Goldstrike’s ore, with very poor liberation of host minerals.
Co-Authorship

All of the work in this study was written by myself, Sugyeong Lee, and I am the primary investigator, the author of all manuscripts, and the performer of all experiments and analysis. Dr. Ahmad Ghahreman and Dr. Farzaneh Sadri contributed to the published articles in Part I as co-authors. The articles in part II were mainly carried out with Dr. Ahmad Ghahreman and Dr. Charlotte Gibson as co-authors and Andrew Borschneck (a 4th year mining engineering undergraduate student) participated in one study. All studies were conducted under the guidance of Dr. Ahmad Ghahreman and Dr. Charlotte Gibson.
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Chapter 1

Introduction

1.1 Gold production

Gold is one of the most valuable metals, which has been widely used since its discovery (Habashi, 2016). Initially, gold was produced by panning, amalgamation, or chlorination until the invention of cyanidation which resulted in a huge increase in gold production in the 1880s (Habashi, 2005 & 2006; Hilson & Monhemius, 2006; Habashi 2016). After this development, cyanidation led gold extraction in the industry due to its excellent performance. However, cyanidation creates environmental and safety issues; hydrogen cyanide and other cyano-compounds are toxic, and the cyanide remaining in waste solution also affects the environment by converting to produce toxic gas of HCN (Donato et al., 2007). In addition to posing environmental issues, cyanidation also suffers from insufficient gold recovery when used to treat refractory gold ores. Refractory gold ores are defined as ores that result in less than 90% gold recovery by direct cyanidation (Fraser et al., 1991; La Brooy et al., 1994).

As the high-grade gold ore has been exhausted, gold extraction from low-grade and refractory gold ores has become increasingly important. This has led to the development of pretreatment methods and alternative lixiviants to process refractory gold ores (Haque, 1987; Prasad et al., 1991). Gold from free milling ores is extracted directly by conventional gold cyanidation, while refractory gold ores are treated by different methods with or without the pretreatment depending on their refactoriness (Haque, 1987). However, gold recovery with the treatment varies depending on ore properties.

Pretreatment methods are roasting, flotation, chemical oxidation, bio-oxidation, and ultrafine grinding (Afenya, 1991; Corrans & Angove, 1991; Fraser et al., 1991). Pretreatment is performed to liberate gold from the ores or remove the problematic materials prior to gold leaching to allow for sufficient gold
recovery. Instead of applying pretreatment, an alternative lixiviant can be used for leaching from refractory gold ores. There are several factors that are considered in assessing the alternative lixiviant to replace cyanide: such as cost, recyclability, selectivity, toxicity, and compatibility with the downstream recovery process (Hilson & Monhemius, 2006). To date researchers have identified and studied various alternative lixiviants, including thiourea, thiosulfate, thiocyanate, ammonia, and halide (Aylmore, 2016).

1.2 Problem statement

Barrick Gold Corp. mines double refractory gold ores from the Goldstrike mine, NV, USA, which contain sulfide and carbonaceous matter (C-matter). Some gold which is locked in the sulfide and C-matter has a preg-robbing effect. To treat these refractory gold ores, Barrick operates a process that includes pressure oxidation (POX) followed by thiosulfate gold leaching with the Resin in Leach (RIL) process (Baron et al., 2016). The POX process oxidizes the sulfide mineral to liberate gold and it is reported that thiosulfate leaching has the benefit of no preg-robbing effect from C-matter compared with cyanide (Schmitz et al., 2001; Sitando et al., 2019). Two POX facilities are operating in the Goldstrike plant: one is run under acidic condition (pH < 3) for high carbonate content ores (CO$_3^{2-}$>10%) and the other is operated under alkaline condition (pH: 7-8) for low carbonate content ores. The ore with high carbonate content is sent to the alkaline autoclave due to its tendency to consume large amounts of acid when treated under acidic conditions; the dissolution of carbonate minerals consumes the acid required for sulfide oxidation and reduces the oxygen pressure by the produced CO$_2$ gas (Thomas & Pearson, 2016).

However, the ore treated by the alkaline POX process, called “alkaline POX discharge”, has suffered from insufficient gold recovery from Barrick’s thiosulfate leaching plant. In general, the alkaline POX results in lower gold recovery than the acidic POX (Thomas & Pearson, 2016). One potential reason for this is iron oxide passivation. During alkaline POX process, the insoluble metal oxide or hydroxide precipitates on the surface of the gold, covering the gold surface, impeding the contact of leaching lixiviant
with the gold (Koslides & Ciminelli, 1992; Hiskey & Sanchez, 1995; Thomas & Pearson, 2016). Further, the iron oxide precipitation during the POX process could cover sulfide minerals, preventing further sulfide oxidation and trapping gold in the unoxidized sulfide matrix, preventing its extraction in the leaching stage. Pangum and Browner (1996) demonstrated that decreasing sulfide oxidation in the POX process results in a higher residual gold concentration in the tailings. Sulfide oxidation between 90% and 100% results in less than 0.5 g t\(^{-1}\) gold in the tailings; it increases to 3.5-4 g t\(^{-1}\) when sulfide oxidation drops to 0-20%, corresponding to major recovery losses. In Barrick’s alkaline POX discharge stream, 40% of the sulfides remained unoxidized. Another potential cause of poor recovery from the alkaline POX discharge may be attributed to the natural complexity of the ore, including gold locked in the sulfide matrix and/or finely disseminated gold particles throughout the ore. The different ore properties between alkaline and acidic POX feed may also contribute to differences in leaching efficiency between the alkaline and acidic POX discharges. Finally, issues with the thiosulfate leaching process itself could be another reason for poor gold recovery.

### 1.3 Proposed work

This study was undertaken to address the problem of the low gold recovery from Barrick’s double refractory gold ore: an insufficient gold recovery from the alkaline POX discharge using thiosulfate leaching. The work was divided into two parts to approach the problem, the research was divided into two parts (Figure 1-1). Part I was the study of the alkaline POX discharge and investigated thiosulfate gold leaching. Then, additional pre-treatments of the alkaline POX discharge were performed. In Part II, flotation was applied to the alkaline POX feed to separate the C-matter from the ore, followed by respective treatments on each C-matter concentrate and tailings. Both parts of the study aimed to solve the problem of low gold recovery, ultimately leading to the improvement of overall gold recovery.
1.4 Thesis overview

The study investigated Goldstrike’s current process using the alkaline POX discharge in Part I and investigated a modification to Goldstrike’s current process, using the alkaline POX feed in Part II. To put this research in context, the literature review presented in Chapter 2 deals with refractory gold ores, the treatment methods of refractory gold ores, and the thiosulfate gold leaching as one of alternative lixiviants.

The main project is comprised of Part I and Part II; each part contains an introduction, a presentation of the research conducted, and a description of materials in Chapter 3. The project is based on the research papers for the journal publication. Part I describes the alkaline POX discharge with the investigation of thiosulfate gold leaching and pretreatment (Chapters 4-6):

- Chapter 4 investigated leaching factors and the determination of the problem with the thiosulfate gold leaching results and analysis. This study was prepared under the title “A case study on the limited gold recovery from non-ammoniacal thiosulfate leaching of a refractory gold ore oxidized in alkaline pressure conditions”, prepared by Sugyeong Lee, Farzaneh Sadri, and Ahmad Ghahreman.
- Chapter 5 covers the mechanical treatment of the alkaline POX discharge, which was published as a paper in the Journal of Sustainable Metallurgy in 2022. The title of the paper is “Enhanced gold
recovery from alkaline pressure oxidized refractory gold ore after its mechanical activation followed by thiosulfate leaching” written by Sugyeong Lee, Farzaneh Sadri, and Ahmad Ghahreman.

- Chapter 6 contains the application of acid dissolution on the alkaline POX discharge as the chemical treatment process for gold recovery improvement. This study is being prepared for the journal submission.

Then, one brief conclusion of part I follows to finish part I and it leads the study to part II.

Part II describes the concentration of C-matter from the alkaline POX feed using flotation (Chapters 7-9):

- Chapter 7 deals with the multi-stage flotation study, which was the published in Minerals: “The separation of carbonaceous matter from refractory gold ore using multi-stage flotation: A case study” in 2021 by Sugyeong Lee, Charlotte E. Gibson, and Ahmad Ghahreman.

- Chapter 8 describes the role of MIBC as a frother, published as “Flotation of carbonaceous matter from a double refractory gold ore: the effect of MIBC on flotation performance and kinetics” in 2021 at Minerals by Sugyeong Lee, Charlotte E. Gibson, and Ahmad Ghahreman. The journal paper was a revised and expanded version of the conference paper “Role of MIBC on the kinetics of carbonaceous matter flotation from gold ores” presented at the 60th Annual Conference of Metallurgists (COM), Canada, August 17-19 (2021); the author information was same as above.

- Chapter 9 compares the effect of kerosene and transformer oil. The revised version of chapter 9 has been submitted as the title of “Investigation into selective collectors for C-matter flotation from a double refractory gold ore: Transformer oil vs. kerosene” for a journal submission. It was prepared by Sugyeong Lee, Charlotte Gibson, Andrew Borschneck, and Ahmad Ghahreman in 2022.

At the end of the study, the summary, contribution, and recommendations for the whole study are described in Chapter 10.
Chapter 2

Literature review

2.1 Refractory gold ores

As discussed in Section 1.2, gold ores are divided into two major types: (1) free-milling ore, and (2) refractory gold ore (Haque, 1987; La Brooy et al., 1994). High gold recovery can be achieved with conventional gold cyanidation from free-milling ores. However, high gold recovery (>90%) cannot be obtained from refractory gold ores by direct cyanidation without any pretreatment. Depending on gold recovery with cyanidation, the refractoriness of the ore is classified into free milling, mildly, moderately, and highly refractory (Table 2-1).

Table 2-1. Refractory gold ores classification (La Brooy et al., 1994)

<table>
<thead>
<tr>
<th>Refractoriness</th>
<th>Recovery with cyanidation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free milling</td>
<td>&gt; 95</td>
</tr>
<tr>
<td>Mildly refractory</td>
<td>80-90</td>
</tr>
<tr>
<td>Moderately refractory</td>
<td>50-80</td>
</tr>
<tr>
<td>Highly refractory</td>
<td>&lt; 50</td>
</tr>
</tbody>
</table>

The refractoriness of an ore is determined by its properties and the effective treatment varies, depending on the refractoriness and ore mineralogy. Thus, a deep understanding of the ore’s refractoriness is required to choose an appropriate treatment, ultimately to obtain sufficient gold recovery from refractory gold ores.

Three main properties of refractory gold ores are locked gold, complex gold ore, and preg-robbing ore.

2.1.1 Locked gold

Locked gold is either physically or chemically existed in the ores. Physically locked gold is submicroscopic and finely disseminated in the ores, thus cyanide cannot reach the gold without pretreatment
to liberate and expose it (Iglesias & Carranza, 1994). Physically locked gold can be found in sulfides, oxides, or silicate ores (Asamoah et al., 2014). Chemically locked gold is present in the sulfide lattice (Fraser et al., 1991; Asamoah et al., 2014). Common materials containing locked gold are sulfide minerals (pyrite and arsenopyrite) and gold minerals such as tellurides (Vaughan, 2004).

2.1.2 Complex ore

The second characteristic of refractoriness is attributed to the cyanide-consuming or oxygen-consuming materials; this type of ore is referred to as a “complex ore”. Contrary to locked gold, gold in a complex ore can be freely reached by cyanide; however, the gangue minerals in complex ores interrupt the efficient extraction of gold as they become the dominant consumers of the leaching reagent (Vaughan, 2004). Copper is an example of a cyanide-consuming material due to its fast reaction with cyanide, and reactive sulfides are known as both cyanide and oxygen-consuming ores (Rees & Van Deventer, 1999 & 2000). Copper makes a complex with cyanide ion and the cupric ion oxidizes the cyanide ion (CN⁻) to cyanate (CNO⁻), leading to a high consumption of cyanide (La Brooy et al., 1994).

2.1.3 Preg-robbing

Preg-robbing is referred to as the removal of gold complexes from solutions (Miller et al., 2016). The preg-robbing mechanisms can be reversible or irreversible (Goodall et al., 2005); the reversible mechanism is due to a simple ion exchange, while the irreversible one is resulting from the gold complex precipitation. The materials causing the preg-robbing effect are known as C-matter, sulfidic, and clays minerals. The main preg-robbing materials from C-matter are organic compounds and elemental carbon (Afenya, 1991). In organic compounds, the long-chain hydrocarbons have no preg-robbing effect, but organic acids adsorb gold cyanide complexes. Pyke et al. (1999) studied the preg-robbing effect of different C-matters (hydrocarbon, humic acid, graphite, activated carbon, native carbon, and acidified native carbon).
The study demonstrated that native and activated carbon have a high preg-robbing effect, while hydrocarbons and humic acid do not affect gold extraction. Rees and Van Deventer (2000) showed the preg-robbing effect of sulfide in cyanide deficient solution with pyrite and chalcopyrite. Bas et al. (2012) also investigated the preg-robbing effect of sulfidic gold ores, indicating that the copper-containing ore and pyrite ore had only 6.7% and 21.5% gold recoveries by cyanidation, respectively. Preg-robbing is also observed in some conditions of thiosulfate leaching with sulfide. Feng and Van Deventer (2001) showed that in thiosulfate deficient solution, chalcopyrite had the highest preg-robbing effect, followed by pyrite and arsenopyrite; furthermore, the preg-robbing phenomenon is magnified at higher gold concentrations and with finer particle sizes. The preg-robbing effect with clays is attributed to the ion exchange to adsorb gold and/or silver (Tremolada et al., 2010).

2.2 Treatment methods of refractory gold ores

Gold extraction from refractory gold ores requires a pretreatment method to achieve high gold recovery. Different techniques are applied to refractory gold ores such as roasting, flotation, oxidation, and ultrafine grinding (Fraser et al., 1991).

2.2.1 Roasting

Roasting is one of conventional processes used to treat refractory gold ores. It decomposes both sulfidic materials and C-matter, leading to the liberation of gold and/or eliminating the preg-robbing effect. The main roasting reactions of sulfide minerals (pyrite and arsenopyrite; the representative sulfidic ores related to gold and expected to be in the studied ore), and C-matter are (Komnitsas & Pooley, 1989):

\[
3\text{FeS}_2 + 8\text{O}_2 = \text{Fe}_3\text{O}_4 + 6\text{SO}_2↑ \tag{2-1}
\]

\[
12\text{FeAsS} + 29\text{O}_2 = 4\text{Fe}_3\text{O}_4 + 3\text{As}_4\text{O}_6↑ + 12\text{SO}_2↑ \tag{2-2}
\]
$$2\text{Fe}_3\text{O}_4 + 0.5\text{O}_2 = 3\text{Fe}_2\text{O}_3$$

$$\text{C} + \text{O}_2 = \text{CO}_2 \uparrow$$

The roasting of the sulfide results in iron oxide and it emits sulfur dioxide gas. The Fe$_3$O$_4$ produced reacts with oxygen and converts to Fe$_2$O$_3$. The product of calcine from roasting consists of maghemite or hematite (Paktunc et al., 2006). The C-matter is oxidized to carbon dioxide gas.

Roasting of sulfidic and carbonaceous sulfidic ores increases gold recovery up to 92% with cyanidation under the optimum roasting conditions from less than 15% of gold recovery without roasting (Fernandez et al., 2000). Another study investigated the effect of roasting on thiourea leaching. In the first stage of roasting, most of the arsenic was removed, after the second stage of roasting, 97% of sulfur was removed and 84% of gold was liberated, leading to 14% and 98% with thiourea leaching as the lowest and the highest gold recovery, respectively (Qin et al., 2021). Jin et al. (2019) studied the phase and structural changes of carbonaceous gold ores during roasting at 400-850°C, concluding that C-matter, sulfide, carbonate, and clays were decomposed, and the preg-robbing effect was reduced by roasting. The gas produced by oxidation makes more pores and cracks in the mineral particles which results in a faster leaching rate. However, over-roasting can lead to the secondary encapsulation of gold, resulting in reduced gold recovery. It was reported that the roasting at high temperature produces less porous iron oxide through fast growth and crystallization (Fernandez et al., 2000). Also, it leads to a smaller surface area, total pore volume, and average pore diameter which has a detrimental effect on the gold leaching rate.

Microwave roasting also has been considered as the refractory gold ore treatment technique by Nanthakumar et al. (2007) and Amankwah and Pickles (2009). In the first study, microwave roasting resulted in the oxidation of pyrite and C-matter, and carbonate decomposition. Using magnetite as a susceptor, microwave roasting reduced the preg-robbing effect, resulting in 98% gold recovery with cyanidation. The second study presented similar results, indicating that carbon and sulfur were oxidized, and the locked gold was liberated by roasting. In another study by Amankwah and Ofori-Sarpong (2020),
a flotation concentrate containing pyrite, arsenopyrite, and C-matter was roasted by microwaves followed by cyanidation. The microwaved sample showed the highest recovery (95.6%), while the samples heated at 650°C and 750°C by conventional heating showed 84% and 91% gold recoveries, respectively. Microwave treatment followed by thiosulfate leaching was explored in two studies: (1) The gold extraction improved at higher roasting temperatures; elevating the temperature from 300 to 500°C increased the gold recovery from 74.4% and 75.0% to 88.5% and 90.2% after 10 and 30 minutes of roasting, respectively (Wang et al., 2019); and (2) Microwave treatment was performed followed by copper-citrate-thiosulfate leaching (Wang et al., 2020a). The as-received sample exhibited a leaching efficiency of less than 70% but increased to 90% after microwave roasting at 500°C for 30 minutes. Furthermore, the thiosulfate consumption rate was reduced by increasing the roasting time and temperature, resulting from decreasing the sulfur content by microwave oxidation. Regardless of the roasting process (conventional or microwave), roasting of refractory gold ores improves gold recovery with various leaching lixivants.

2.2.2 Flotation

As an efficient method to improve gold recovery, flotation has been considered for pre-concentrating gold or separating the problematic materials from refractory gold ores (O’Connor & Dunne, 1994). Gold, sulfide minerals, or C-matter are the materials typically concentrated by flotation from gold ores. Gold is easily floated when it is well-liberated from the other gangue in the ore. Forrest et al. (2001) showed that selective gold flotation can be achieved at pH values above 11.5 and moderate dosages of the collector (Aerofloat 7249: 30 g t⁻¹), and particle size of P90 at 106 µm. The bulk flotation of sulfidic ores improves gold recovery to 90% with the reduction of arsenic and antimony (Badri & Zamankhan, 2013; Faraz et al., 2014). Murthy et al. (2003) studied sulfidic gold ore flotation, indicating that gold was concentrated from 1.4 g t⁻¹ to 6.1 g t⁻¹ with 75.6% of gold recovery which is a significant economical enhancement. The gold recovery from this concentrate increased to 74% by the POX process and thiourea leaching. Using flotation, C-matter having low gold contents can be separated, then discarded; C-matter
possessing high gold concentration can be enriched, then can be sent to roaster for oxidation of C-matter followed by cyanidation (Afenya, 1991; Fraser et al., 1991). Yang et al. (2015) studied the flotation of refractory gold ore followed by roasting and leaching. Before flotation, the gold recovery was only 12.9% due to the preg-robbing effect, while flotation enriched the gold to 29.7 g t\(^{-1}\) and a gold recovery of 93.66% was achieved by roasting followed by cyanidation.

### 2.2.3 Pressure Oxidation

The POX process can be conducted under acidic and alkaline conditions. Ores containing a low amount of carbonate minerals are typically treated by acidic POX. The few carbonates present in the ore are dissolved by the acidulation process with H\(_2\)SO\(_4\) before the acidic POX process. During the acidic POX process, the heat generated from sulfide oxidation can promote the reaction. The acidic POX is conducted under 170-225\(^\circ\)C with dissolved oxygen (La Brooy et al., 1994; Marsden & House, 2006). The main reactions of sulfide oxidation are:

\[
\begin{align*}
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \\
4\text{FeAsS} + 11\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{HAsO}_2 + 4\text{FeSO}_4 \\
4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{O}_2 & \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}
\end{align*}
\]

\[\text{(2-5)}\]
\[\text{(2-6)}\]
\[\text{(2-7)}\]

\[
2\text{HAsO}_2 + \text{Fe}_2(\text{SO}_4)_3 + \text{O}_2 + 2\text{H}_2\text{O} = 2\text{FeAsO}_4 + 3\text{H}_2\text{SO}_4
\]

\[\text{(2-8)}\]

Gudyanga et al. (1999) used acidic POX to treat refractory gold ore concentrates which had exhibited 75% gold recovery by roasting followed by cyanidation. In this study, the POX process at 180\(^\circ\)C, 15 bars of O\(_2\) partial pressure for 2 h improved gold recovery to over 90% with cyanidation but silver recovery was reduced. The reduction of silver recovery was attributed to the formation of jarosite during the acidic POX process. For the treatment of gold in arsenopyrite and pyrrhotite, acidic POX was conducted at 180\(^\circ\)C for 3 h (Lehmann et al., 2000). This treatment resulted in a maximum of 75% sulfide
decomposition and 79% gold recovery after 10 h cyanidation, which is 15-20% higher than non-treated concentrate. Ammoniacal thiosulfate gold leaching showed a high gold recovery of 89% from the pressure oxidized gold concentrate (Lampinen et al., 2015).

Alkaline POX is used to treat ores with high content of carbonate (> 10%) and low sulfur (< 2%) (La Brooy et al., 1994). It is performed under similar conditions to acidic POX, except the pH is neutral or alkaline (Marsden & House, 2006). The main reactions are:

\[
\begin{align*}
4\text{FeS}_2 + 15\text{O}_2 + 14\text{H}_2\text{O} & = 4\text{Fe(OH)}_3 + 16\text{H}^+ + 8\text{SO}_4^{2-} \quad (2-9) \\
4\text{Fe}_7\text{S}_8 + 69\text{O}_2 + 74\text{H}_2\text{O} & = 28\text{Fe(OH)}_3 + 64\text{H}^+ + 32\text{SO}_4^{2-} \quad (2-10) \\
2\text{FeAsS} + 7\text{O}_2 + 8\text{H}_2\text{O} & = 2\text{Fe(OH)}_3 + 2\text{Fe(OH)}_3 + 2\text{H}_3\text{AsO}_4 + 4\text{H}^+ + 2\text{SO}_4^{2-} \quad (2-11) \\
4\text{CuFeS}_2 + 17\text{O}_2 + 18\text{H}_2\text{O} & = 4\text{Cu(OH)}_2 + 4\text{Fe(OH)}_3 + 16\text{H}^+ + 8\text{SO}_4^{2-} \quad (2-12)
\end{align*}
\]

Contrary to the acidic POX process, the metal oxide or hydroxide produced during the alkaline POX process is insoluble, resulting in its precipitation on the surface. This precipitation could interfere with the sulfide oxidation process and gold leaching. Koslides and Ciminelli (1992) demonstrated that the oxide coating covers the sulfide particles at high pH values, and thin and dense oxides are precipitated under neutral conditions. In one investigation by Hiskey and Sanchez (1995), gold-bearing arsenopyrite concentrate was oxidized by alkaline POX, resulting in 98% sulfur oxidation along with 86% arsenic and 82% gold dissolution. With the same degree of sulfur oxidation, gold recovery after alkaline POX treatment was shown to be lower than acidic POX, due to the formation of hematite, arsenate, and sulfate as the by-products of alkaline POX.

### 2.2.4 Ultrafine grinding

Ultrafine grinding is considered as an alternative method for the liberation of refractory gold ores. Conventional grinding can liberate gold from the ore, while some fine gold particles remain in the ore and
are unaffected by normal grinding. However, further size reduction by ultrafine grinding can expose more gold particles from inside the ore (Ellis, 2003). A study on ultrafine grinding using an Isamill showed that cyanidation recovery of refractory gold ore was significantly improved when the 80% passing size of 10 µm was achieved (Harbort et al., 1998). However, depending on the ore’s mineralogy and contained gold, ultrafine grinding cannot always improve the gold recovery. Corrans and Angove (1991) compared the gold recovery from arsenopyrite and pyrite before and after ultrafine grinding. Arsenopyrite has more affinity for gold compared to pyrite, therefore arsenopyrite possesses a higher gold content. Additionally, the gold recovery varied from 20% to 95%, depending on the nature of the gold contained in the sulfide. One arsenopyrite concentrate showed only 20% gold recovery, even with an ultrafine particle size (Corrans & Angove, 1991). The low recovery was attributed to fine gold particles remaining in the arsenopyrite, despite ultrafine grinding. Ultrafine grinding of pyrite showed a more significant effect on gold leaching recovery, resulting from the coarser gold size in the pyrite as compared to arsenopyrite.

2.3 Thiosulfate gold leaching

2.3.1 Thiosulfate leaching as an alternative lixiviant

Aurocyanide suffers from preg-robbing by C-matter and sulfide, leading to insufficient gold recovery. Applying a pretreatment technique, C-matter can be removed prior to cyanidation by roasting or flotation. However, if the gold ore has several refractory characteristics, multiple stages of treatments are required to reduce the refractoriness by different effective methods. As another method to treat refractory gold ores, several alternative lixiviants for cyanide have been investigated by many researchers, including thiosulfate, thiocyanate, thiourea, and chlorination (Zhang & Senanayake, 2016). Among these, thiosulfate leaching has the advantage of a lowered preg-robbing effect (Grosse et al., 2003; Sitando et al., 2019), while the gold complexes with other lixiviants have shown a high preg-robbing effect in the presence of C-matter. Sitando et al. (2019) demonstrated that without free thiosulfate, gold thiosulfate complex adsorbs on sulfide
minerals and carbon, while its preg-robbing effect is highly reduced by adding free thiosulfate from 0 to 0.2 M. The affinity of ions to activated carbon is in the following order: thiocyanate > thiourea > cyanide >> thiosulfate (Gallagher et al., 1990; Arima et al., 2003). The reason for a low affinity for thiosulfate has not determined clearly, but it may be due to higher negative charge, molecular structure, and the weak interaction between thiosulfate ions and carbon (Miller et al., 2016). With free thiosulfate ions, thiosulfate had no preg-robbing effect on sulfide ores because of the stabilized thiosulfate ion and reversible adsorption of gold (Feng & Van Deventer, 2001). Thus, thiosulfate leaching is a suitable method to treat the double refractory gold ores containing both C-matter and sulfide. It makes a complex with gold; the dissolution of gold in thiosulfate solution proceeds with oxygen as follows:

\[
\begin{align*}
\text{Au} + 2\text{S}_2\text{O}_3^{2-} &= \text{Au(S}_2\text{O}_3)_2^{3-} + e^-; \quad E^0 = 0.153 \text{ (V)} \quad (2-13) \\
2\text{Au} + 4\text{S}_2\text{O}_3^{2-} + 0.5\text{O}_2 + \text{H}_2\text{O} &= 2\text{Au(S}_2\text{O}_3)_2^{3-} + 2\text{OH}^- \quad (2-14)
\end{align*}
\]

However, thiosulfate gold leaching is slow with oxygen, thus a catalyst is required. A widely used catalyst in thiosulfate leaching is cupric ion (Breuer & Jeffrey, 2002). The cupric ion is an effective catalyst for thiosulfate leaching and is used in both ammoniacal thiosulfate and non-ammoniacal thiosulfate leaching systems. It forms a stable complex with ammonia (Equation 2-15) in the ammoniacal system or thiosulfate (Equation 2-16) in a non-ammoniacal system (Senanayake, 2005b; Mohammadi et al., 2017).

\[
\begin{align*}
\text{Cu}^{2+} + 4\text{NH}_3 &= \text{Cu(NH}_3)_4^{2+} \quad (2-15) \\
\text{Cu}^{2+} + 2\text{S}_2\text{O}_3^{2-} &= \text{Cu(S}_2\text{O}_3)_2^{2-} \quad (2-16)
\end{align*}
\]

The stabilized cupric ion in the solution can be used for gold leaching reactions. With copper ions in ammoniacal thiosulfate gold leaching, the overall reaction is as follows:
\[
\text{Au} + \text{Cu(NH}_3\text{)}_4^{2+} + 5\text{S}_2\text{O}_3^{2-} = \text{Au(S}_2\text{O}_3\text{)}_2^{3-} + \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + 4\text{NH}_3
\]  
(2-17)

This overall reaction is a result of the following reactions (Aylmore & Muir, 2001; Jeffrey, 2001):

\[
\text{Au} + \text{Cu(NH}_3\text{)}_4^{2+} = \text{Au(NH}_3\text{)}_2^{+} + \text{Cu(NH}_3\text{)}_2^{+} 
\]  
(2-18)

\[
\text{Au(NH}_3\text{)}_2^{+} + 2\text{S}_2\text{O}_3^{2-} = \text{Au(S}_2\text{O}_3\text{)}_2^{3-} + 2\text{NH}_3 
\]  
(2-19)

\[
\text{Cu(NH}_3\text{)}_2^{+} + 3\text{S}_2\text{O}_3^{2-} = \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + 2\text{NH}_3 
\]  
(2-20)

\[
2\text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + 8\text{NH}_3 + 0.5\text{O}_2 + \text{H}_2\text{O} = 2\text{Cu(NH}_3\text{)}_4^{2+} + 2\text{OH}^- + 6\text{S}_2\text{O}_3^{2-} 
\]  
(2-21)

The reduced cuprous ion is oxidized again to the cupric ion with added oxygen. In the anodic area, gold is oxidized, and in the cathodic area, the cupric ion is reduced. The ammoniacal thiosulfate system makes a more stable complex, leading to lower reagent consumption; however, ammonia also raises environmental issues and a complicated reaction system (Sitando et al., 2018).

### 2.3.2 Ammoniacal thiosulfate system

In the ammoniacal thiosulfate system, ammonia can stabilize copper ions by forming a complex of Cu(NH\text{)}_3)_4^{2+}. However, it is influenced by pH and reagent concentrations (Aylmore & Muir, 2001). At high reagent concentrations, Cu(NH\text{)}_3)_4^{2+} is stable at pH 8-10, while at low reagent concentrations, it has a limited stability between pH. Sitando et al. (2020) demonstrated that gold recovery decreased significantly at pH 12 and the brown precipitate produced at pH 12 was confirmed to be Cu(OH)_2 and CuO by XRD.

Gold recovery is also affected by total NH\text{)}_3 concentration and thiosulfate concentration in the ammoniacal leaching system. Under high and low reagent contents at pH 10, more cupric ion converts from Cu(S\text{}_2\text{O}_3\text{)}_3^{5-} to Cu(NH\text{)}_3)_4^{2+} as the NH\text{)}_3 concentration increases. Furthermore, increasing Cu(NH\text{)}_3)_4^{2+} can reduce the thiosulfate consumption resulting from the formation of tetrathionate (Ha et al., 2010). On the
contrary, increasing thiosulfate concentration leads to the formation of \( \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} \) rather than \( \text{Cu(NH}_3\text{)}_4^{2+} \) (Aylmore & Muir, 2001).

### 2.3.3 Non-ammoniacal thiosulfate leaching

In non-ammoniacal thiosulfate gold leaching systems, the overall reaction occurs as Equation 2-14. Cupric ion is reduced to cuprous with the oxidation of Au. Reduced \( \text{Cu}^+ \) is again oxidized to \( \text{Cu}^{2+} \) by the available oxygen in the solution (Equation 2-22) (Jeffrey et al., 2003).

\[
4\text{Cu}^+ + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{Cu}^{2+} + 4\text{OH}^-
\]  

(2-22)

In the non-ammoniacal thiosulfate leaching system, stable copper species depend on the ratio of copper and thiosulfate (Cui et al., 2011). \( \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} \) is dominant at low ratios of Cu-thiosulfate, while \( \text{Cu(S}_2\text{O}_3\text{)}^{+} \) is the stable species at a high ratio of Cu to thiosulfate. Cupric ion has a positive effect on thiosulfate gold leaching by increasing the kinetics of the leaching process. However, cupric ion can be decomposed at high temperatures, leading to low gold recovery by the formation of \( \text{CuS} \) (Equation 2-23) (Abbruzzese et al., 1995).

\[
\text{Cu}^{2+} + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} = \text{CuS} + \text{SO}_4^{2-} + 2\text{H}^+
\]  

(2-23)

### 2.3.4 Thiosulfate decomposition during leaching

During thiosulfate leaching, thiosulfate converts to other sulfur species (Molleman & Dreisinger, 2002; Xia et al., 2003). It is reported that in the presence of oxygen, thiosulfate consumption increases (Chu et al., 2003; Breuer & Jeffrey, 2003; Senanayake, 2005a). Thiosulfate ions can be decomposed by oxidation, but at the same time, they can also react with other species (Equation 2-24, 25, 26, 27, & 28).
The stability of polythionates is given by the following sequence: \( \text{SO}_4^{2-} > \text{S}_2\text{O}_3^{2-} > \text{S}_3\text{O}_6^{2-} >> \text{S}_4\text{O}_6^{2-} \) and the mechanism of \( \text{S}_2\text{O}_3^{2-} \) decomposition is described in Figure 2-1.

![Figure 2-1. Thiosulfate decomposition route (Xu et al., 2017)](image)

Cupric ion can decompose thiosulfate and convert it to tetrathonate (Breuer & Jeffrey, 2003). To reduce the thiosulfate consumption, sulfite (\( \text{SO}_3^{2-} \)) was considered as the additive. Adding sulfite ions can stabilize thiosulfate ions through the regeneration reactions (Equation 2-29, 30, & 31) (Kerley, 1983). Sulfite reacts with sulfur species and produces thiosulfate again.

\[
\begin{align*}
\text{S}_3\text{O}_6^{2-} + \text{SO}_3^{2-} & = \text{S}_4\text{O}_6^{2-} + \text{S}_2\text{O}_3^{2-} \\
\text{S}_4\text{O}_6^{2-} + \text{SO}_3^{2-} & = \text{S}_2\text{O}_6^{2-} + \text{S}_2\text{O}_3^{2-} \\
2\text{S}^{2-} + 3\text{SO}_3^{2-} + 3\text{H}_2\text{O} & = 2\text{S}_2\text{O}_3^{2-} + 6\text{OH}^- + \text{S}
\end{align*}
\]

2.3.5 The effect of minerals on thiosulfate gold leaching
Alkaline POX discharge consists of various minerals that could affect the thiosulfate leaching process. Thus, investigating the effect of each mineral is necessary to explain the behavior of real ores in thiosulfate leaching. Researchers have investigated the effect of different minerals on thiosulfate leaching.

Understanding the role of sulfide on gold thiosulfate leaching is important as sulfide minerals are one of main sources of gold. Researchers have studied the effects of sulfidic minerals (arsenopyrite, chalcocite, chalcopyrite, galena, pyrrhotite, pyrite, and sphalerite) on thiosulfate gold leaching in an ammoniacal thiosulfate solution (Feng & Van Deventer, 2003 & 2006; Liu et al., 2017). The results indicated that most sulfide minerals negatively impacted thiosulfate leaching, leading to decreasing gold dissolution and increasing thiosulfate consumption. Pyrrhotite promoted gold recovery with increasing gold dissolution rate, but only at low solids concentration. Aylmore et al. (2014) and Sitando et al. (2019) demonstrated the effect of pyrite in gold thiosulfate solution, concluding that gold adsorption on pyrite increases at a higher pyrite concentration; however, the adsorption is reduced when the thiosulfate concentration increases (Feng & Van Deventer, 2001).

Hematite is one of the sulfide oxidation products, so it can appear in gold leaching. Feng and Van Deventer (2007) studied the effect of hematite on thiosulfate leaching in an ammoniacal thiosulfate solution. They assumed that hematite covers gold during the leaching process, leading to reduced gold extraction through the physical barrier. Also, the catalytic effect of hematite hastens the decomposition of thiosulfate (Feng & Van Deventer, 2007). With goethite, gold adsorption increases at lower thiosulfate and higher ammonia concentrations (Sitando et al., 2019). Goethite strongly adsorbs copper ion from the solution, which could be the detrimental effect on gold leaching by reducing cupric ion concentration for gold oxidation (Aylmore et al., 2014).

C-matter is a well-known preg-robbing material for the gold complex (Santiago & Ladeira, 2019). However, gold thiosulfate complex has less prog-robbing characteristics than other lixiviants (Arima et al., 2003; Ofori-Sarpong & Osseo, 2013). The adsorption of gold complex on quartz was recently investigated
(Li et al., 2021). This study used XPS, and SEM analysis and demonstrated that Au(S\textsubscript{2}O\textsubscript{3})\textsuperscript{2-} can physically or chemically adsorb on quartz minerals.

For the extraction of gold, grinding was necessary to achieve the proper particle size for leaching. When grinding with iron media, iron contamination is inevitable. Feng and Van Deventer (2010a) studied the effect of iron contamination on thiosulfate leaching. Iron powder and ferric ions were added in thiosulfate gold leaching and demonstrated that iron reduces both gold extraction and leaching kinetics; metallic iron added into the grinding was found to have a more negative effect than ferric ions. The more detrimental effect of metallic iron than ferric ions is due to the passivation of iron particles on the minerals and/or gold surfaces during grinding (Feng & Van Deventer, 2010a).

2.3.6 The effect of additives on thiosulfate gold leaching

Various additives in thiosulfate leaching have been studied. Sitando et al. (2018) reviewed additives and stated that they often contain carboxylates or amine functional groups, which can make a stable complex with copper or iron. EDTA (Ethylenediaminetetraacetic acid) is one of the organic additives and contains four carboxylic acid and two amine groups. The effect of EDTA as an additive was studied in an ammoniacal thiosulfate system (Aazami et al., 2014). With ammonia, the addition of EDTA increases the gold recovery by forming a complex with copper and reducing copper adsorption. Nie et al. (2019) demonstrated that the addition of EDTA and EN (Ethyleneimine) prevents surface passivation by copper sulfide and polysulfides and the copper complex can be easily reduced. Feng and Van Deventer (2010b) also showed that EDTA increases gold recovery and reduces thiosulfate consumption. However, a high concentration of EDTA had a detrimental effect on gold dissolution due to the complexation of all copper ions for catalyzing with EDTA. It makes a stable cupric ion.

Copper-EN-thiosulfate leaching has been investigated by many researchers. EN can make a stable complex with copper, thus it replaces the ammoniacal system (Deng et al., 2020). EN in thiosulfate gold leaching reacts as follows:
Au + 5S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} + Cu(EN)\textsubscript{2}\textsuperscript{2+} = Au(S\textsubscript{2}O\textsubscript{3})\textsubscript{2}\textsuperscript{3−} + 2EN + Cu(S\textsubscript{2}O\textsubscript{3})\textsubscript{3}\textsuperscript{5−} \quad (2-32)

4Cu(S\textsubscript{2}O\textsubscript{3})\textsubscript{3}\textsuperscript{5−} + 8EN + O\textsubscript{2} + 2H\textsubscript{2}O = 4Cu(EN)\textsubscript{2}\textsuperscript{2+} + 4OH\textsuperscript{−} + 12S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} \quad (2-33)

The produced complex of Cu(EN)\textsubscript{2}\textsuperscript{2+} oxidizes gold, then copper is again oxidized, resulting in the regeneration of Cu(EN)\textsubscript{2}\textsuperscript{2+}. In this system, with a low concentration of EN, gold recovery increases, and thiosulfate consumption decreases (Wang et al., 2019). Additionally, it can occur over a wide range of pH from 7 to 11.

The effect of copper citrate on a thiosulfate leaching system has been investigated without ammonia (Wang et al., 2020a & 2020b). In the copper-citrate-thiosulfate system, the reactions are as follows (Wang et al., 2020a):

\[2 \text{ Au} + 10S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} + \text{Cu}_{2}\text{Cit}_{2}H\textsubscript{2}\textsuperscript{4+} = 2\text{Au}(S\textsubscript{2}O\textsubscript{3})\textsubscript{2}\textsuperscript{3−} + 2\text{Cu}(S\textsubscript{2}O\textsubscript{3})\textsubscript{3}\textsuperscript{5−} + 2\text{CitH}\textsubscript{4}^{+}. \quad (2-34)\]

\[2\text{Cu}(S\textsubscript{2}O\textsubscript{3})\textsubscript{3}\textsuperscript{5−} + 2\text{CitH}\textsubscript{4}^{+} + 0.5O\textsubscript{2} + H\textsubscript{2}O = \text{Cu}_{2}\text{Cit}_{2}H\textsubscript{2}\textsuperscript{4+} + 6S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} + 2OH\textsuperscript{−}. \quad (2-35)\]

Cupric citrate acts as both a catalyst and an oxidant: gold is oxidized by cupric citrate and the formed copper thiosulfate complex will be again converted to cupric citrate, facilitating additional gold leaching. For free milling ores, the copper-citrate-thiosulfate leaching system showed similar results to cyanidation. It is more environmentally friendly and has faster leaching kinetics (Wang et al., 2020b). Leaching of a carbonaceous concentrate resulted in over 70% gold recovery (Wang et al., 2020a). However, copper citrate can be decomposed to CuO or CuS (Equation 2-36 & 2-37) at high copper concentrations, causing low gold recovery.

\[\text{Cu}_{2}\text{Cit}_{2}H\textsubscript{2}\textsuperscript{4+} + 4OH\textsuperscript{−} = 2\text{CuO} + 2\text{CitH}\textsubscript{4}^{+} + 2H\textsubscript{2}O \quad (2-36)\]

\[\text{Cu}_{2}\text{Cit}_{2}H\textsubscript{2}\textsuperscript{4+} + 2S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} + 4OH\textsuperscript{−} = 2\text{CuS} + 2SO\textsubscript{4}^{2−} + 2\text{CitH}\textsubscript{4}^{+} + 2H\textsubscript{2}O \quad (2-37)\]
Similar passivation phenomenon was observed in silver leaching with the ammonia-copper-citrate-thiosulfate system (Puente-Siller et al., 2014 & 2021). A copper sulfide layer is formed on silver sulfide, resulting in 80% silver recovery.

Amino acid is an organic compound containing both amino and carboxyl functional groups. The effect of amino acid was investigated with 4 different types of amino acids (L-valine, glycine, DL-α-alanine, and L-histidin) in thiosulfate leaching (Feng & Van Deventer, 2011). The results indicated that all amino acids increased gold recovery and reduced thiosulfate consumption. This was attributed to the generation of a stable complex with copper ions, preventing the precipitation of copper. As an additive, humic acid in thiosulfate leaching can increase gold recovery, resulting from the reduction in both thiosulfate consumption and passivation of the gold surface (Xu et al., 2017b).

2.4 The commercial thiosulfate gold leaching circuit in Goldstrike

In Barrick’s Goldstrike plant, the double refractory gold ore is treated by the POX process followed by the resin in leach (RIL) process (Figure 2-2). In 2014, the thiosulfate leach circuit successfully replaced the cyanidation leach circuit, making it the first commercial thiosulfate leach plant in the world (Deal et al., 2020). The low carbonate-containing ore enters an autoclave under acidic conditions after the acidulation process by H2SO4 to remove some of the carbonates. On the other hand, the high carbonate ore (> 10% CO32-) is oxidized under alkaline conditions. After POX, the process discharge is neutralized and used for thiosulfate gold leaching under alkaline conditions, then the gold is extracted by the RIL process with calcium thiosulfate. The elution process is conducted for copper, followed by gold elution (Fleming et al., 2003). Eluted gold is precipitated by NaSH (sodium hydrogen sulfide), and the resin is regenerated. The solution from the tailings is processed by reverse osmosis (RO); the thiosulfate can be recycled for the RIL process, and the reagent-free process water can be recycled back to the milling circuit.
Gold deportment analysis was conducted for the acidic POX feed from the mill feed to the lab tails (laboratory scale testing tailings) (Figure 2-3). The mill feed contained only 15% free gold before the POX process. After grinding, acidulation by sulfuric acid and POX were carried out to remove carbonates and oxidize sulfides, respectively. After the POX process, the gold deportment shows that more gold was liberated from the sulfides, resulting in 56% free gold. As the by-product of POX, iron oxide was produced, and 4% gold was locked in the iron oxides. 38% of the gold was detected on the C-matter in the acid POX discharge; gold is adsorbed on the surface of C-matter after being released from oxidized pyrite. Most of the gold was extracted after the RIL process, so that the tailings contained 0.0140 oz t⁻¹ of gold.
The alkaline POX feed contained 18% free gold, and 23% and 26% of the gold content was distributed in free pyrite and disseminated pyrite, respectively (Figure 2-4). After the alkaline POX process, 14% of gold was trapped in iron oxide and 12% of the gold was still disseminated in the pyrite, due to the insufficient oxidation of sulfide in alkaline POX conditions. After the RIL process, 0.459 oz t⁻¹ of gold was left in the tailings from which 64% of unextracted gold was adsorbed on the C-matter. An analysis of surface-bound gold showed that AuCS⁻ and AuSCN⁻ were naturally present in the alkaline POX feed, while the majority of the gold complexes in the alkaline POX discharge were AuO⁻, AuNO⁻, AuCS⁻, AuSCN⁻, and AuS(CN)₂⁻ which were detected on the surface of the C-matter.
From the gold deportment study in Barrick’s report, the surface gold was naturally detected in both the alkaline and acidic POX feed, and this is referred to as “surface gold”. Adams (2016) explained that surface gold is produced by sorption, gold plating, precipitation, and ion exchange; the preg-robbed gold during cyanidation is another example of surface gold. Dimov et al. (2003) demonstrated the presence of surface gold on C-matter by TOF-SIMS and TOF-LIMs analysis. They showed that chloride treatment can increase the amount of gold adsorbed on the C-matter, similar to adsorption on activated carbon. In both alkaline and acidic POX feeds, surface gold was naturally available and the gold species on C-matter changed during the process.

The literature review covered the general information from refractory gold ores to thiosulfate gold leaching. The studied ores are typical of refractory gold ores and have several problematic materials including sulfide, C-matter, and the locked gold. In this study, different treatment processes are examined.
including mechanical activation (MA) and chemical treatment, followed by thiosulfate gold leaching (Chapter 4-6), and carbonaceous matter flotation (Chapter 7-9).
Chapter 3

Part introduction and materials

3.1 Part I: Treatment on alkaline POX discharge

3.1.1 Introduction of part I

In Part I, the alkaline POX discharge was used to investigate the reasons for low gold recovery from the alkaline POX discharge. Part I consisted of three projects which are described in Chapters 4, 5, and 6 (Figure 3-1). In the first step of the study (Chapter 4), the maximum gold recovery was determined by the optimization study following a design of experiments (DOE) practice. Based on the results, the efficacy of each factor was investigated to determine the causes of low gold recovery. Followed by the optimization study, the mineralogical analysis was performed to demonstrate the causes of low gold recovery in Chapter 4. Chapter 5 and Chapter 6 present the treatment process and its effect on the gold recovery. Chapter 5 and Chapter 6 investigate the mechanical and chemical treatment processes, respectively; the treatment techniques were both identified as potential options through the work conducted in Chapter 4. Treatments were aimed to liberate more gold from the alkaline POX discharge. Each chapter includes its own introduction, results, discussion, and conclusion.
3.1.2 Materials of Part I

The POX discharge sample from the Barrick Gold alkaline POX circuit at the Goldstrike mine mainly consisted of quartz, dolomite, and gypsum, as determined by X-ray diffraction analysis (XRD). Additional carbon/sulfur, peroxide fusion, fire assay, and inductively coupled plasma – optical emission spectrometry (ICP-OES) analysis indicated that the sample contained gold, sulfur, and carbon as well as other elements (Table 3-1). Two sample batches were received from Barrick Goldstrike mine (referred to as ‘old’ and ‘new’ based on the order they were received) and their properties were slightly different, as described in Table 3-1. The ‘old’ alkaline POX discharge was used in the study presented in Chapter 5 and the ‘new’ alkaline POX discharge was investigated in the studies presented in Chapters 4 and 6. The detailed analysis of the ore samples is provided in Appendix A (Table A-1&A-2).

<table>
<thead>
<tr>
<th>Element</th>
<th>Ca, %</th>
<th>Mg, %</th>
<th>Fe, %</th>
<th>S, %</th>
<th>C, %</th>
<th>Au, g t⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old</td>
<td>6.38</td>
<td>3.23</td>
<td>1.56</td>
<td>1.26</td>
<td>6.12</td>
<td>2.94</td>
</tr>
<tr>
<td>New</td>
<td>7.70</td>
<td>3.50</td>
<td>1.60</td>
<td>1.79</td>
<td>5.23</td>
<td>3.08</td>
</tr>
</tbody>
</table>

Particle size was measured with a laser particle size analyzer (LPSA) (Malvern, Mastersizer 3000) and specific geometric surface area (S_G) was obtained from the particle size. In laser particle size analysis, the laser diffraction angle is converted to particle size and the particle number is measured by the diffracted beam intensity (Di Stefano et al., 2010). The specific surface area from LPSA is converted from particle size with assumption for some parameters for different materials (Arvaniti et al., 2015). The specific surface area by gas adsorption (S_A) was obtained with a Brunauer-Emmett-Teller (BET) area analyzer (Micromeritics, TriStar 3000). The 80% passing size, S_G, and S_A of the as-received old alkaline POX discharge were 56.5 μm, 1.352 m² g⁻¹, and 9.729 m² g⁻¹, respectively. The new alkaline POX discharge had a passing size of 91 μm.
POX process was carried out to liberate the locked gold inside the host minerals, more specifically the sulfide minerals. Chemical analysis of the alkaline POX discharge sample showed that a large amount of sulfur was removed due to oxidation; however, the issue of complex mineralogy was not fixed by the POX process, as gold was still scattered all over the host minerals (Figure 3-2). Additional TEM micrographs of the alkaline POX discharge sample are added in Appendix A (Figure A-1, A-2, & A-3), depicting the complex mineralogy of the sample under investigation.

![Figure 3-2. TEM images and mapping of the alkaline POX discharge](image)

### 3.2 Part II: Treatment on alkaline POX feed

#### 3.2.1 Introduction of Part II

To improve the overall gold recovery, C-matter flotation was considered as a pretreatment method, with the objective to concentrate the C-matter for treatment at the Goldstrike roaster, rather than by the POX process. The concentrate and tailings of the flotation process will be treated separately, according to Figure 3-3. The C-matter concentrate is treated by the roaster to decompose the C-matter, resulting in high
gold recovery. Flotation tailings will then be the feed for alkaline POX process to liberate gold from the sulfides in the tailings.

![Flowchart of the proposed process for the treatment of refractory gold ore]

**Figure 3-3. The proposed process for the treatment of refractory gold ore**

The proposed process still requires an alkaline POX process for the tailings; however, an increase in total gold recovery is expected by enhancing gold recovery from the C-matter. In Barrick Goldstrike mine, two different facilities are operating depending on the ores properties: one is a roaster followed by carbon in leach (CIL) process and the other one is POX followed by the calcium thiosulfate (CaTS) RIL process. As shown in Figure 3-4, the ore processed by the roaster resulted in higher gold recovery than the alkaline POX discharge in Barrick’s plant. However, the roaster facility in Goldstrike has limited capacity, thus selective flotation of C-matter is required to minimize the presence of other minerals in the flotation concentrate. It is possible that more selective flotation might be achieved with novel reagents, an optimized flowsheet, and/or different operating conditions.
3.2.1.1 Investigation into multi-stage flotation

As a pretreatment method for refractory gold ores, C-matter flotation was investigated with multi-stage flotation by rougher, scavenger, and cleaner stages in Chapter 7. Different dosages of kerosene and MIBC were applied, and one condition was selected by testing in each flotation stage. With the combination of each stage, four circuit designs were suggested, which were a single-stage rougher flotation I, rougher-scavenger flotation (R+S), rougher-scavenger-scavenger cleaner flotation (R+S+SC), and rougher-rougher cleaner-scavenger-scavenger cleaner flotations (R+S+RC+SC). The results demonstrated the need for the multi-stage flotation of C-matter from refractory gold ores to achieve selective separation and suggested the promising potential of C-matter flotation as a pretreatment for efficient gold production.

3.2.1.2 Reagent study I: Frother – MIBC effect on C-matter flotation
In Chapter 8, the effect of MIBC on C-matter flotation was investigated to understand the role of the frother in bubble and froth formation and on flotation kinetics. MIBC dosages between 30 and 150 g t\(^{-1}\) were used in combination with 500 g t\(^{-1}\) of kerosene as a collector. The results of this study explained the role of MIBC in C-matter flotation and can be used as a design basis for scavenger-cleaner flotation testing. Overall, the results show the potential of flotation to improve gold recovery in thiosulfate leaching through the removal of C-matter.

3.2.1.3 Reagent study II: Collector – The conventional and novel collector with emulsion study

In Chapter 9, the effect of conventional and novel collectors was explored on C-matter flotation. Kerosene, which is one of the representative collectors for C-matter flotation, was considered as the conventional collector. Transformer oil was introduced as a novel collector and its effect on C-matter flotation was studied. Collector type, dosage, and emulsification were investigated as effective parameters.

3.2.2 Materials of Part II

The sample used in all the flotation experiments was the ore from the Goldstrike mine. The sample mainly consisted of quartz, dolomite, and minor quantities of pyrite and calcite, as analyzed by XRD (Figure 3-5). Additional analysis was carried out to determine other elemental contents, which were not detected in XRD. Carbon and sulfur (by ELTRA, CS 2000, Haan, Germany), peroxide fusion, fire assay, and ICP-OES analysis indicated that the sample contained gold, sulfur, and carbon as well as other elements (Table 3-2). In addition, the sample contained 252 ppm of As, 347 ppm of Cr, 165 ppm of Mn, 447 ppm of V, and 340 ppm of Zn and minor quantities (<100 ppm) of other elements. More characterization results are presented in Appendix A (Table A-3).
Table 3-2. Elemental composition of the sample ore

<table>
<thead>
<tr>
<th></th>
<th>Al, %</th>
<th>Ba, ppm</th>
<th>Ca, %</th>
<th>Mg, %</th>
<th>Fe, %</th>
<th>K, %</th>
<th>Na, %</th>
<th>P, ppm</th>
<th>Total C (C-matter), %</th>
<th>Total S, %</th>
<th>Au, g t⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.21</td>
<td>926</td>
<td>7.92</td>
<td>3.96</td>
<td>1.32</td>
<td>0.95</td>
<td>0.04</td>
<td>1,000</td>
<td>5.93 (1.95)</td>
<td>1.33</td>
<td>2.14</td>
</tr>
</tbody>
</table>

The ore contained finely disseminated gold throughout the gangue minerals (Figure 3-6). Elemental carbon from both C-matter and carbonates is scattered all over the minerals. Carbon as carbonate (related to Ca and Mg; lower part in figure) is more liberated than C-matter (C element, but not related to Ca and Mg), meaning that C-matter has a poor liberation degree. In addition, some gold is associated with the C-matter; thus, a higher gold recovery is expected by the C-matter decomposition through the roasting process. More TEM analysis graphs are presented in Appendix A (Table A-4, A-5, & A-6).
Figure 3-6. TEM micrographs and elemental mapping of the ore sample (alkaline POX feed)
Part I Treatment on alkaline POX discharge

Chapter 4

An investigation on the limited gold recovery from non-ammoniacal thiosulfate leaching of a refractory gold ore oxidized in alkaline pressure conditions

4.1 Introduction

Cyanidation is the conventional method to recover gold from ores; however, the cyanidation process for refractory gold ores results in insufficient gold leaching rate and recovery. Refractory gold ores are referred to as the ores containing preg-robbing matter (e.g., C-matter), encapsulated gold in sulfides and/or silicates, and cyanide-/oxygen-consuming materials (Komnitsas & Pooley, 1989; La Brooy et al., 1994; Chen et al., 2002). For gold recovery from refractory gold ores to be a viable process, pretreatment techniques and alternative lixiviants have been applied to the ores. In this chapter, the study was performed on the as-received ore from Barrick’s Goldstrike mine, NV, USA which is the oxidized refractory gold ore with double refractoriness, containing sulfide and C-matter. POX is a suitable method to oxidize the sulfide minerals in the ore/concentrate and liberate the locked gold. High carbonate-containing ores are treated under alkaline conditions. The alkaline POX process has the problem of lower gold recovery than the acidic process due to the iron oxide/hydroxide passivation (Koslides & Ciminelli, 1992; Thomas & Pearson, 2016). The formation of the passive layer on the gold and sulfide surfaces leads to restriction of the contact between the lixiviant and the solute. The passivated sulfide during the POX process cannot be further oxidized, resulting in an insufficient gold liberation to be attained in this process.
Thiosulfate is a promising lixiviant to replace with cyanide, especially for the refractory gold ore containing C-matters. The gold thiosulfate complex has a low affinity for C-matter, leading to high gold recovery (Aylmore & Muir, 2001; Feng & Van Deventer, 2001; Sitando et al., 2019). The downside of using thiosulfate gold leaching is its metastable characteristic and the complex leaching system as well as high reagent consumption due to its decomposition by oxygen and the added cupric ions as the catalyst (Rolia & Chakrabarti, 1982; Breuer & Jeffrey, 2000; Jeffrey et al., 2003). The decomposed thiosulfate products and cupric ions can impede the efficiency of the gold leaching process. For instance, disulfite ($S_2O_5^{2-}$) interferes with the gold leaching process, or the sulfur and ammonia copper polysulfide were observed to precipitate on the gold surface during thiosulfate gold leaching (Jeffrey et al., 2003; Chu et al., 2003; Jeffrey et al., 2008). In addition, an excess of cupric ions leads to a high thiosulfate consumption as well as CuS precipitation, resulting in low gold recovery (Langhans et al., 1992; Azami et al., 2014). Thus, the proper concentration of thiosulfate and cupric ion should be evaluated for each ore, and the interactions among factors need special attention in the thiosulfate gold leaching system.

In Barrick’s Goldstrike mine, the ore was treated by the POX process to liberate the gold content, followed by thiosulfate gold leaching to avoid the preg-robbing issue. However, Barrick’s Goldstrike plant still suffers insufficient gold recovery from the alkaline POX discharge. The low gold recovery could be attributed to the alkaline POX process, the thiosulfate leaching system, as was mentioned above, or the original ore characteristics and mineralogy. This study has been suggested to reveal the problem of low gold recovery associated with the alkaline POX discharge line at Barrick’s plant to propose a solution to enhance the recovery in the current process. In this regard, the optimization study was carried out with the DOE to determine the maximum gold recovery from alkaline POX discharge, followed by a thorough investigation to discover the reason behind the low gold recovery.
4.2 Experimental methods

4.2.1 Optimization investigation of gold leaching

DOE was used to optimize the leaching conditions and determine the highest gold recovery from the alkaline POX discharge in the thiosulfate leaching system. The Box-Behnken Design (BBD) method, which is one of the Response Surface Designs (RSD), was selected for the DOE study (Figure 4-1). The designed test by BBD was run with the edge of conditions and the center points were repeated, which has the advantages of achieving higher efficiency (The number of coefficients/number of experiment) than other RSD models as well as avoiding the extreme test conditions (Ferreira et al., 2007). Thus, the BBD is the suitable model to test the alkaline POX discharge which had a limited quantity. Design Expert® version 13 by Stat-Ease, Inc. (Minneapolis, MN, USA) was used for the experimental design and analysis.

![Figure 4-1. The Box-Behnken Design (BBD)](image)

Thiosulfate (TS) concentration, cupric ion (Cu) concentration, and temperature were the test parameters under investigation. TS concentration varied in the range of 0.05-0.25 M, Cu concentration was set between 0.5-2.0 mM, and the temperature was explored in the range of 25-50℃ (Table 4-1). 15 tests were designed with three repetitions at the center points (Table 4-2).
Table 4-1. Selected factors for the optimization experiments with the BBD

<table>
<thead>
<tr>
<th>Key</th>
<th>Factor</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>TS conc. (M)</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td>B</td>
<td>Cu conc. (mM)</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
<td>Temp. (°C)</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 4-2. Test conditions with BBD for the optimization experiments

<table>
<thead>
<tr>
<th>Test #</th>
<th>A (M)</th>
<th>B (mM)</th>
<th>C (°C)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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<td>1.25</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
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<td>25</td>
</tr>
<tr>
<td>3</td>
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<td>50</td>
</tr>
<tr>
<td>4</td>
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<td>0.5</td>
<td>50</td>
</tr>
<tr>
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<td>1.25</td>
<td>50</td>
</tr>
<tr>
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</tr>
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<td>0.5</td>
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</tr>
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</tr>
<tr>
<td>13</td>
<td>0.15</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>14</td>
<td>0.05</td>
<td>2</td>
<td>37.5</td>
</tr>
<tr>
<td>15</td>
<td>0.25</td>
<td>2</td>
<td>37.5</td>
</tr>
</tbody>
</table>

4.2.2 Thiosulfate gold leaching procedure

The other leaching factors were kept constant at a pulp density of 33 wt.% solids, stirring speed of 400 rpm, airflow rate of 0.1 L min⁻¹, and 24 h of leaching time. Sodium thiosulfate salt (Na₂S₂O₃·5H₂O, Certified ACS Crystalline, Fisher Chemical) and copper sulfate (CuSO₄·5H₂O, ≥ 98.0%, Fisher BioReagents™) were added to the leaching reactor, and NaOH (Sodium Hydroxide Solution 1N, Certified, Fisher Chemical™) was used to adjust the initial pH to 9.5. For the kinetics study, 10 ml of pulp samples were taken at 1, 3, 5, and 24 h, and each test was repeated three times to check accuracy and precision of the data. After 24 hours of running the leaching tests, the final solution was filtered with vacuum filtration using filter paper of grade 2 (< 8 μm). Solutions were then filtered by a syringe filter (< 0.45 μm) to be analyzed by AAS (Atomic absorption spectroscopy; iCE™ 3300, Thermo Scientific™) for their gold and
copper concentrations. Thiosulfate concentration was measured with IC (Ion Chromatography; 930 Compact Flex with 944 Professional UV/VIS Detector Vario, Metrohm AG). Gold concentration in the residue was determined by fire assay followed by ICP-OES analysis.

4.2.3 Mineralogical investigation

TEM (Transmission Electron Microscopy) techniques were used to explore the characteristics of the alkaline POX discharge and gold distribution in the host minerals. The slurry sample was filtered and dried prior to the analysis. The sample was ground to below 100 nm of thickness, and energy-dispersive X-ray spectroscopy (EDX) mapping was performed to map the distribution of gold particles in the samples. The diagnostic test was conducted to decompose the minerals in order to define the extractable percentage of gold by thiosulfate leaching. HCl dissolution, HNO₃ dissolution, and roasting were the three treatment steps to decompose the minerals, each followed by thiosulfate gold leaching under optimum conditions (Table 4-3). During each step and after the thiosulfate leaching, an estimate of the leachable gold in the host minerals was obtained by AAS analysis of the leach solutions. Then, carbon and sulfur contents were analyzed by a C/S analyzer to confirm the efficacy of the treatment. The remainder of gold after applying all treatment and leaching steps was defined as the gold locked in silicate minerals and so, the unextractable percentage of gold by thiosulfate was determined.
Table 4-3. Diagnostic test steps to determine the extractable percentage of gold from the alkaline POX discharge

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Conditions</th>
<th>Extracted gold from</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiosulfate leaching 1</td>
<td>The obtained optimum conditions</td>
<td>Free gold</td>
</tr>
<tr>
<td>HCl dissolution</td>
<td>HCl 32%, 60°C, 2h, L/S ratio = 2:1 w/w</td>
<td>Dolomite, Calcite, Iron oxides passivation</td>
</tr>
<tr>
<td>Thiosulfate leaching 2</td>
<td>The obtained optimum conditions</td>
<td></td>
</tr>
<tr>
<td>HNO₃ dissolution</td>
<td>HNO₃ 55%, 60°C, 6 h, L/S ratio = 10:1 w/w</td>
<td>Pyrite</td>
</tr>
<tr>
<td>Thiosulfate leaching 3</td>
<td>The obtained optimum conditions</td>
<td></td>
</tr>
<tr>
<td>Roasting</td>
<td>700°C, 8 h</td>
<td>C-matter</td>
</tr>
<tr>
<td>Thiosulfate leaching 4</td>
<td>The obtained optimum conditions</td>
<td></td>
</tr>
</tbody>
</table>

4.3 Results and discussion

4.3.1 Gold leaching optimization

Thiosulfate gold leaching experiments were designed and carried out based on the output of the BBD method, and the predicted model is presented (with coded factors):

\[
\text{Au recovery (\%)} = 46.38 - 1.57A - 1.40B + 9.19C + 0.6694AB - 0.6337AC + 3.66BC - 1.70A^2 - 4.23B^2 + 1.36C^2
\]  

(4-1)

The model well describes the actual values with a coefficient of determination value \( R^2 \) of 0.9817 and \( p-value \) of 0.0008 with 95% confidence interval (Figure 4-2; Table 4-4). The \( p-value \) of less than 0.05 indicated that the model was significant and C, BC, and \( B^2 \) were the significant factors affecting the gold recovery from the thiosulfate leaching system. In the model, the insignificant factors were considered together to see the interaction effect and the impact of the interactions were compared in the next section; even with the consideration of the insignificant factors, the insignificant lack of fit still means that there is
less possibility to deviate from the derived model and supports the adequacy of the fitted model and the high $R^2$ value.

Figure 4-2. Plot of predicted vs. actual data of the modified model in BBD ($R^2$: 0.9817, $p$-value: 0.0008)

Table 4-4. Analysis of Variance (ANOVA) table for the designed experiments

<table>
<thead>
<tr>
<th></th>
<th>$F$-value</th>
<th>$p$-value</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>29.86</td>
<td>0.0008</td>
<td>significant</td>
</tr>
<tr>
<td>A-TS conc.</td>
<td>6.24</td>
<td>0.0547</td>
<td></td>
</tr>
<tr>
<td>B-Cu conc.</td>
<td>4.92</td>
<td>0.0773</td>
<td></td>
</tr>
<tr>
<td>C-Temp.</td>
<td>212.96</td>
<td>&lt;0.0001</td>
<td>significant</td>
</tr>
<tr>
<td>AB</td>
<td>0.5643</td>
<td>0.4863</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>0.5058</td>
<td>0.5087</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>16.84</td>
<td>0.0093</td>
<td>significant</td>
</tr>
<tr>
<td>A²</td>
<td>3.38</td>
<td>0.1255</td>
<td></td>
</tr>
<tr>
<td>B²</td>
<td>20.77</td>
<td>0.0061</td>
<td>significant</td>
</tr>
<tr>
<td>C²</td>
<td>2.15</td>
<td>0.2027</td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>0.5721</td>
<td>0.6861</td>
<td>not significant</td>
</tr>
</tbody>
</table>

Due to no significant effects of TS concentration (A) and Cu concentration (B) on gold recovery, over 100 optimum conditions were obtained at the same temperature (around 50°C), one of which was selected as
the optimum condition with the consideration of TS and Cu consumption factors. The attained TS and Cu consumption models are described as the following:

\[
\log(\text{TS consumption}) = 2.40 - 0.5859A + 0.3686B + 0.2880C + 0.2457AB - 0.4120AC - 0.5920BC, \\
R^2 = 0.9248, \ p-value = 0.0004
\]  

(4-2)

\[
\frac{1}{\sqrt{\text{Cu consumption}}} = 0.2075 + 0.0085A + 0.0270B - 0.0358C, \\
R^2 = 0.7462, \ p-value = 0.0013
\]  

(4-3)

The optimum conditions in which the maximum gold recovery was obtained are TS concentration of 0.14 M, Cu concentration of 0.78 mM, and temperature of 49.98 (50) °C. Under the conditions, the gold recovery was predicted to be 58.66%; the test with the selected conditions was repeated three times, resulting in 57.69 ± 1.90% gold leaching recovery which is in good agreement with the value predicted from the mathematical model, as well as high repeatability based on the repeated test values.

4.3.2 Effect of leaching factors on gold recovery

Figure 4-3 illustrates the effect of investigated factors in the optimization study. As observed from the model discussed (Equation 4-1), gold recovery was not significantly manipulated by either TS or Cu concentration in the ranges under investigation in this study (Figure 4-3 (a); Table 4-1). As shown in Figure 4-3 (b), gold recovery was enhanced by an increase in temperature from 25 to 50°C, while TS concentration again exhibited a minor effect on the gold recovery (Figure 4-3 (b)). However, a more considerable change in the gold recovery was observed when Cu concentration was changed along with temperature (Figure 4-3 (c)). It indicated the influence of BC parameter on gold recovery which was previously shown in the presented model (\(p-value < 0.05\), Table 5). The considerable changes in the gold recovery by changing temperature could be attributed to the high activation energy of the leaching reaction (gold-thiosulfate
complexation) due to its chemically controlled associated mechanism (Breuer & Jeffrey, 2000; Jeffrey, 2001). At lower temperatures, Cu concentration had a larger effect on gold recovery than TS concentration, i.e., higher Cu content resulted in higher gold recovery. However, at elevated temperatures, higher Cu concentration had a detrimental effect on gold recovery (Figure 4-3 (c)). At lower temperatures, the leaching kinetics were slower, therefore, the catalytic effect of Cu became more beneficial to accelerate the gold dissolution reactions; Conversely, at higher temperatures, the energy state of the system was high enough that only a small amount of cupric ion was sufficient to enhance the leaching kinetics. Excessive Cu concentration led to its precipitation on the surface of gold particles, as well as elevating thiosulfate decomposition in the system. The detrimental effect of excessive cupric ion at high temperatures exceeds its catalytic effect, resulting in lower gold recovery (Aazami et al., 2014; Lampinen et al., 2015; Mohammadi et al., 2017). The results emphasized again that examining the interaction between the parameters is important. The minimal effect of the TS concentration on gold recovery could be attributed to selecting a range of thiosulfate concentrations that maintain enough free thiosulfate available in the system in all the experiments.
4.3.3 Gold thiosulfate leaching kinetics

The kinetic test was performed under optimum conditions as well as lower temperature levels (25 and 37.5°C). The kinetic investigation showed the significant effect of temperature on gold recovery in thiosulfate gold leaching as illustrated in Figure 4-4. In addition, a leaching test was run at 62.5°C, above the maximum temperature selected in the DOE, to secure the highest gold recovery obtained in this study.
As is presented in Figure 4-4, a sharp increase was obtained in gold recovery at the first 1 h of leaching, then the gold dissolution kinetics slowed down and the same pattern was seen for all temperatures. Elevating the temperature from 25 to 50℃ accelerated the initial kinetics (after 1 h of leaching); however, above 50℃, the initial kinetics did not further increase. Additionally, the gold recovery at 62.5℃ was only marginally higher (2%) than 50℃ within the error range, indicating that no further improvement was achieved by increasing the temperature above 50℃. The leaching rate reduction after 1h could be attributed to the decomposition of thiosulfate and cupric ion reduction in the solution (Breuwe & Jeffrey, 2000).

Figure 4-4. Gold thiosulfate leaching kinetics trend at different temperatures under the optimum copper and thiosulfate concentrations (TS: 0.14 M, Cu: 0.78 mM).

Figure 4-5 demonstrates TS and Cu consumptions during leaching under the optimum conditions and at different temperatures. Higher temperatures resulted in a larger TS consumption rate (Figure 4-5 (b)) and a more significant increase in Cu consumption (Figure 4-5 (a)). The consumption at high temperature is attributed to the decomposition of TS and Cu precipitation as CuS (Abbruzzese et al., 1995). Temperature has a more substantial impact on Cu consumption than TS consumption, possibly resulting from the availability of an excessive amount of thiosulfate in the leaching medium. Temperatures above 50℃ did
not have a beneficial effect on gold recovery (Figure 4-4), while increasing the consumption rate of both TS and Cu. This confirmed that the optimum test conditions identified resulted in the highest gold recovery possible in the leaching system.

Figure 4-5. (a) Cu consumption (b) TS consumption during 24 h leaching at different temperatures

4.3.4 Determination of the limited gold recovery

The study on the optimization and leaching kinetics was performed on the alkaline POX discharge, revealing a decline in the leaching kinetics after 1 h and insufficient gold recovery for the optimum conditions was achieved. The limited gold recovery could be attributed to the hindered leaching rate or the physical limitation resulting from the ore mineralogy. Therefore, further investigations were conducted to find the reason(s) behind the low leaching recovery from the alkaline POX discharge.

4.3.4.1 The hindered gold recovery at 1 h

The hindered leaching recovery at 1 h could be due to the passive layer formation on the gold surface, resulting from TS decomposition and Cu precipitation. To investigate the impact on overall gold recovery at 1 h, two tests were carried out under the optimum conditions, and the tests were stopped after
1 h leaching. The final solutions were then filtered in preparation for the second leaching step. One of the residues was ground to clean any potential passive layers and, for comparison purposes, the other residue was left untreated. Grinding was conducted in a laboratory stirred media mill with a ball to powder ratio of 2:1 and pulp density of 50 wt.% solids for 30 min. These conditions were confirmed to have only an abrasion effect and no effect on further gold liberation from the host minerals (Lee et al., 2022; chapter 5). Both residues were then leached in fresh thiosulfate solution (TS: 0.14 M; Cu: 0.78 mM) for another 23 h (Figure 4-6). The leaching recovery was slightly enhanced at the beginning of the second leaching stage with fresh solution; however, the overall gold recovery after 24 h of leaching stayed constant and was not influenced by grinding or the introduction of fresh leach solution. Furthermore, the ground residue and the unground residue showed similar patterns for gold leaching (except for the minor reduction in gold leaching after grinding the residue, which can be attributed to the loss of gold from grinding media to leaching reactor. After grinding, the slurry sample was filtered, then washed by DI water from the grinding media ball). The results indicated that grinding did not affect the final gold recovery and as a result, the passivation during thiosulfate gold leaching was not the main reason for reduced gold recovery of alkaline POX discharge from the thiosulfate leaching medium. The observed enhancement in the gold recovery can be assigned to the addition of fresh solution with an optimum concentration of Cu and TS (which was previously discussed in section 3.2, as parameters affecting the gold leaching rate), and the absence of oxy-sulfur species which can interfere with the leaching process (Breuer & Jeffery, 2002; Chu et al., 2003). Therefore, it can be concluded that encapsulation of gold in the host minerals led to limited contact between the lixiviant and the gold, inhibiting leaching.
4.3.4.2 The properties of the alkaline POX discharge

One potential issue associated with the alkaline POX discharge is the formation of an iron oxide passive layer on the gold and the sulfide particles during the POX process (Thomas & Pearson, 2016). This phenomenon leads to insufficient sulfide oxidation and consequently, blocks the contact between the gold particles and the leaching lixiviant. In our previous study, SEM analysis showed the passive layer to be formed of iron oxide mixed with other minerals (Lee et al., 2022). In the current study, SEM and TEM analysis were attempted to detect the locked gold spots in the ore; however, because of the low gold content in the ore (3.08 g t⁻¹), its complex mineralogy, and too fine size of the disseminated gold particles, no pure gold peak was detected by SEM analysis. This supported the hypothesis that finely locked gold particles could be the reason for the limited gold recovery. TEM-EDX mapping showed that the gold particles were finely scattered all over the minerals (Figure 4-7 & 4-8), indicating its poor liberation and complex mineralogy. In Figure 4-7, a locked mineral is shown which is more likely to be a pyrite phase according

![Figure 4-6. Gold leaching behavior in a regular leaching solution (no treatment) and fresh solution addition to ground and unground residues after 1 h leaching (TS: 0.14 M, Cu: 0.78 mM)](image-url)
to the EDX mapping analysis, and it shows a more concentrated gold spot inside this area. This demonstrates that the encapsulated gold inside the pyrite matrix was not liberated, and some pyrite was not oxidized during the POX process. The presence of unoxidized pyrite in the ore after the POX process is one of the shortcomings of the alkaline POX process, rendering inefficient gold leaching as a noticeable gold amount remains locked in the pyrite phase.

![TEM-EDX mapping of locked pyrite in silicates and concentrated gold spot located on the pyrite area](image)

**Figure 4-7.** TEM-EDX mapping of locked pyrite in silicates and concentrated gold spot located on the pyrite area

In addition to the presence of unoxidized pyrite that contains a high concentration of gold, disseminated fine gold particles were observed in all other minerals such as quartz, dolomite, or gypsum (Figure 4-8). These gold particles are more likely to be locked as very fine particles that are not extractable by any treatment technique as it is hard for them to be liberated and exposed to the leaching lixiviant.
Figure 4-8. Scattered gold particles in all minerals by TEM-EDX mapping (yellow box: expected as gypsum (CaSO₄·2H₂O); red box: expected as dolomite (CaMg(CO₃)₂; other areas: expected as quartz (SiO₂))

Hence, the limited gold recovery from the alkaline POX discharge could be due to the chemically locked gold in the unoxidized pyrite. Also, the poor liberation and the complex mineralogy of the feed ore were investigated.

A diagnostic procedure was used to evaluate the leachability of the alkaline POX discharge from thiosulfate media. The objective of the procedure was to decompose specific minerals in the ore followed by thiosulfate leaching to determine the amount of gold encapsulated in those minerals (Table 4-4), representing the unextractable portion of gold in the ore. The C/S content of the materials after each treatment is presented in Figure 4-9 (a); S content reduced after the first thiosulfate leaching stage, resulting from gypsum dissolution by NaOH during leaching (Asamoah et al., 2018a). HCl dissolution decomposed the carbonates and HNO₃ dissolution removed the pyrite. An additional roasting process was applied to decompose the remainder of the carbon and sulfur, leaving behind less than 0.08% of carbon and sulfur in the solid residue.
Figure 4-9. (a) Alkaline POX discharge and leaching residue’s changes in carbon and sulfur contents after each treatment (b) gold recovery after each treatment and the cumulative gold recovery

Through the decomposition steps, more gold was extracted by thiosulfate leaching (Figure 4-9 (b)). This indicated that once gold is liberated, it can be recovered by thiosulfate leaching; thus, thiosulfate leaching is not the cause of the low gold recovery. The diagnostic test results showed that the cumulative gold recovery after applying the treatment steps was 102% ±10%, with the majority of the error occurring in the leaching results after the first treatment (HCl decomposition, Figure 4-9 (b)). This high recovery could be attributed to the impact of HCl dissolution treatment on liberating other gold-containing minerals as well, as the ore has a complex mineralogy and some major minerals are encapsulated inside some other ones, which generated a higher error at this level. Additionally, the remainder of the gold which was not leached after applying the treatment techniques was locked inside silicate minerals that were not decomposable throughout the diagnostic test steps. According to the mineralogical analysis of the alkaline POX discharge, it contains 60% silicates; however, discharge decomposition results showed that the gold particles were mostly disseminated in other minerals (carbonates, sulfides, and C-matter) and less than 8% were expected to be locked in silicate minerals. Fire assay results of the residues confirmed that the total gold recovery was 92.2%, meant that 7.8% of the gold was remained in the residue. The results of the diagnostic tests support the TEM analysis that showed gold particles were scattered all over the minerals.
and locked inside them. In addition, it confirmed that thiosulfate leaching was an efficient process for gold leaching, and the low gold recovery from the alkaline POX discharge was assigned to the mineralogical complexities (e.g., locked gold in host minerals, locked host minerals inside other minerals, and insufficient sulfide oxidation rate) associated with the ore and not the thiosulfate leaching process. Therefore, it can be concluded that optimizing the alkaline POX process to enhance the oxidation rate for sulfides as well as liberating the locked gold particles from inside the host minerals are the key factors to be considered to achieve a higher gold recovery from thiosulfate leaching.

4.4 Conclusion

To address the issue of low gold recovery from thiosulfate leaching of alkaline POX discharge from Barrick Gold Corporation, an optimization investigation was conducted to achieve the maximum gold recovery capacity using the thiosulfate leaching medium. 59% of gold was recovered under the optimum conditions of 0.14 M TS, 0.78 mM Cu, and 50°C temperatures during 24 h of leaching. Kinetic experiments revealed that the leaching rate significantly slowed down after one hour, resulting from the reduced cupric ion concentration in the leaching medium during leaching. Furthermore, the reduction in the leaching rate did not affect the gold recovery value after 24 h and it was not the cause of the low gold recovery. TEM micrographs showed the gold distribution in the alkaline POX discharge and demonstrated that gold particles were mainly disseminated as fine particles all over the minerals. Furthermore, unoxidized pyrite (from the POX process) was shown to contain a high concentration of gold locked inside which was not leachable. The diagnostic test results confirmed that the locked gold could be easily leached after its liberation. Thus, the low gold recovery was not a result of the thiosulfate leaching process itself but was due to mineralogical issues and insufficient sulfide oxidation in the alkaline POX process. Higher gold recovery can only be attained by enhancing the liberation of gold. Improving the oxidation efficiency of
the alkaline POX process and/or additional treatment after the POX process were identified as possible ways to improve gold liberation, and thus increase gold recovery.
Chapter 5

Enhanced gold recovery from alkaline pressure oxidized refractory gold ore after its mechanical activation followed by thiosulfate leaching

5.1 Introduction

Refractory gold ores contain preg-robbing matter, cyanide-/oxygen-consuming matter, and/or gold locked in sulfide or silicate minerals (Afenya, 1991; La Brooy et al., 1994; Asamoah et al., 2021). To efficiently liberate and extract gold from these ores, pretreatment methods are often used, including roasting, bio-oxidation, pressure oxidation (POX), and ultrafine grinding (Corrans & Angove, 1991; Fraser et al., 1991). When used alone or in combination with other pretreatment methods, mechanical activation (MA) via grinding has been shown to enhance gold recovery by cleaning the passivating layer from the mineral surface, decreasing the particle size, and thus increasing the mineral surface area exposed to leaching reagents, and by causing liberation of gold from gold-bearing minerals. For example, gold recovery after chloride-hypochlorite leaching of a refractory pyritic concentrate increased from 37.2 to 100% with MA pretreatment, with the additional benefit of the much shorter leach time (30 vs 480 min) (Hasab et al., 2013). MA has also been shown to improve the efficiency and rate of thiosulfate leaching (Ficeriová et al., 2002; Hashemzadehfini et al., 2011) and cyanidation (Corrans & Angove, 1991; Harbort et al., 1998; Birol & Uçurum, 2016). Ultrafine grinding of a pyrite ore to reduce the 80% passing size (P80) from 74 to 10 μm increased gold recovery from 23.4 to 70.2% by cyanidation (Harbort et al., 1998). MA of bio-oxidized gold ores improved gold recovery by up to 1.8 times by cyanidation (Asamoah et al., 2018b).

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Laboratory-scale stirred media mills have been successfully used to study MA (Table 5-1) because they are suitable for wet grinding and fine/ultrafine grinding (Kwade, 1999; Jankovic, 2003). Their grinding performance (i.e., fineness) is determined by the number of stress (SN) and stress intensity (SI) proportional to the total energy input (Kwade & Schwedes, 2002). Under constant SN and SI, particle fineness is constant and can be estimated by measuring the total energy input. SN and SI are affected by grinding factors. SN depends on the number of media contacts \(N_c\), the probability of caught and stressed particles at a media contact \(P_s\), and the number of feed particles inside the mill \(N_F\) (Equation 5-1) (Kwade & Schwedes, 2007):

\[
SN = \frac{N_cP_s}{N_p} \propto \frac{\varphi_{GM}(1-\varepsilon)}{(1-\varphi_{GM}(1-\varepsilon))} \cdot \frac{n \cdot t}{d_{GM}^2} \quad \text{(for real grinding)} 
\]

where \(\varphi_{GM}\) is the grinding media filling ratio (-), \(\varepsilon\) is the grinding media bulk porosity (-), \(c_v\) is the solids concentration of the product suspension (-), \(d_{GM}\) is the grinding media diameter (m), \(n\) is the number of revolutions per second \((s^{-1})\), and \(t\) is the grinding time \((s)\) (Kwade & Schwedes, 2007). SI is proportional to \(S_{IGM}\) (stress intensity of the grinding media) determined by the grinding media diameter \(d_{GM}\), grinding media density \(\rho_{GM}\) \((\text{kg} \cdot \text{m}^{-3})\), and stirred tip speed \(v_t\) \((\text{m} \cdot \text{s}^{-1})\) (Equation 5-2) (Kwade & Schwedes, 2002):

\[
SI \propto S_{IGM} = d_{GM}^3 \rho_{GM} v_t^2 
\]
Table 5-1. Mechanical activation for metal extraction with the PE 075 laboratory batch mill (NETZSCH, Shanghai, China); steel ball diameter 2.0 mm

<table>
<thead>
<tr>
<th>Sample mass, g</th>
<th>Speed, rpm</th>
<th>Time, min</th>
<th>Ball mass, g</th>
<th>Solution volume, mL</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>nd</td>
<td>10–160</td>
<td>2,000</td>
<td>200</td>
<td>(Balaz et al., 1996)</td>
</tr>
<tr>
<td>20</td>
<td>500–1,300</td>
<td>15–60</td>
<td>2,000</td>
<td>200</td>
<td>(Balaz, Achimovicova, et al., 2000)</td>
</tr>
<tr>
<td>100</td>
<td>nd</td>
<td>15–60</td>
<td>2,000</td>
<td>200</td>
<td>(Balaz Boldizarova, et al., 2000)</td>
</tr>
<tr>
<td>50</td>
<td>1,000</td>
<td>15–60</td>
<td>2,000</td>
<td>200</td>
<td>(Ficeriová et al., 2002)</td>
</tr>
<tr>
<td>50–200</td>
<td>600–1,200</td>
<td>15–60</td>
<td>2,000</td>
<td>200</td>
<td>(Godocikova et al., 2002)</td>
</tr>
<tr>
<td>24–66</td>
<td>1,000</td>
<td>24–66</td>
<td>2,000</td>
<td>200</td>
<td>(Balaz et al., 2003)</td>
</tr>
<tr>
<td>24–66</td>
<td>1,000</td>
<td>24–66</td>
<td>2,000</td>
<td>200</td>
<td>(Ficeriova et al., 2005)</td>
</tr>
<tr>
<td>50</td>
<td>1,000</td>
<td>60</td>
<td>2,000</td>
<td>200</td>
<td>(Ficeriova et al., 2005)</td>
</tr>
<tr>
<td>20</td>
<td>1,000</td>
<td>30</td>
<td>2,000</td>
<td>200</td>
<td>(Balaz &amp; Achimovicova, 2006)</td>
</tr>
<tr>
<td>100</td>
<td>1,000</td>
<td>60</td>
<td>1,800</td>
<td>210</td>
<td>(Alex et al., 2014)</td>
</tr>
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<td>50–150</td>
<td>600–1,200</td>
<td>30–120</td>
<td>2,000</td>
<td>200</td>
<td>(Mussapyrova et al., 2021)</td>
</tr>
</tbody>
</table>

nd: no data

By adjusting the MA conditions described in Table 5-1, the surface and bulk properties of the samples were changed, affecting the leaching recovery of gold or the kinetics of the process (Balaz et al., 1996; Balaz, Achimovicova, et al., 2000; Balaz, Boldizarova, et al., 2000; Godocikova et al., 2002; Balaz et al., 2003; Ficeriova et al., 2005). Balaz et al. (Balaz et al., 1996; Balaz, Achimovicova, et al., 2000) reported that increasing ratio of surface area to bulk disordering shows a positive effect on the leaching kinetics. In some studies, it was shown that leaching rate increases when the degree of destruction (D) exceeds 30% (Balaz et al., 2003; Ficeriova et al., 2005).

The objective of this study is to evaluate the effectiveness of MA with a stirred media mill to improve gold recovery from alkaline POX discharge with a fine particle size (P80: 56.8 μm). POX is routinely performed on ore from Barrick Goldstrike mine, NV, USA, a refractory gold ore consisting of C-matter and sulfide. Alkaline or acidic POX is used to liberate gold from the sulfide followed by RIL thiosulfate leaching, thus avoiding the preg-robbing effect of the C-matter (Baron et al., 2016). However, gold recovery from alkaline POX discharge is only 59%, in part because of incomplete oxidation of pyrite...
(FeS₂) and passivation of gold with hematite (Fe₂O₃) and other iron oxide and hydroxide precipitates produced by oxidation of iron sulfide minerals (Koslides & Ciminelli, 1992; Thomas, 2005). During the MA experiments, the water volume, and media conditions (and thus SI) were kept constant. The SN was modified by changing the ball to powder ratio (BPR), which affects the grinding media filling ratio and bulk porosity ($\varphi_{GM}$ and $\varepsilon$ in Equation 5-1), and the pulp density (PD), which affects the solids concentrations ($c_v$ in Equation 5-1). In this study, thiosulfate gold leaching was implemented to use the same conditions at Barrick’s gold leaching plant; Furthermore, cyanide was not an effective leaching lixiviant due to the pregrubbing effect from the remaining C- matter. Modifying these process variables will provide 1) data to determine the reason for low gold recovery and 2) guidance on new approaches to enhance gold recovery from alkaline POX discharge.

5.2 Experimental

5.2.1 Mechanical activation

MA via wet grinding was performed in a PE 075 (NETZSCH, Shanghai, China) laboratory stirred media mill (Figure 5-1). Tap water was circulated through the outer layer of the chamber to maintain the temperature at room temperature. Zirconia balls were used instead of steel balls, which can have a detrimental effect on thiosulfate gold leaching (Feng & Van Deventer, 2010a). MA tests were conducted under the conditions in Table 5-2, then samples were dried. The dried residue was analyzed with a particle size analyzer, BET analyzer, SEM with and without EDX, XRD, and thermogravimetric analysis (TGA; NETZCH STA 449 F3 Jupiter® thermal analyzer; N₂ gas rate 10 K min⁻¹, 30-800°C) to determine the effects of MA on surface and bulk structures and morphology.
Table 5-2. MA conditions employed in this study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed, rpm</td>
<td>1,000</td>
</tr>
<tr>
<td>Ball diameter, mm</td>
<td>2.0</td>
</tr>
<tr>
<td>Mill volume, L</td>
<td>0.5</td>
</tr>
<tr>
<td>Loaded powder (sample) weight, g</td>
<td>100</td>
</tr>
<tr>
<td>Grinding duration, h</td>
<td>1</td>
</tr>
<tr>
<td>Ball to powder weight ratio</td>
<td>2:1, 3:1, 5:1 7:1 at 50 wt.% pulp density</td>
</tr>
<tr>
<td>Pulp density, wt.% solids</td>
<td>25, 33, 50 at 2:1 ball to powder ratio</td>
</tr>
</tbody>
</table>

5.2.2 Thiosulfate gold leaching

Mechanically activated samples were separated from used balls with a sieve. The residue on the balls was recovered by washing with deionized water. 24 h thiosulfate leaching tests were performed immediately after MA to avoid any changes in the particles (Table 5-3). Leaching was conducted in glass reactors and stirred at 700 rpm with an overhead mixer. The temperature was maintained at 50°C with a water bath, and air was injected into the reactor at a flow rate of 0.1 L min⁻¹. Sodium thiosulfate pentahydrate (Na₂S₂O₅·5H₂O, Certified ACS Crystalline, Fisher Chemical) was used for leaching. With oxygen only, thiosulfate gold leaching has slow kinetics, so cupric ions as cupric sulfate pentahydrate
(CuSO₄·5H₂O, ≥ 98.0%, Fisher BioReagents™) were added as a catalyst. The initial pH was adjusted to 9.5 using sodium hydroxide (NaOH), but the pH was not regulated during leaching.

<table>
<thead>
<tr>
<th>Leaching parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium thiosulfate concentration, M</td>
<td>0.2</td>
</tr>
<tr>
<td>Cu²⁺ concentration, mg L⁻¹</td>
<td>50</td>
</tr>
<tr>
<td>Air flow rate, L min⁻¹</td>
<td>0.1</td>
</tr>
<tr>
<td>Initial pH</td>
<td>9.5</td>
</tr>
<tr>
<td>Pulp density, g L⁻¹</td>
<td>200</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>50</td>
</tr>
<tr>
<td>Stirring speed, rpm</td>
<td>700</td>
</tr>
<tr>
<td>Leaching time, h</td>
<td>24</td>
</tr>
</tbody>
</table>

The leaching solution was filtered through 8 μm pore size filter paper (Grade No. 2) and then a 0.45 μm pore size syringe filter. The gold concentration in the filtered solution was analyzed with AAS. Gold in the residue was quantified by fire assay followed by ICP-OES.

5.3 Results and discussion

5.3.1 MA results

Preliminary testing at a BPR of 2:1 and PD of 50 wt.% showed that the P80 of the alkaline POX slurry decreased from 56.5 μm in the as-received sample to 36.5 μm after 60 min of MA (Figure 5-2). Although a smaller P80 could be achieved with a longer grinding time (19.1 μm after 300 min), the higher slurry density—possibly due to evaporation of water from the slit between the stirred rod and lids—made material flow difficult. Additionally, the sample ground for 300 min was difficult to recover due to the high amount of evaporation. From a practical standpoint, long grinding times would also increase energy consumption. Based on these preliminary results, 60 min of MA was chosen.
5.3.1.1 Effect of ball to powder ratio

At 50 wt.% PD, the particle size decreased with increasing BPR; P80 size of 3.46 µm was achieved at a BPR of 7:1 (Figure 5-3). The higher grinding efficiency at a higher BPR is due to a high mill filling ratio (Celep & Yazici, 2013), that is, less space between the grinding balls increases the number of contacts between the particles and the grinding balls (Equation 5-1) (Kwade & Schwedes, 2007). A higher filling ratio also increases the grinding throughput (Schnatz, 2004). The three main particle grinding mechanisms are abrasion, impact, and compression (Lowrison, 1974). The bimodal distribution at 2:1 and 3:1 BPR (Figure 5-3) indicates a complex grinding mechanism by abrasion, impact, or compression, which produces both coarse particles from the original sample and very fine particles that broke off from the coarse particles (Hennart et al., 2009). Finally, the monomodal distributions at 5:1 and 7:1 BPR indicate either impact or compression, which produced finer fractures as cleavage across all size ranges (P80 < 9 µm).
Figure 5-3. Particle size distribution cumulative volume (solid lines) and volume density (dashed lines) at four ball to powder ratios of alkaline POX discharge (50 wt.% pulp density) after 60 min of MA by wet grinding.

As the BPR was increased, both $S_G$ and $S_A$ generally increased (Figure 5-4). $S_G$ is calculated from particle size; therefore, it is directly related to particle size. However, several additional factors affect $S_A$, which may have caused the lack of a response when BPR was increased from 2:1 to 3:1 (Figure 5-4). For example, surface roughness ($R_s$) is related to $S_A$ by Equation 5-3 (Jaycock & Parfitt, 1981):

$$R_s = A_B \cdot d \cdot \frac{D}{6}$$  \hspace{1cm} (5-3)

where, $A_B$, $d$, and $D$ indicate the $S_A$, solid density, and average particle diameter, respectively. Surface roughness is lower for particles subjected to abrasion than impact (Ahmed, 2010; Zhang et al., 2021). At BPRs of 2:1 and 3:1, more abrasion was shown, which would have lowered the surface roughness due to surface cleaning and $S_A$. By comparison, both $S_G$ and $S_A$ increased at BPRs of 5:1 and 7:1 due to the significantly smaller particle sizes achieved.
5.3.1.2 Effect of pulp density

The P80s of the POX discharge slurry were 36.4 and 19.9 µm at 50 and 25 wt.% PD, respectively (Figure 5-5). A cushioning effect between the grinding media and the particles could have led to inefficient grinding at the higher PD (Santosh et al., 2021). By comparison, at a lower PD, the particles are less resistant to the balls, which increases the effective dispersion volume and enhances grinding kinetics (Shinohara et al., 1999). In addition, the higher viscosity at higher PD could have inhibited effective grinding by reducing the stress intensity of collision as the velocity of the media decreased (He & Forssberg, 2007). Increasing the viscosity causes an increase in breakage by attrition rather than breakage by compression, due to more tightly packed particles at a higher PD (Tucker, 1984). Therefore, the coarser particle size was due to more abrasion, as shown by the bimodal particle size distribution in Figure 5-3. The abrasion effect would be less apparent at low PD, where impact or compression would be dominant, and a finer particle size would be generated in all size ranges.
Figure 5-5. Particle size distribution cumulative volume (solid lines) and volume density (dashed lines) at three pulp densities of alkaline POX discharge after 60 min of MA by ultrafine wet grinding at a 2:1 ball to powder ratio.

The $S_G$ and $S_A$ of the POX slurry were slightly lower and higher, at 50 wt.% than 25 wt.% PD, respectively (Figure 5-6). The SEM was used to compare the solids at these two PD values, demonstrating that clean and smooth surfaces (red blocks) were more prevalent at 25 wt.% PD (Figure 5-7). Efficient collisions that split particles in half resulted in new clean surfaces at lower PD. The rougher particles (yellow blocks) that were more prevalent in the 50 wt.% PD sample had more fine debris on their surfaces. Fine debris was attributed to more abrasion at 50 wt.% PD. Producing new surface area increases $S_A$, while reduced roughness decreases $S_A$. Thus, the sum of positive and negative effects on $S_A$ resulted in lower $S_A$ at lower pulp density by producing new surfaces, which were cleaner and smoother.
Figure 5-6. Specific geometric area ($S_G$) and specific surface area by gas adsorption ($S_A$) vs pulp density of alkaline POX slurry after 60 min of MA by ultrafine wet grinding at a ball to powder ratio of 2:1
Figure 5-7. Scanning electron micrographs of alkaline POX slurry after 60 min of MA by ultrafine wet grinding (ball to powder ratio 2:1) at (a) 50 wt.% and (b) 25 wt.% pulp density; blue blocks: selected section for magnified micrographs ((a)-1 and (b)-1); red blocks: clean and smooth surfaces; yellow blocks: rougher particles.

Changes in the MA factors not only affected the particle size reduction, but also the difference in the main grinding mechanism by abrasion, impact, or compression. In the next section, the effect of caused changes would discuss with gold recovery results.

5.3.2 The effect of mechanical activation on gold recovery

Thiosulfate gold leaching of alkaline POX slurry in the absence of MA yielded a gold recovery of 59.5% (Table 5-4). Gold recovery was most improved (72.1%) after 60 min of MA with a BPR of 5:1 and
PD of 50 wt.%. Gold recovery was >70% for slurry samples with a P80 < 9 µm. At a similar P80 and using the same BPR of 2:1, the MA of alkaline POX slurry had a slightly higher gold recovery at 25 wt.% PD (67.1%) and 33 wt.% PD (66.1%) than 50 wt.% PD (64.0%). At a lower PD, more fracturing of particles would have occurred, exposing new particle surfaces to the leaching reagent, and liberating gold locked inside the minerals. However, the MA period required to achieve that gold recovery (63.1%) was three times higher at the higher PD, which has cost implications.

Table 5-4. P80, specific surface area (Sₐ), and gold recovery from alkaline POX slurry (pulp density, 200 g L⁻¹) after MA followed by sodium thiosulfate leaching (0.2 M S₂O₃²⁻; 50 mg L⁻¹ Cu²⁺; 24 h leaching time)

<table>
<thead>
<tr>
<th>MA period, min</th>
<th>Ball to powder ratio</th>
<th>Pulp density, wt.%</th>
<th>P80, µm</th>
<th>Sₐ, m² g⁻¹</th>
<th>Au recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>–</td>
<td>50</td>
<td>56.5</td>
<td>9.73</td>
<td>59.5</td>
</tr>
<tr>
<td>30</td>
<td>2:1</td>
<td>50</td>
<td>45.2</td>
<td>8.71</td>
<td>59.9</td>
</tr>
<tr>
<td>60</td>
<td>2:1</td>
<td>50</td>
<td>36.4</td>
<td>9.24</td>
<td>64.0</td>
</tr>
<tr>
<td>180</td>
<td>2:1</td>
<td>50</td>
<td>22.9</td>
<td>8.47</td>
<td>63.1</td>
</tr>
<tr>
<td>60</td>
<td>2:1</td>
<td>33</td>
<td>22.9</td>
<td>8.70</td>
<td>66.1</td>
</tr>
<tr>
<td>60</td>
<td>3:1</td>
<td>50</td>
<td>20.1</td>
<td>9.09</td>
<td>63.3</td>
</tr>
<tr>
<td>60</td>
<td>2:1</td>
<td>25</td>
<td>19.9</td>
<td>8.47</td>
<td>67.1</td>
</tr>
<tr>
<td>60</td>
<td>5:1</td>
<td>50</td>
<td>8.54</td>
<td>10.55</td>
<td>72.1</td>
</tr>
<tr>
<td>60</td>
<td>7:1</td>
<td>50</td>
<td>3.46</td>
<td>14.64</td>
<td>70.4</td>
</tr>
</tbody>
</table>

There was opposing relationship between P80 and Au recovery up to a certain P80 size of 8.54 µm (Figure 5-8 (a)), and the minor increase in the gold recovery was attributed to the fine gold particle size (Corrans & Angove, 1991). The residual error was higher at finer P80 (Figure 5-8 (a)), suggesting that the mechanisms driving gold recovery differed with particle size. During POX, some of the mineral surface in the alkaline POX slurry was covered by a passivation layer. Abrasion of the mineral surface removed some of this layer. However, at finer particle sizes, more gold was liberated from inside the particles. The Au recovery had no distinct relationship with Sₐ change (Figure 5-8 (b)).
5.3.2.1 Gold recovery via de-passivation

SEM with EDX of the surface of the as-received alkaline POX discharge showed the co-existence of Si and O with Al, Ca, Mg and Fe in some spots (Figure 5-9 (a)). The selected point is most probably showing a passive layer of iron oxide on silicate and carbonate—a by-product of the alkaline POX process. Additionally, some debris with the same EDX peak was detected after MA (Figure 5-9 (b)), which suggests that grinding cleans the particle surfaces of the passivation layer. This is also supported by clean surfaces on particles after MA (Figure 5-10; see also Tables B-1, 2, & 3 and Figure B-1, 2, & 3). The EDX results reinforce the hypothesis that an iron oxide passivating layer is formed which could be removed by MA, leading to an enhancement in the Au leaching recovery.
Figure 5-9. Scanning electron microscopy with energy dispersive X-ray spectroscopy of the scanned area as iron oxide passivation (a) before and (b) after MA for 60 min (pulp density 25 wt.%, P80 19.9 μm)
5.3.2.2 Gold recovery from amorphization

After MA, the XRD peaks were similar at the three PD values tested (Figure 5-11 (a)), except peaks related to gypsum, which decreased in intensity and occurred at smaller 2 theta values (shifted left) with decreasing PD (Figure 5-11 (b)). The peak shift is attributed to the uniform strain and/or the moisture contents of sample (Balaz, 2000; Agarwal et al., 2017). The effect of moisture contents may be related to gypsum (CaSO\(_4\)·2H\(_2\)O), which forms a hydration product. Thus, the sample with shifted peaks likely had lower moisture content due to less gypsum in the sample after MA. The lack of a peak in the 2-theta range corresponded to the dissolution of gypsum for a slurry with a P80 of 8.54 μm (data not shown). The dissolution of gypsum is likely due to the amorphization of gypsum in finer samples. The higher grinding efficiency resulting in more impact or compression at lower PD and higher BPR induced increased amorphization of gypsum. Reduction and shifting of peaks by amorphization after MA have been previously reported and has been attributed to exposing interlocked gypsum and making amorphous
gypsum more soluble (Baláž et al., 1996; Baláž et al., 2003; Alex et al., 2014; Asamoah et al., 2018b; Asamoah et al., 2020). Both effects would have facilitated liberating gold trapped inside the gypsum, leading to the highest gold recovery achieved (Table 5-4). It should be noted that further size reduction from a P80 of 8.54 to 3.46 μm did not further improve gold recovery.

![Figure 5-11](image)

**Figure 5-11.** (a) X-ray diffraction patterns and (b) magnified view of peaks in the 2-theta range of 13.0–14.0 of alkaline POX slurry at three pulp densities after MA

During TGA between 30℃ and 175℃, the weight loss from the alkaline POX slurry was higher at 50 wt.% PD than 25 or 30 wt.% PD (Figure 5-12; Table 5-5). Finer particles (P80 8.54 μm at 50 wt.% PD) lost less weight (~0.96%). At temperatures < 175℃, the weight loss from POX slurry is mostly related to the dehydration of gypsum, iron oxyhydroxides, and dolomite (Gunasekaran & Anbalagan, 2007; Lou et al., 2011; Tripathi et al., 2018). Based on the XRD results (Figure 5-11), dehydration of gypsum could be the dominant mechanism; thus, the weight loss at temperatures < 175℃ depends on the gypsum content of the sample. The TGA results, therefore, indicate again that finer particles (P80: 8.54 μm) contained less gypsum. Differences in weight loss between samples at 175–500℃ and 500–800℃ were minor (Table 5-5). In this temperature range of 500-800°C, the weight loss results from decomposition of pyrite and dolomite
(Schoenlaub, 1969; Gunasekaran & Anbalagan, 2007), and at 500°C, pyrite is also converted to pyrrhotite (Xu et al., 2019). As the gypsum content decreased with MA, the relative content of other minerals increased. Thus, the minor changes between the samples at 175–800°C was attributed to the amount of gypsum. The result indicated that the MA mostly affected the gypsum contents, with minor/no differences in the other minerals. Thus, the additional increase in Au recovery at finer particle size was mostly from the gypsum amorphization. However, no more gold was extracted with the further size reduction (P80: 3.46 μm), which concluded that the remained gold was finely disseminated and/or locked in the sulfide matrix.

![Figure 5-12. TGA graph of alkaline POX slurry after 60 min of MA at three pulp densities (P80: 19.9 μm (25 wt.%), 22.9 μm (33 wt.%), 36.4 μm (50 wt.%) ball to powder ratio 2:1)](image)
Table 5-5. TGA results of alkaline POX slurry after 60 min of MA at three pulp densities (P80: 19.9 μm (25 wt.%), 22.9 μm (33 wt.%), 36.4 μm (50 wt.%) ball to powder ratio 2:1) and at 50 wt.% pulp density (P80 8.54 μm, ball to powder ratio 5:1)

<table>
<thead>
<tr>
<th>Weight change, %</th>
<th>25 wt.%</th>
<th>33 wt.%</th>
<th>50 wt.%</th>
<th>P80: 8.54 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-175°C</td>
<td>-1.30</td>
<td>-1.39</td>
<td>-1.76</td>
<td>-0.96</td>
</tr>
<tr>
<td>175-500°C</td>
<td>-0.45</td>
<td>-0.48</td>
<td>-0.45</td>
<td>-0.53</td>
</tr>
<tr>
<td>500-800°C</td>
<td>-12.24</td>
<td>-12.14</td>
<td>-12.06</td>
<td>-12.13</td>
</tr>
<tr>
<td>Total</td>
<td>-13.99</td>
<td>-14.00</td>
<td>-14.27</td>
<td>-13.51</td>
</tr>
</tbody>
</table>

5.4 Conclusion

MA by grinding for 60 min at a BPR of 5:1 and PD of 50 wt.% increased the gold recovery from alkaline POX slurry during thiosulfate leaching from 59.5 to 72.1%. This was attributed to removal of the passivation layer from the mineral surfaces, exposure of more surface area to the leaching reagent via particle size reduction (P80 56.5 μm to 8.54 μm), and amorphization of gold-bearing minerals, gypsum as the dominant phase. This study suggested that low gold recovery from the alkaline POX slurry partially resulted from passivation by the alkaline POX, but the main problem was caused by the original properties of ores. Thus, new approaches to enhance gold recovery from the alkaline POX discharge should focus on liberating gold that is finely disseminated in the gangue minerals or locked in the sulfide matrix from feed ores.
Chapter 6

The application of acid pretreatment on the alkaline pressure oxidized refractory gold ores and its effect on gold thiosulfate leaching process

6.1 Introduction

From Barrick Gold Corp.’s Goldstrike mine, NV, USA, the run of mine double refractory gold ore contains C-matter and sulfide minerals. The ore is first treated by the POX process followed by thiosulfate leaching to liberate gold from the sulfides and to avoid the preg-robbing effect from the C-matter (Baron et al., 2016). The gold recovery from the alkaline POX discharge is low, at approximately 59% (Lee et al., 2022; chapter 4 & 5). To improve gold recovery, mechanical treatment by ultrafine grinding has been investigated, resulting in a 12% recovery improvement at the 80% passing size of 8.54 μm; however, no additional gold is extracted with further size reduction (Lee et al., 2022; chapter 5).

In this study, acid was used to chemically treat the alkaline POX discharge. The expected impacts were 1) the de-passivation of the by-product (iron oxide/hydroxide) from the alkaline POX process (e.g., iron oxide passivation) (Koslides & Ciminelli, 1992; Thomas & Pearson, 2016), 2) gold liberation from the carbonate minerals by carbonate dissolution, and 3) an increase in porosity, resulting in more contact between thiosulfate and the locked gold. For the acid dissolution, H₂SO₄ was first considered due to its relatively low cost and its local availability (there is a production facility for acidulation prior to the acid POX process at Barrick’s Goldstrike plant in NV, USA). However, H₂SO₄ precipitates gypsum through its reaction with calcium ions from the dissolved dolomite and/or calcite in the alkaline POX discharge (Alimi et al., 2003). The gypsum precipitated during acid dissolution could have a detrimental effect on gold recovery through potential passivation of the gold surface. Thus, HCl was compared with H₂SO₄ as a means
to determine the effect of precipitation as no precipitation occurs when HCl and calcium ions are in contact (Baba et al., 2014).

A limited number of studies have investigated acid dissolution as a pretreatment technique followed by gold or silver leaching (Wang et al., 2018; Portilla et al., 2020). Wang et al. (2018) studied H₂SO₄ leaching for the treatment of pyrite cinder and the copper-silver ores and found that acid pretreatment removed the arsenic and iron from the pyrite cinder prior to gold leaching, resulting in higher gold recovery by non-cyanidation leaching (reagent: Jinchan™; containing SC(NH₂)₂, NaSiO₃, NaOH, (NaPO₃)₆) (Beyuo et al., 2016). Further, H₂SO₄ dissolution before cyanidation led to lower cyanide consumption and faster silver leaching, which was attributed to the reduced amount of copper extraction during cyanidation (Portilla et al., 2020). Both studies showed improvement in gold recovery by acid dissolution pretreatment; however, it was attributed to the removal of the detrimental elements prior to gold leaching, and not due to increased liberation. Acid dissolution as a pretreatment is not a common process; however, the alkaline POX discharge used in this study had complicated mineralogy and poor liberation with 30% carbonate content. Thus, the efficacy of acidulation on the gold recovery is worth considering.

Both H₂SO₄ and HCl treatments were performed under various acid concentrations (HCl: 1.0/2.0/3.0 M and H₂SO₄: 0.5/1.0/1.5 M) and pulp densities (5/10/20 wt.% solids) to determine the dissolution endpoint, when no more acid consumption occurs. With the same concentration, H₂SO₄ contains twice as many hydrogen ions as HCl; thus, double the concentration of HCl was used in this study to maintain constant molar ratios of acid hydrogen ion/sample for both acids. Acid treated samples were then leached in thiosulfate solution. The study aimed to improve the gold recovery in the leaching process and determine the reason for the low gold dissolution. In addition, the results of chemical treatment were compared with those from mechanical treatment by ultrafine grinding (carried out in the previous chapter) (Lee et al., 2022).
6.2 Experimental

6.2.1 Acid dissolution procedure

Acid dissolution was carried out under different conditions. The dissolution tests were performed at various pulp densities (5/10/20 wt.%) and 1.0 M HCl or 0.5 M H₂SO₄. Then, with the selected pulp density, the effect of acid concentration was investigated. The acid concentration was kept constant during the treatment process at HCl concentrations of 1.0/2.0/3.0 M and H₂SO₄ concentrations of 0.5/1.0/1.5 M by adding more acid. Acid concentration was measured by acid-base titration at different time intervals (0.5/1/3/5/8/24 h) and the required amount of additional acid was calculated accordingly. The endpoint of the reaction was determined when more acid was not required to maintain the target acid concentration. Phenolphthalein solution was used as the indicator in acid-base titration and diluted NaOH solution was added using a titrating burette. Each dissolution test was carried out for 24 hours. The results were processed, and the selected optimum conditions were used to carry out the main test followed by thiosulfate leaching. The acid dissolution residues were dried and analyzed using SEM (Scanning Electron Microscopy) analysis and EDX mapping, as well as LPSA (Laser Particle Size Analyzer; Malvern) to determine the particle size distribution of the obtained sample.

6.2.2 Thiosulfate gold leaching procedure

Thiosulfate leaching experiments were performed in an Erlenmeyer flask on a hot plate equipped with a magnetic stirrer with a stirring speed of 400 rpm, temperature of 50°C, and pulp density of 200 g L⁻¹. NaOH (Sodium Hydroxide Solution 1N, Certified, Fisher Chemical™) was used to adjust the initial pH to 9.5 and 0.2 M of sodium thiosulfate salt (Na₂S₂O₃·5H₂O, Certified ACS Crystalline, Fisher Chemical) and 50 ppm of cupric ion as copper sulfate (CuSO₄·5H₂O, ≥ 98.0%, Fisher BioReagents™) were added to the reactor prior to leaching. Subsamples were taken at 1, 3, 5, 8, and 24 h. The leaching solution was then filtered with filter paper (Grade 2, < 8 μm), and then a syringe filter (< 0.45 μm). The samples were all
analyzed by AAS (Atomic adsorption spectroscopy; iCE™ 3300, Thermo Scientific™) for their gold contents. The gold concentration in the residue was determined by fire assay analysis followed by ICP-OES.

6.3 Results and discussion

6.3.1 The effect of acid dissolution conditions

The acid dissolution process was carried out at various pulp densities and acid concentrations. HCl dissolution results indicated that the end point, at which no more acid consumption occurs, was attained faster at lower pulp density which was expected due to less amount of samples at a lower pulp density (Figure 6-1 (a)). Under all HCl concentrations, acid was consumed during the initial 2 h of the dissolution period (Figure 6-1 (b)). Overall, the acid was completed consumed within the first 2 h of the process; after this point no more acid was needed to maintain the acid concentration at the target concentration value. The total acid consumption increased with the increase in pulp density as more reagent was needed to react with a larger amount of sample (Figure 6-1 (a)). The total acid consumption at different acid concentrations varied from 50 ml to 58 ml (Figure 6-1(b)). This could be attributed to the error from the acid titration detection limit and slight differences in the samples’ formed phases. Thus, it can be concluded that maintaining acid concentration above 1 M had no effect on the total acid consumption. The results indicate that HCl dissolution slightly affected the dissolution kinetics, but no effect was observed on the overall acid consumption, suggesting that acid levels were sufficient to facilitate the dissolution reaction. The purpose of acid dissolution pretreatment in the current investigation was to liberate more gold particles mostly from carbonate minerals; thus, enough acid was provided to maximize the effect of the acid dissolution.
Figure 6-1. The effect of (a) pulp density (5-20 wt.%) (the final acid concentration: 1.0 M HCl) (b) the final acid concentration (1.0-3.0 M HCl) (pulp density: 20 wt.% solids) on the acid dissolution performance for 24 h

H₂SO₄ dissolution revealed similar results to HCl dissolution (Figure 6-2). The acid consumption was completed faster at lower pulp densities and the total acid consumption increased at higher pulp densities (Figure 6-2 (a)). The final acid consumption was between 15 ml to 18 ml to maintain target H₂SO₄ concentration (Figure 6-2 (b)). It was also concluded that target acid concentration did not change the total acid consumption at a constant pulp density. Under all test conditions, the overall reaction between the alkaline POX discharge and H₂SO₄ was completed within the initial 2 h. Again, the results indicated that the acid dissolution conditions only affected the rate of acid consumption. Experiments were conducted with sufficient HCl and H₂SO₄ to ensure that the maximum liberation of gold particles will be achieved through the dissolution of carbonates.
Figure 6-2. The effect of (a) pulp density (the final acid concentration: 0.5 M H₂SO₄) (b) the final acid concentration (pulp density: 20 wt.% solids) on the acid leaching performance for 24 hours

A 20 wt.% pulp density was selected to conduct dissolution tests at different acid concentrations to dissolve a larger amount of discharge materials. Acid treatment was then followed by thiosulfate leaching to dissolve gold and assess the efficiency of the acid dissolution procedure on gold leaching. With the acid pretreatment residues, the preliminary leaching test was performed (Figure 6-3). The results revealed that HCl treatment caused a drop in the leaching recovery of gold, and higher HCl concentrations resulted in further reduction in gold leaching recovery. On the contrary, H₂SO₄ dissolution elevated gold recovery to around 70% regardless of the acid concentration (Figure 6-3). Gold recovery was more sensitive to HCl concentration than H₂SO₄ concentration.
Based on the preliminary results, the lowest and the highest acid concentrations (HCl: 1.0 and 3.0 M; H₂SO₄: 0.5 and 1.5 M) were selected to compare the effect of acid concentration on gold leaching. Dissolution durations of 2 h and 24 h were also selected for comparison. Again, the aim of the treatment was the liberation of gold, thus 2 h which showed the endpoint of acid consumption was selected as the shortest dissolution time.

6.3.2 The effect of acid pretreatment on gold recovery

6.3.2.1 Thiosulfate gold leaching after HCl dissolution

With the selected conditions, HCl dissolution was performed followed by thiosulfate gold leaching under the leaching conditions presented in the experimental section. The results presented in Figure 6-4 revealed that in a constant acid concentration, longer acid dissolution duration (24 h compared with 2 h) reduced the gold leaching efficiency. Additionally, a lower acid concentration (1.0 M compared with 3.0 M) resulted in achieving in higher gold dissolution efficiencies. The highest gold leaching recovery (63%) was obtained from the acid treated solid at 1.0 M HCl and 2 h acidulation and the lowest gold leaching
recovery (49%) was achieved for the acid treated materials under 3.0 M HCl and 24 h dissolution conditions. Depending on the HCl dissolution test conditions, higher or lower than baseline (58%) gold recovery values were obtained (Lee et al., 2022; chapter 4 & 5). As can be seen in Figure 6-4, acid treated solids under a shorter dissolution duration (2 h) exhibited faster leaching kinetics with a sharp increase in the first hour of leaching, followed by a slight change in the next 23 h of thiosulfate leaching; however, the solids pretreated for a longer time (24 h) resulted in lower gold leaching recovery after 1 h of leaching, followed by a gradual increase in the leaching recovery over the next 23 h of the leaching period.

Figure 6-4. Au recovery for 24 h with different HCl dissolution conditions (HCl concentration and dissolution time)

The acid treated residues at different HCl concentrations were analyzed by LPSA before and after thiosulfate leaching. According to the size distribution curves presented in Figure 6-5, after HCl dissolution and before leaching, the residue treated under lower HCl concentration (1.0 M) had a slightly larger number of coarse particles than the residue treated under 3.0 M HCl. Additionally, particles finer than 0.2 μm were not detected in any sample before leaching; however, after leaching, fine particles (< 0.2 μm) were produced, and the samples treated under 1.0 M HCl dissolution had a higher volume density of finer particle sizes. This could be attributed to adhesion of finer particles on coarse particles during acidulation, which will
disperse again during leaching. The presence of fine particles in the alkaline POX discharge supported the possibility of adhesion during the HCl dissolution. The coarser particle size distribution after leaching of the sample pretreated under 3.0 M HCl compared with 1.0 M HCl could be indicative of more fine particles adhering on the surface of the coarser ones. The attached particles could result in lower gold recovery, attributed to interfering with the contact between thiosulfate and gold particles. In addition, the different trends obtained for gold leaching kinetics presented in Figure 6-4 could also be explained. With shorter HCl dissolution times, there was weaker/less adhesion between fine and coarse particles, resulting in improved and rapid dispersion following pretreatment. However, longer acid treatment likely increased the magnitude (both strength and quantity) of adhesion of fines to coarse particles, requiring more time for detachment and leaching. Thus, samples with a shorter pretreatment period (i.e., 2 h), showed faster leaching kinetics, with gold recovery reaching a plateau after only 1 h. On the other hand, the samples pretreated for longer periods (24 h) saw a continuous increase in gold recovery over a 24 h period (without reaching a plateau) and the final gold recovery was lower than that for samples pretreated for 2 h. The delayed recovery after a long pretreatment period was likely due to the continuous detachment and leaching of firmly adhered fine particles over the 24 h leaching period.
6.3.2.2 Thiosulfate gold leaching after H$_2$SO$_4$ treatment

Thiosulfate gold leaching tests were performed after H$_2$SO$_4$ pretreatment. The initial gold recovery at 1 h was the highest for the sample treated under 0.5 M H$_2$SO$_4$ concentration for 24 h, and the final recovery values for all samples were in a close range of 63% to 67% (Figure 6-6). Overall, H$_2$SO$_4$ treatment resulted in enhanced gold leaching recovery with regards to the untreated sample (59%). However, there was no distinct relation between H$_2$SO$_4$ dissolution conditions and Au recovery.
Figure 6-6. Gold leaching recovery behavior of acid treated samples under different H₂SO₄ dissolution conditions (H₂SO₄ concentration and acid dissolution time)

Figure 6-7 presents the total C and S contents in the acid treatment residues. Acid treatment under higher H₂SO₄ concentration and longer dissolution time resulted in lower total C and higher total S contents in the acid dissolution residue. The higher S value indicates that more gypsum was precipitated during H₂SO₄ treatment. The change in the C content was attributed to carbonate dissolution; however, it more likely originated from the increasing the mass of the sample resulting from gypsum precipitation, leading to a drop in the relative C weight percentage. The duplicate leaching test resulted in a final gold recovery between 64.5% to 67.0% (Figure 6-6). Altogether, it can be concluded that H₂SO₄ dissolution liberated locked gold by decomposing carbonate minerals with little influence from dissolution conditions (in the range under investigation in the current study), ultimate improving gold recovery in thiosulfate leaching. The minor difference in gold recovery was attributed to the gold distribution from samples.
6.3.3  HCl and H$_2$SO$_4$ dissolution: a comparison

It was shown that HCl dissolution reduced gold recovery at higher concentrations and longer acid dissolution times, while H$_2$SO$_4$ dissolution enhanced thiosulfate gold leaching recovery under all acid dissolution experimental conditions. The results contradicted the hypothesis that precipitated gypsum on the surface of gold could interfere with gold extraction. SEM analysis was performed on acid-treated samples under different acid dissolution conditions investigated so far, and the results are presented in Figure 6-8. The SEM image of the HCl-treated samples (Figure 6-8 (a) & (b)) clearly shows the adhesion of the particles which resulted in formation of larger agglomerates and a decrease in the amount of the finer needle shape particles. This confirms the reason for the lower gold leaching recovery which was discussed in section 6.3.2.1 and for the LPSA results (Figure 6-5). In this regard, the SEM graphs of the samples treated under different H$_2$SO$_4$ concentrations show more separate particles and clean surfaces (yellow boxes) compared with the HCl treated samples, as well as finer rod and needle shaped particles (Figure 6-8 (c) & (d)).
HCl dissolution generally decreased the gold recovery, but the dissolution at 1.0 M and 2 h slightly enhanced gold leaching recovery (63%) with regards to the baseline recovery (59%). Therefore, the acid treatment can positively affect the gold leaching recovery, but the detrimental effect of particle adhesion inhibits efficient leaching of gold particles. Diluted acid dissolution was performed to assess the effect of the liberation and find the conditions in which the detrimental effect was more prevalent. The acid concentrations were 1%, 5%, and 10% (HCl: 0.3/1.5/3 M; H₂SO₄: 0.1/0.5/1 M without additional acid to maintain acid concentration). The results indicated that HCl dissolution with diluted acid resulted in 58-63% of gold recoveries and H₂SO₄ treatment resulted in 59-60% of gold recoveries (Figure 6-9). The slightly
higher gold recovery with HCl treatment than for the baseline indicated that HCl dissolution could liberate gold particles to some extent, and the weak HCl concentration has no detrimental effect on gold recovery; therefore, a more concentrated acid solution is required to liberate a higher proportion of the gold. Thus, the detrimental effect might only occur at an elevated concentration of HCl, leading to a reduction in gold leaching recovery. In H₂SO₄ treated samples it was shown that the enhancement in gold leaching recovery started at concentrations over 10%, and the dilute acid solution did not affect the gold leaching recovery.

![Figure 6-9. Au recovery results after the acid treatment with dilute acid (1, 5, and 10%)](image)

In summary, acid dissolution treatment on the alkaline POX discharge could enhance gold recovery in the thiosulfate leaching step; this enhancement could be attributed to liberating the encapsulated gold particles. In addition, during the alkaline POX process, the formed iron oxide can cover the surface of reactive gold-containing minerals such as sulfide minerals, resulting in an insufficient sulfide oxidation and consequently low gold recovery. Figure 6-10 shows the SEM image of an HCl treated sample. The elemental mapping of the blue box denotes higher pyrite content, which was expected to be oxidized in the alkaline POX process; its presence in the acid-treated sample could be indicative of its prior passivation by POX products such as iron oxide, which were dissolved in the acid treatment process and rendered a clean liberated surface.
This de-passivation process would likely expose a proportion of encapsulated gold particles in the cover layers to the leaching lixiviants and lead to a higher gold leaching recovery.

Figure 6-10. SEM and EDX mapping results of acid dissolution residue (HCl 3.0 M, 24 h) (Blue box: expected as the unoxidized pyrite which was covered by the passivation before the acid dissolution).

The chemical process of H$_2$SO$_4$ treatment boosted the gold recovery in the thiosulfate leaching step. However, the gold recovery never exceeded 70%, and overall, less enhancement was achieved than mechanical treatment (Lee et al., 2022, chapter 5). The remaining 30% of gold is finely locked in the gangue and/or matrix so that chemical and mechanical treatments cannot expose them to the leaching lixiviant and thus enhance gold leaching recovery. Both pretreatment investigations indicate that the gold remaining in the leach residue was finely disseminated in minerals other than carbonates, which must be decomposed to recovery the gold.
6.4 Conclusion

Acid treatment with HCl and H$_2$SO$_4$ was applied to the alkaline POX discharge as a chemical treatment to obtain better gold dissolution. Pulp density and acid concentration only affected the dissolution kinetics. Overall, the reaction between the acid and the sample was completed within 2 h under all test conditions. Based on the acid treatment test results, 2 h and 24 h and the lowest and highest acid concentrations (HCl: 1.0 M and 3.0 M; H$_2$SO$_4$: 0.5 M and 1.5 M) were selected as the acidulation conditions for subsequent thiosulfate gold leaching experiments. HCl treatment under higher concentrations and longer treatment durations resulted in reduced gold recovery due to the formation of agglomerates. However, H$_2$SO$_4$ treatment increased the gold recovery, and the treatment conditions had no significant effect on the obtained recovery values; the higher gold leaching recovery obtained from acid treatment was attributed to the liberation of the locked gold particles by dissolution of the passive layer in the acid. In comparison with the gold recovery with the mechanical treatment, it was further confirmed that the remaining 30% of gold in the leach residue was unreachable locked gold in other minerals, which cannot be exposed to the leaching lixiviant.
Brief conclusion of part I and move to Part II

In conclusion, poor gold recovery from the alkaline POX discharge was identified to be a function of the original ore properties, which could not be addressed through the current process of the alkaline POX process followed by thiosulfate gold leaching. The main cause of low gold recovery was attributed to the finely scattered and locked gold in the ore, which was not liberated in the current process even with the additional pretreatment methods. Based on the conclusion of Part I, Part II evaluated pre-flotation of the alkaline POX feed as an alternative process to improve gold recovery. Since roasting is known to be effective in liberated gold locked in C-Matter, it is expected that removal of C-matter through flotation, followed by roasting of C-matter flotation concentrate and pressure oxidation of the low C-Matter content flotation tailings will result in improved overall gold recovery.
Part II Treatment on alkaline POX feed

Chapter 7

The separation of carbonaceous matter from refractory gold ore using multi-stage flotation: a case study²

7.1 Introduction

In the flotation of C-matter from gold ore, C-matter with low gold concentration is separated and then discarded, while C-matter possessing high gold concentration is treated by roasting before extracting gold by cyanidation (Afenya, 1991; Fraser et al., 1991; Yang et al., 2015). The main objective of this study was to separate C-matter from refractory gold ore with high recovery and selectivity such that the C-matter concentrate can be treated in a Goldstrike’s roaster, which has limited capacity. Thus, the mass of the C-matter concentrate must be low, while removing as much C-matter as possible from the feed to POX; the flotation tailings can then be treated in an autoclave to oxidize sulfides and liberate more gold, followed by thiosulfate leaching for gold extraction. By roasting C-matter concentrate, more gold can be liberated from the C-matter, which is not decomposed by the present process, leading to improved gold recovery. The gold recovery from the tailings may not be improved because it is treated by the same procedure of alkaline POX, followed by thiosulfate gold leaching; however, the finer particle size required for the flotation than the present process (P80 size of the alkaline POX discharge: 56.5 μm) could result in greater liberation of sulfide and gold, leading to higher oxidation efficiency and gold recovery. Through the proposed process,

all gold in the ore is processed, but this is carried out separately by each effective treatment on the concentrate and tailings.

Due to the natural hydrophobicity of C-matter, flotation without collector (pre-flotation) can be carried out for its separation. However, it has been reported that collector-less flotation results in low selectivity, insufficient recovery, and high consumption of frother (Gredelj et al., 2009); the use of collector in combination with frother contributed to improved performance. In the flotation of C-matter, adding diesel as collector increases both recovery and kinetics, and lowers the amount of frother (typically MIBC; 4-Methyl-2-pentanol) required for effective flotation by preventing MIBC adsorption on the surface of the particles (Gredelj et al., 2009; Zhang & Honaker, 2015). Fuel oils, such as kerosene and diesel, result in improved recovery by increasing hydrophobicity. However, overdosing the collector leads to poor selectivity by collecting more minerals or ash (in the case of coal flotation), either through the recovery of middling particles, or through hydraulic entrainment (Polat et al., 2003; Naik et al., 2005). For C-matter flotation, the combination of a conventional oil collector and alcohol frother provides a satisfactory result; however, the optimum dosage should be determined for high selectivity and sufficient recovery.

Flotation performance is influenced by the conditions in each stage, and by the circuit’s configuration and design—the optimum design is determined by simulation and/or testing (Sutherland, 1981; Calisaya et al., 2016). For most types of ore, a multi-stage flotation circuit (i.e., a combination of rougher/scavenger/cleaner) is required to accomplish better separation efficiency (Sutherland, 1981; Honaker & Mohanty, 1996; Tao et al., 2000). Calisaya et al. (2016) compared five alternative circuits obtained using simulation and showed that the optimum metallurgical conditions (e.g., reagent dosages, additional milling, scraping speed) in each stage are all the same regardless of the circuit design. However, with the selected optimum conditions, the overall performance is changed by the circuit design. Sutherland (1981) determined that the best performance is achieved when the circuit is arranged as rougher and cleaner with equal residence time. The simulation results indicated that the addition of a cleaner flotation stage improved the flotation selectivity with kinetic rate limited flotation and non-selective detachment.
conditions; in addition, the number of cleaner stages for further selectivity improvement is determined by the middling contents (Honaker & Mohanty, 1996). In coal column flotation testing, the highest separation efficiency is attained using either a rougher-scavenger-scavenger-cleaner or a rougher-scavenger-cleaner flotation configuration (Tao et al., 2000). In graphite flotation with scrubbing treatment by attrition mill for high selectivity, more stages of cleaner flotation only resulted in decreased recovery, with no improvement in grade (Lu & Forssberg, 2001). The study concludes that the efficacy of the cleaner flotation is influenced by the nature of the feed-to-cleaner circuit. For the best flotation performance, both the optimization of each stage flotation and the investigation of flotation circuit design should be considered.

In typical flotation circuits, the rougher and scavenger concentrates are combined to form the feed to cleaner flotation. However, in this study, the cleaner flotation of the rougher concentrate and the scavenger concentrate were carried out separately to evaluate the effectiveness of different circuit configurations using a limited number of tests. Considering this, four flotation circuit designs were evaluated to assess their potential for recovery of C-matter from Goldstrike’s double refractory gold ore (Figure 7-1): (1) single-stage rougher flotation (R), (2) rougher flotation followed by scavenger flotation (R+S), (3) rougher-scavenger flotation followed by cleaning of the scavenger concentrate (R+S+SC), and (4) rougher-scavenger flotation followed by cleaning of the rougher and scavenger concentrates, separately (R+S+RC+SC). In addition, the optimum conditions of each stage were determined by testing different reagent dosages. The flotation products from each configuration were evaluated in terms of overall C-matter recovery and combined concentrate grade.
Figure 7-1. The flotation circuit design from the results (a) R: single-stage rougher flotation (b) R+S: rougher and scavenger flotation (c) R+S+SC: rougher, scavenger, and scavenger cleaner flotation (d) R+S+RC+SC: rougher, rougher cleaner, scavenger, and scavenger cleaner flotation.

This study aims to determine the best flowsheet to separate C-matter from the gold ore with the highest selectivity; the desired recoveries and grades were above 90% and 10%, respectively. To perform selective and efficient C-matter flotation, each stage of flotation was carried out with different reagent conditions (selected to achieve the best performance), and the results were compared for the different circuit configurations to identify the circuit design yielding the best selectivity.

7.2 Experimental

Rougher and scavenger flotations were performed followed by cleaner flotation for each concentrate (Figure 7-2). Rod mill (400 mm×175 mm) grinding was carried out prior to flotation testing to reduce the particle size with 11 kg of various size rods for 10/15/20 min at 33 wt.% solids. All the tests were performed in a Denver laboratory flotation machine. Kerosene (>99%, Fisher Chemical™, Hampton,
USA) and methyl isobutyl carbinol (MIBC) (4-Methyl-2-pentanol, 98%, Sigma-Aldrich, Saint Louis, USA) were selected as the collector and frother, respectively.

Figure 7-2. The proposed flotation process for the separation of C-matter

Additionally, a laboratory-stirred media mill (PE 075, Netsch, Shanghai, China) was used for further fine grinding for the determination of the limited flotation performance.

7.2.1 Rougher flotation

The rougher flotation was carried out with different particle sizes (P80: 36.5, 44.6, and 67.7 μm) and reagent dosages (Kerosene: 50/100/200/300/500 g t⁻¹; MIBC: 30/60/90/120/150 g t⁻¹). The ground ore was mixed with tap water at 25 wt.% solids for 3 min, then kerosene and MIBC were added into the 2.5 L cell and conditioned for 1 min at 1,200 rpm. The froth was collected at different time intervals (0.5/1.5/2.5/4.5/6.5 min). The impeller speed was 1200 rpm for both the conditioning and the froth collection.

7.2.2 Scavenger flotation
Following the rougher flotation, tap water (200 mL) was added to increase the water level. Different dosages of kerosene (70/210/350 g t\(^{-1}\)) and MIBC (21/42/63 g t\(^{-1}\)) were added to the 2.5 L flotation cell. The conditioning time was again 1 min for kerosene and MIBC and separate froth products were collected as flotation time elapsed (0.5/1.5/2.5/4.5 min). The impeller speed was 1200 rpm for both conditioning and froth collection.

7.2.3 Cleaner flotation

For each rougher and scavenger concentrate, the cleaner flotation was conducted with additional water (500 mL for rougher-cleaner and 350 mL for scavenger cleaner) and reagents in a 1.0 L flotation cell at 1200 rpm. For rougher cleaner flotation, 36–108 g t\(^{-1}\) of kerosene and 11-32 g t\(^{-1}\) of MIBC were added with 1 min of conditioning time for each, and flotation was performed for a total of 4.5 min with separate concentrate products collected after 0.5, 1.5, 3.0, and 4.5 min. Scavenger cleaner flotation was conducted with 42-125 g t\(^{-1}\) of kerosene and 11-32 g t\(^{-1}\) of MIBC for 1 min of conditioning each; the froth was collected for a total of 3 min with separate concentrate products collected after 0.5, 1.5, and 3.0 min.

Each concentrate and tailings product were dried, then weighed. The C-matter was determined as total carbon content, except for carbon from carbonate. For the analysis of the C-matter, HCl dissolution was carried out on a representative subsample. A 3 g subsample was dissolved in 20% HCl solution (Certified ACS Plus, 36.5 to 38.0%, Fisher Chemical) at 60°C for 1 h. The dissolved sample was filtered, then washed well with deionized water (D.I water). A C/S analyzer (ELTRA, CS 2000) was used to determine the carbon and sulfur contents of the samples before and after HCl dissolution. For the kinetics study, the classical first order model was fit to the test results (Equation 7-1).

\[
R = R_\infty (1 - e^{-kt})
\]  

(7-1)

R is recovery, \(R_\infty\) is the ultimate recovery with infinite time, and k is the rate constant (min\(^{-1}\)).
7.3 Results and discussion

7.3.1 Rougher flotation

In rougher flotation, across the conditions tested, C-matter recovery ranged from 40% to 70%, with grades between 2% and 4% (Table 7-1). Tests 7, 9, 10, and 11 showed higher C-matter recovery (> 67%) than the others. These tests featured finer particle sizes (P80: 36.5 μm) and resulted in a higher concentrate grade, attributed to higher MIBC dosages between 60 to 150 g/t (Table 7-1). Tests 5-7 were conducted with the same reagent dosages, but the feed particle size distribution varied; as the particle size decreased, recovery increased. The concentrate grade was the lowest in the intermediate size range tested (P80: 44.6 μm; Test 6), likely resulting from a combination of fine particles and poor liberation. As the particle size decreases, the entrainment factor increases, leading to reduced selectivity (Neethling & Cilliers, 2009; Yianatos & Contreras, 2010). However, the flotation rate and recovery tend to increase as liberation improves with finer size while the recovery of gangue (carbonate and silicate) decreases (Albijanic et al., 2015; Hoang et al., 2018). Thus, the results showed that as the particle size decreased from a P80 of 67.7 µm to a P80 of 44.6 μm, gangue entrainment increased with the minor change in mineral liberation, leading to a decrease in the concentrate grade. However, when the particle size was further reduced to a P80 of 36.5 μm, improved liberation resulted in slightly higher recovery and grade through the reduction of gangue recovery. In Test 8, C-matter recovery was significantly lower (51%) with the fine particle size (P80: 36.5 μm). This result was due to a low dosage of MIBC (30 g t⁻¹), which was insufficient to form stable froth and small bubbles. Further information on the effect of MIBC dosage on C-matter flotation recovery from Goldstrike’s ore is detailed in a separate study (Lee et al., 2021a, chapter 8). Significantly lower recovery (41%) with 30 g/t of MIBC was also observed in Test 12, with coarser feed. Additionally, C-matter recovery was low with coarser feed material (P80: 67.7 μm) in Tests 1 and 2, with a low dosage of kerosene (50 and 100 g t⁻¹). Hence, in rougher flotation, it was concluded that a sufficient reagent dosage and finer feed particle sizes were required to obtain high C-matter recovery.
Table 7-1. Rougher flotation test conditions (agitation speed: 1,200 rpm, pulp density: 25 wt.%, flotation time: 6.5 min)

<table>
<thead>
<tr>
<th>Test</th>
<th>Kerosene dosage, g t⁻¹</th>
<th>MIBC dosage, g t⁻¹</th>
<th>P80, μm</th>
<th>Recovery, %</th>
<th>Grade, %</th>
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The purpose of the rougher flotation was high C-matter recovery; thus, Test 10 was selected as the optimal conditions for rougher flotation, as this test corresponded to maximum recovery (69.87%), with a high C-matter grade (3.42%) in the rougher concentrate. Test 11 also resulted in high recovery (70.09%) with high grade (3.62%); however, the difference in recovery and grade was insignificant and Test 10 was chosen as it used a lower MIBC dosage (120 g t⁻¹). Figure 7-3 describes the flotation results again with yield and grade; both the C-matter recovery and yield increased together with the increased flotation time, but after 2.5 min, the increased C-matter recovery began to plateau, while the yield continued to increase. Above this point, further improvement in selectivity was not possible. Thus, the flotation time for the rougher flotation was limited to 2.5 min for subsequent test work.
Figure 7-3. Rougher flotation results with the selected conditions (Test 10 – kerosene: 500 g t⁻¹; MIBC: 120 g t⁻¹; P80: 36.5 μm).

7.3.2 Scavenger flotation

Additional kerosene and MIBC effects were investigated in the scavenger flotation testing. The scavenger overall recovery—the recovery in the scavenger as a function of the feed to rougher flotation is presented in Table 7-2. In contrast to the rougher flotation showing a 30% difference in recovery, the scavenger overall recovery saw limited change as a function of reagent dosage (the variation in recovery was less than 4% between all the conditions tested). The limited change to the C-matter recovery with different reagent dosages could be attributed to the presence of residual reagents from the rougher flotation and the low floatability of the remaining particles. In the rougher flotation, the most floatable particles are collected first, leaving behind locked or middling particles, which are more difficult to float (Tsatouhas et al., 2006). Thus, the limited floatability, likely resulting from the locked or composite particles, led to the minimal change in C-matter recovery in the scavengers with changes in the reagent dosage.
Table 7-2. Scavenger flotation results (rougher flotation for 2.5 min: C–matter recovery mean 54.49% (SD: 2.19%) (agitation speed: 1,200 rpm, flotation time: 4.5 min, pulp density: 20 wt.%)

<table>
<thead>
<tr>
<th>Test</th>
<th>Kerosene Dosage, g t⁻¹</th>
<th>MIBC Dosage, g t⁻¹</th>
<th>Scavenger Overall Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>21</td>
<td>24.12</td>
</tr>
<tr>
<td>2</td>
<td>210</td>
<td>21</td>
<td>24.98</td>
</tr>
<tr>
<td>3</td>
<td>350</td>
<td>21</td>
<td>28.69</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>42</td>
<td>26.29</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>63</td>
<td>25.95</td>
</tr>
<tr>
<td>6</td>
<td>350</td>
<td>42</td>
<td>25.84</td>
</tr>
<tr>
<td>7</td>
<td>350</td>
<td>63</td>
<td>27.70</td>
</tr>
</tbody>
</table>

Although the influence of the reagent dosage on the recovery in the scavenger was weaker than in the rougher flotation, the scavenger helped to collect more C–matter than with a single rougher flotation stage (Figure 7-4). The additional kerosene and the longer conditioning time likely increased the hydrophobicity of slow-floating middling particles, increasing their floatability. The selected test results for the highest recovery in the scavenger are presented in Figure 7-4, along with the rougher results; however, the C–matter grade was much reduced by the scavenger flotation. This resulted from the higher-grade matter collected in the rougher stage and the greater entrainment in the scavenger stage.
Figure 7-4. The selected rougher-scavenger flotation results (Kerosene: 350 g t\(^{-1}\); MIBC: 21 g t\(^{-1}\)) compared with the rougher flotation results.

7.3.3 Cleaner flotation

The cleaner flotation for each rougher concentrate (C-matter recovery mean: 52.04%; SD: 1.65%) and scavenger concentrate (C-matter recovery mean: 27.04%; SD: 2.99%) was carried out with the further addition of reagents. Changes to the reagent dosage had a minor effect on cleaner flotation performance. Cleaner stage flotation performance was evaluated based on the feed to the cleaner circuit (i.e., it was assumed the rougher and scavenger concentrates contained 100% of the C-matter). The rougher cleaner showed a higher stage recovery (90-94%) compared with the scavenger cleaner (84-89%). The test conditions that resulted in the highest selectivity were 36 g t\(^{-1}\) of kerosene and 11 g t\(^{-1}\) of MIBC for the rougher-cleaner and 83 g t\(^{-1}\) of kerosene and 11 g t\(^{-1}\) of MIBC for the scavenger-cleaner. Under these conditions, in the rougher cleaner, the stage recovery was 90.11%, corresponding to 45.95% overall recovery (i.e., based on the feed to the rougher circuit) with 5.18% grade. The scavenger-cleaner flotation
required more kerosene (83 g t\(^{-1}\)) to achieve an 86.68% stage recovery (overall recovery 26.27% with 2.87% grade).

### 7.3.4 Comparison of flotation circuit configurations

The flotation circuit design options are shown in Figure 7-1. The flotation performances in each circuit were compared in terms of C-matter recovery and grade (Figure 7-5). The R+S flowsheet resulted in higher C-matter recovery (85.31%) than the single-stage flotation (R: 69.87%), although increased recovery corresponded to a significant reduction in C-matter grade from 3.42% to 2.20%. This was due to the increased recovery of the middling particles and hydraulic entrainment during the scavenger flotation. As more middling particles were collected, the C-matter recovery increased. However, it also reduced the concentrate grade. With the scavenger cleaner flotation (R+S+SC), C-matter recovery decreased (77.26%) compared with R+S flotation; however, it upgraded the C-matter concentrate to 3.39%, suggesting that the scavenger cleaner flotation stage was necessary for effective separation. This can be attributed to the difference in the kinetics. The increase in the grade at the cleaner stage is discussed with the kinetics in the next section. By adding a rougher cleaner flotation stage, C-matter recovery decreased again to 72.22% with a further improvement in concentrate grade (4.01%), which was a higher recovery and grade than the single-stage flotation I. Again, the cleaner stage had an effect on the improvement of the grade from the rougher concentrate, but the increased grade was less than the scavenger cleaner. This was attributed to the reduced middling recovery and the entrainment in the rougher concentrate compared with the scavenger concentrate.
Figure 7-5. Flotation test results with the selected conditions in each flotation circuit (R-kerosene: 500 g t\(^{-1}\), MIBC: 120 g t\(^{-1}\), 6.5 min; R+S: R-kerosene: 500 g t\(^{-1}\), MIBC: 120 g t\(^{-1}\), 2.5 min and S-kerosene: 250 g t\(^{-1}\), MIBC: 21 g t\(^{-1}\), 4.5 min; R+S+SC: SC-kerosene: 83 g t\(^{-1}\), MIBC: 11 g t\(^{-1}\), 3.0 min, R+S+RC+SC: RC-kerosene: 36 g t\(^{-1}\), MIBC: 11 g t\(^{-1}\), 4.5 min and SC-kerosene: 83 g t\(^{-1}\), MIBC: 11 g t\(^{-1}\), 3.0 min)

Overall, by adding a cleaner flotation stage, the selectivity was greatly improved. The flotation rate constant was obtained by using Equation (7-1), indicating that the cleaner flotation had a higher flotation rate constant than the rougher flotation (Figure 7-6). Thus, in the cleaner flotation, much faster flotation kinetics with shorter flotation times resulted in higher selectivity by reducing the recovery of middling, composite particles, or gangue, which have slower kinetics. Additionally, the rougher cleaner stage was generally faster than the scavenger cleaner. This result can also be attributed to the presence of more liberated C-matter having lower attachment times in the rougher cleaner feed than in the scavenger cleaner feed (Figure 7-6 (b)) (Albijanic et al., 2015). The faster flotation kinetics with higher dosages of kerosene in the scavenger cleaner indicated that the kerosene improved the collection of more liberated C-matter particles, which led to higher selectivity.
In this study, the cleaner flotation was effective for further improvement in the selectivity. In a simulation study, conducted by Honaker and Mohanty (1996), on column flotation for fine coal cleaning, it was shown that the efficacy of the cleaner stage depends on non-selective detachment conditions and the collected amount of middling (Honaker & Mohanty, 1996). Thus, the scavenger flotation may help to collect more C-matter, which was detached during the rougher stage. However, the scavenger flotation collected middling as well, leading to reduced grade. Improved selectivity in the scavenger cleaner flotation stage indicated that more middling and gangue were collected as scavenger concentrate; middling and gangue were rejected in the cleaner stage.

Figure 7-6. Rate constant changes by (a) kerosene dosage level (b) MIBC dosage level in rougher and cleaner flotation (sca. cleaner (low): with low dosage of kerosene, 42 g t\(^{-1}\) and sca. cleaner (high): with high dosage of kerosene, 125 g t\(^{-1}\) in scavenger cleaner) obtained by the classical first order model \((R^2 > 0.96)\)

7.3.5 The investigation of the limited flotation performance

A superior flotation performance was achieved through multi-stage flotation than through single-stage flotation. However, even under the most promising flotation conditions, C-matter recovery was less
than 90% and the flotation concentrate grade was less than 10%. Flotation performance less than the target grade-recovery value could be attributed to the poor liberation of C-matter in the feed even at a fine grind size (P80: 36.5 μm). For the analysis, mineral liberation analysis (MLA) was attempted; however, MLA was not able to detect the presence of C-matter. This may be because of the low concentration of C-matter in the feed (1.95%), the fine grain size of the C-matter, and the complex mineralogy, again supporting the theory that the ore comprised of very finely disseminated C-matter. The particle size analysis (P80 value) results showed that the rougher concentrate was finer than the scavenger concentrate, and all the concentrates featured smaller particle sizes than tailings (Table 7-3). This may suggest that the floatability was related to the particle size, with increased floatability at finer particle sizes due to better liberation of finely disseminated C-matter.

Table 7-3. Particle size analysis results of each concentrate and tailings

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P80, μm</td>
<td>30.3</td>
<td>42.5</td>
<td>38.5</td>
<td>43.0</td>
<td>46.6</td>
</tr>
</tbody>
</table>

Instead of MLA, tests were performed to determine the relationship between the floatability and the particle size. To investigate the effect of further size reduction on floatability, two tests (Test 1 and Test 2) were conducted with the same size of samples with the rougher flotation study (P80: 36.5 μm) and one more test (Test 3) was performed with ultrafine grinding (P80: 11.3 μm). Additionally, to achieve flotation with minimal entrainment, flotation was carried out by only collecting the black froth using the naked eye, regardless of kinetics. It is thus postulated that only true flotation occurred in this test, with minimal entrainment. The test conditions were varied in terms of reagent dosage, agitation speed, and aeration rate to obtain the black froth, as described in the Appendix (Tables C-1, C-3, and C-5). All the tests were continued until no more black froth floated. The results of Tests 1 and 2 were almost the same, regardless of the test conditions (Figure 7-7; Tables C-2 and C-4), which indicated that the black froth was collected selectively and that this test effectively estimated the amount of collectable material by true flotation.
effectively. Flotation after fine grinding by the stirred media mill (P80: 11.3 μm of the whole ore sample) resulted in a significant improvement in the selectivity compared with the coarser grind sizes (Figure 7-7; Table C-6). It supported the assumption that finer grinding led to improved liberation, ultimately achieving better flotation selectivity.

![Figure 7-7. C–matter recovery vs. grade by test 1, 2, and 3](image)

Additionally, the Test 1 and Test 2 (P80: 36.5 μm) results indicated that the recovery was lower (60%) than the test result from the multi-stage flotation (R+S+RC+SC-recovery: 72%, grade: 4%), while the grade was higher (7.6%) (Table 7-4), suggesting that the C-matter collected by the multi-stage flotation was likely the result of both true flotation and the entrainment of particles (which is inevitable in flotation testing). It also supported the notion that the efficacy of the cleaner stage is determined by the amount of middlings; with the middling in the feed, the cleaner stage is effective for better selectivity (Honaker & Mohanty, 1996). In addition, the C-matter grade (7.68%) with 60.45% recovery was still low, meaning that the collected C-matter featured a strong association with gangue minerals due to its poor liberation. The higher C-matter recovery (71.81%) with increased grade (8.76%) with fine grinding suggested that the
locked C-matter was a limiting factor in flotation performance, and that the finer particle size can lead to better selectivity. However, 30% of the C-matter remained as non-floatable matter even with the selective flotation and a fine particle size of P80 11.3 μm. It is likely that the remaining C-matter was very finely disseminated, and even ultrafine grinding was insufficient to achieve high floatability with high selectivity.

Table 7-4. The selective flotation test results

<table>
<thead>
<tr>
<th></th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cum. C-matter recovery, %</td>
<td>60.45</td>
<td>59.61</td>
<td>71.81</td>
</tr>
<tr>
<td>Cum. C-matter grade, %</td>
<td>7.68</td>
<td>7.61</td>
<td>8.76</td>
</tr>
</tbody>
</table>

The different circuit designs can be ranked in the following order, from best to worst: R+S+SC+RC > R > R+S+SC > R+S. Through R+S+RC+RC flotation, 72% C-matter with a 4.01% grade and 28% of C-matter with a 0.87% grade remained in the concentrates and tailings, respectively; 45.3% of gold was collected with the concentrate (33.2% yield) and 54.7% (66.8% yield) of gold remained in the tailings. The final C-matter recovery was less than 70%, which is not sufficient. As a subject for future study, the application of novel flotation reagents and oil collector emulsion, which are effective at ultrafine grind sizes, may help to improve selectivity in flotation. Studies have shown that certain neutral oils perform very well at ultrafine grind sizes in the flotation of minerals such as molybdenite (Lin et al., 2018), but have yet to be tested on other mineral systems.

7.4 Conclusion

As a first stage of pretreatment, a C-matter flotation study was investigated with the assessment of multiple flotation circuit configurations. Through the testing of rougher, scavenger and cleaner flotation, the optimum conditions for each stage were determined, and the flotation performance was assessed considering a combined final concentrate product. For the highest combined grade and recovery, a
flowsheet including R+S+RC+SC demonstrated the most potential, resulting in 72% C-matter recovery with 4% C-matter grade. Through the additional testing, it was determined that the limited overall C-matter recovery was attributed to poor liberation. With the optimized flotation process presented in this study, it is recommended that the concentrate and tailings products be subjected to further testing using a suitable downstream process (i.e., roasting followed by cyanidation for the concentrate, and the POX process followed by thiosulfate leaching for the tailings) to determine the effect of C-matter flotation on overall gold recovery.
Chapter 8

Flotation of carbonaceous matter from a double refractory gold ore: the effect of MIBC on flotation performance and kinetics

8.1 Introduction

For identifying the optimal conditions for C-matter flotation from Goldstrike ore, the effect of methyl isobutyl carbonyl (MIBC) as a frother was investigated, with a focus on bubble and foam/froth formation. In flotation, it is well known that the frother reduces the bubble size by preventing bubble coalescence (Cho & Laskowski, 2002; Grau et al., 2005); therefore, bubble size decreases with increasing frother concentration until it reaches a minimum. The frother concentration after which bubble size remains constant is known as the critical coalescence concentration (CCC) (Cho & Laskowski, 2002; Grau et al., 2005). The CCC is a function of the frother type; MIBC is reported to have a CCC between 9 and 12 ppm (Cho & Laskowski, 2002; Laskowski, 2004; Gupta et al., 2007; Guven et al., 2020). As the MIBC concentration increases, the Sauter mean diameter of the bubble ($D_{32}$) decreases from 2.0-4.0 mm at 0 ppm to around 1.0 mm at the CCC, depending on the test conditions (Cho & Laskowski, 2002; Laskowski, 2004; Gupta et al., 2007; Finch et al., 2008). With an increase in MIBC concentration from CCC to 15-100 ppm, the $D_{32}$ shows a minor change of less than 0.3 mm. It has been demonstrated that bubble size is reduced by breakup, which is promoted by an unstable bubble surface, as more frother is added (Finch et al., 2006; Finch et al., 2008; Kracht & Finch, 2009). The frother changes the bubble velocity as bubbles with a frother rise more slowly than those without a frother (Zhou et al., 1992; Sam et al., 1996; Rafie et al., 2011). This

decreased bubble rise speed in the presence of a frother is attributed to a change in drag force, caused by bubble size, and bubble shape (more spherical bubbles are formed with a frother), and interaction between the frother and water molecules (Zhou et al., 1992; Zhou et al., 1993; Wu & Gharib, 2002; Kracht & Finch, 2010). The rise speed of bubbles influences the probability of collision in flotation, ultimately influencing flotation performance (Zhou et al., 1992).

In addition to its impact on the bubbles, the frother contributes to changes in foamability and froth structure. Unstable froth can lead to recovery loss, and therefore froth structure is an important parameter in effective flotation (Tsatouhas et al., 2006). Several studies have reported that foamability increases with increasing frother concentration (Barbian et al., 2003; Laskowski et al., 2003; Gupta et al., 2007; Moreno et al., 2021). Zheng et al. (2006) demonstrated that increased froth height and retention time result in reduced entrainment. Further, the frother induces changes in the froth structure. Foam is classified as either wet foam or dry foam; wet foam has a thicker liquid wall between bubbles and while it carries more water, it can also have better drainage (Malysa, 1992; Melo & Laskowski, 2006). In spite of this, studies by Smith and Warren (1989) and Zheng et al. (2006) showed that fine particle entrainment decreases as water recovery to the concentrate decreases. This observation is supported by Barbian et al. (2005), who demonstrated that foam stability affects flotation performance in terms of grade.

Researchers have also shown that flotation kinetics is influenced by the frother addition. It has been demonstrated that specific bubble surface area (\(S_b\)) positively correlates with the first-order rate constant (Gorain et al., 1997); as bubble size decreases (\(S_b\) increases), the probability of collision and solid carrying capacity increases, increasing flotation rate. It has also been proposed that the frother influences flotation kinetics by decreasing the induction time (i.e., the time required for the thin film of water between the air bubble and the mineral particle to rupture, allowing the particle to attach to the air bubble). Reduced induction time is attributed to an interaction between the collector and the frother, where the collector adsorbed at the mineral surface interacts with the frother at the gas/water interface when the particle and bubble collide and attach, increasing the critical film thickness and attachment (Laskowski, 1993; Gorain
et al., 1997). The higher the frother concentration in the solution, the stronger the interaction with the collector, which results in a higher flotation rate. Flotation kinetics is related to the probability of collection (P), which in flotation is explained by the probability of adhesion (P_a) and collision (P_c) (Yoon & Luttrell, 1989; Ek, 1992). Changes in P_a and P_c caused by the frother lead to a flotation kinetics difference.

In this study, a total of four kinetics models were selected: classical first order, modified first-order (Agar), improved gas/solid adsorption, and first-order with rectangular distribution (continuous uniform distribution) (Klimpel). Typically, the classical first-order model is applied to systems with monodisperse feed under the assumption that all particles have the same floatability (Sahoo et al., 2019). The Agar and Klimpel models are derived from the classical first-order model with the addition of a time correction factor (b) and the assumption of a rectangular distribution of particle floatability (Bu et al., 2017). The improved gas/solid adsorption model is similar to the fully mixed model, which inverts the rate constant (Gharai & Venugopal, 2016). Due to the presence of the aforementioned modifying factors, the Agar, Klimpel, and improved gas/sold adsorption models have been observed to better describe flotation kinetics compared to the classical first-order model. Other flotation models were not considered in this study, as they have generally been observed to have a poorer fit to most flotation systems (Sahoo et al., 2019) and the first-order kinetics model is viewed as sufficient to explain flotation kinetics (Tao, 2005). The selected models are summarized in Table 8-1, where R_∞, k, and b are the ultimate recovery, the rate constant, and the time correction factor, respectively.

<table>
<thead>
<tr>
<th>Model</th>
<th>Flotation Rate Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical first order</td>
<td>( R = R_\infty (1 - e^{-kt}) )</td>
</tr>
<tr>
<td>Modified first-order (Agar)</td>
<td>( R = R_\infty (1 - e^{-k(t+b)}) )</td>
</tr>
<tr>
<td>Improved gas/solid adsorption</td>
<td>( R = R_\infty \left( \frac{kt}{1 + kt} \right) )</td>
</tr>
<tr>
<td>First-order with rectangular distribution (Klimpel)</td>
<td>( R = R_\infty \left[ 1 - \frac{1}{kt} (1 - e^{-kt}) \right] )</td>
</tr>
</tbody>
</table>
As discussed above, the frother affects both the bubbles and the foam/froth in flotation. However, the frother also interacts with the particles and the froth structure is affected by solids (Melo & Laskowski, 2006; Rafiei et al., 2011). Thus, the effect of the frother can differ depending on the ore type. This study examines how MIBC influences C-matter rougher flotation performance (e.g., recovery, selectivity, and kinetics). Our results not only determine the effect of MIBC on C-matter, but also suggest the possibility of flotation as the alternative method for refractory gold ore containing C-matter, leading to overall increased gold recovery.

8.2 Experimental

The flotation experiments were carried out using a Denver laboratory flotation machine in a 2.5 L flotation cell. The impeller speed was 1,200 rpm for both conditioning and collecting. The experiment was performed at a natural pH of 7-8. The ground sample was mixed with tap water for 3 min in the flotation cell at 25 wt.% pulp density, and then the kerosene and MIBC were added as the collector and the frother, respectively. Kerosene dosage was constant at 500 g t\(^{-1}\) and the MIBC dosage increased from 30 to 150 g t\(^{-1}\) (9-47 ppm in the pulp, Table 8-2). The dosage of kerosene (500 g t\(^{-1}\)) was identified through a series of bench scale flotation tests conducted with varying concentrations of kerosene at a constant MIBC dosage. These tests showed that as the kerosene dosage increased from 50 to 500 g t\(^{-1}\), C-matter recovery improved from 40% to 55% (with a feed particle size with a P80 size of 67.7 μm and 60 g t\(^{-1}\) of MIBC). Thus, subsequent testing on the effect of MIBC was conducted using 500 g t\(^{-1}\) of kerosene. The conditioning time for the kerosene and MIBC was 1 min each (kerosene was added first, followed by MIBC). For the flotation kinetics study, the froth was collected at 0.5, 1.5, 2.5, 4.5, and 6.5 min. The 5 distinct concentrates and the final tailings were dried, then weighed. All tests were repeated, showing less than 3% difference in the final recovery. These samples were dissolved in a HCl solution at 60°C to analyze C-matter with the removal of
carbonates. Carbon and sulfur contents before and after acid dissolution were determined by a C/S analyzer (ELTRA, CS 2000).

<table>
<thead>
<tr>
<th>Table 8-2. MIBC dosages and the converted concentrations in the pulp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g t⁻¹)</td>
</tr>
<tr>
<td>(ppm)</td>
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</table>

8.3 Results and discussion

8.3.1 The effect of MIBC dosage on recovery

Flotation tests were carried out with 500 g t⁻¹ of kerosene on ground ore samples (P80: 36.5 μm) and the dosage of MIBC was changed from 30 g t⁻¹ to 150 g t⁻¹. The results showed improved recovery by increasing MIBC dosage from 30 g t⁻¹ to 60 g t⁻¹ (Figure 8-2). As the MIBC dosage increased to 150 g t⁻¹, recovery in the initial moments of flotation increased. However, the final recovery after 6.5 min of flotation was nearly the same (~69%) with 60–150 g t⁻¹ of MIBC, indicating that MIBC addition greater than 60 g t⁻¹ had no effect on the ultimate C-matter recovery, only on flotation kinetics. The CCC of MIBC was between 9 ppm and 12 ppm (Cho & Laskowski, 2002; Laskowski, 2004; Gupta et al., 2007; Guven et al., 2020). Thus, it was expected that the MIBC concentration reached the CCC somewhere between 30 and 60 g t⁻¹ (9 ppm and 19 ppm, Table 8-2), resulting in a significant increase in C-matter recovery at 60 g t⁻¹. The lower recovery observed at 30 g t⁻¹ of MIBC can be attributed to an insufficient amount of MIBC, preventing the formation of fine bubbles and stable froth. As bubble size decreases, the collision and attachment between bubbles and particles increase since the total bubble surface area increases, leading to increased recovery (Savassi et al., 1998). Above 60 g t⁻¹, excess MIBC was shown to influence the flotation rate, but it offered no advantage in terms of the ultimate C-matter recovery.
8.3.2 The effect of MIBC dosage on the selectivity

The grade-recovery curves, presented in Figure 8-2, compare flotation performance and selectivity at different MIBC dosages. The higher MIBC dosages exhibited better overall flotation performance, as indicated by the shift in the curves from left to right (Figure 8-2). Increased selectivity in C-matter flotation was related to changes in entrainment and flotation kinetics as the MIBC dosage increased.
Figure 8-2. C-matter grade vs. C-matter recovery for different MIBC dosages: kerosene dosage, 500 g t\(^{-1}\); agitation speed, 1,200 rpm

Ideally, the recovery of C-matter to the flotation concentrate occurs by true flotation with a high degree of selectivity. However, some amount of hydraulic entrainment of gangue minerals is inevitable, particularly in the flotation of fine particles. Entrainment is related to water recovery (Savassi et al., 1998); to better understand the effect of the MIBC dosage on gangue entrainment, Figure 8-3 shows the water recovery to the concentrate as a function of flotation time. The results showed no significant difference in water recovery at 0.5 min of flotation for all MIBC dosages tested. This result is supported by a study conducted by Boylu and Laskowski (2007) on water transfer rate with MIBC and emulsified diesel. The authors showed that the MIBC concentration does not affect the initial water transfer rate with a high concentration of collector. Thus, due to the high concentration of kerosene (500 g t\(^{-1}\)) in this study, the MIBC dosage did not influence water recovery in the initial moments of flotation. However, as flotation time increased, a greater increase in water recovery was observed at lower dosages of MIBC, resulting in a lower final water recovery with higher MIBC dosages, with the exception of 30 g t\(^{-1}\) of MIBC. The lowest water recovery was shown in the test with 30 g t\(^{-1}\) dosage of MIBC at 6.5 min. This anomaly can be
attributed once again to an insufficient frother concentration, preventing the formation of fine bubbles—finer bubbles result in increased water recovery (Dobby & Finch, 1986; Finch et al., 2006). This result is supported by Yoon and Luttrell (1986), whose work showed that reducing the bubble diameter increased both water recovery rate and coal recovery rate in flotation. However, the increase of coal recovery was much faster than that of water recovery, resulting in higher selectivity. Thus, the poor selectivity and lower water recovery observed at 30 g t\(^{-1}\) of MIBC in the present study can be attributed to larger bubbles, as the frother dosage was below the CCC. Above 60 g t\(^{-1}\), despite no difference in water recovery at 0.5 min, selectivity was higher with a higher MIBC dosage (Figure 8-3). This can be explained in terms of both the flotation kinetics and the froth properties. As can be seen in Figure 8-2, before 4.5 min, both C-matter grade and recovery increased with higher MIBC dosages.

![Graph](image)

**Figure 8-3. Water recovery changes for different MIBC dosages**

Improved selectivity observed with increasing MIBC dosages can also be related to entrainment. Kracht et al. (2016) showed that PEG 300 (Polyethylene glycol) has a thicker and drier foam than octanol. With PEG 300, the selectivity of copper was higher than with octanol, even when the water recovery was
equal. The authors presented recovery by entrainment ($R_{ENT}$) as a function of entrainment factor (ENT) and water recovery ($R_w$) (Zheng et al., 2006; Kracht et al., 2016):

$$R_{ENT} = ENT \times R_w$$

(8-1)

The study showed that PEG 300 has a lower ENT than octanol, resulting in less entrainment at equal water recovery values, attributed to differences in froth structure. Neethling et al. (2003) claimed that closely packed bubbles have less water in the plateau border (i.e., where three lamellae (thin water film)—separate bubbles in foam—meet (Wang et al., 2015)) at the pulp–froth interface than in randomly packed bubbles. As previously discussed, it is also well known that wet foam contains more water than dry foam (Malysa, 1992; Melo & Laskowski, 2006). Figure 8-4 shows the froth collected using 120 g t$^{-1}$ of MIBC for each flotation time interval, illustrating that the froth was drier and more abundant in the initial stages of flotation (0.5 and 1.5 min), while the froth dissipated with longer flotation times. During flotation testing, it was observed that the froth collected in the later stages collapsed instantly after collection. Further, the rate at which the froth collapsed increased with decreasing MIBC dosages, as did the perceived “wetness” of the froth. This observation suggests that at higher MIBC dosages, after 0.5 min of flotation, the froth was drier, leading to reduced hydraulic entrainment. Thus, a higher MIBC dosage likely affected the froth structure, as demonstrated by changes in water recovery and selectivity. Although froth height was not measured in this study, other studies have shown that higher froth height and retention time increase with frother concentration (Cho & Laskowski, 2002; Laskowski, 2003; Gupta et al., 2007), and they are therefore related to lower entrainment factor values, which tend to result in reduced gangue entrainment and high concentrate grade (Zheng et al., 2006; Wang et al., 2016).
8.3.3 The effect of MIBC dosage on kinetics

Flotation results were fitted to four different kinetics models and the results are presented in Table 8-3. All models show acceptable fit, showing a high $R^2$ value (> 0.96). The rate constant increases with increasing MIBC dosages, while the ultimate recovery is similar for all MIBC dosages except for 30 g t$^{-1}$. The time correction factor ($b$) in the Agar model mostly increased as the MIBC concentration increased. A positive $b$ value indicates the attachment of hydrophobic particles to air bubbles during the conditioning period, before the air is added to the flotation cell (Sahoo et al., 2019). Thus, the $b$ value obtained in this study suggests that a higher MIBC dosage helps to promote froth stability and the flotation of the hydrophobic particles. Among the four models, the improved gas/solid adsorption model was selected as the representative one due to its highest $R^2$ value ($R^2 > 0.997$ at all dosages). However, once again, the other kinetics models also show good fits and a trend similar to that of the improved gas/solid model against MIBC dosage changes.
Table 8-3. Kinetic model fitting results: $R_\infty$, %, ultimate recovery; $k$ (min$^{-1}$), rate constant; $b$ (min), time correction factor.

<table>
<thead>
<tr>
<th>(g t$^{-1}$)</th>
<th>Classical</th>
<th>Agar</th>
<th>Klimpel</th>
<th>Improved Gas/Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_\infty$</td>
<td>$k$</td>
<td>$R^2$</td>
<td>$R_\infty$</td>
</tr>
<tr>
<td>30</td>
<td>55.4</td>
<td>0.38</td>
<td>0.9990</td>
<td>56.0</td>
</tr>
<tr>
<td>60</td>
<td>69.6</td>
<td>0.50</td>
<td>0.9986</td>
<td>70.1</td>
</tr>
<tr>
<td>90</td>
<td>66.8</td>
<td>0.70</td>
<td>0.9863</td>
<td>68.9</td>
</tr>
<tr>
<td>120</td>
<td>67.9</td>
<td>0.83</td>
<td>0.9846</td>
<td>69.6</td>
</tr>
<tr>
<td>150</td>
<td>67.0</td>
<td>0.96</td>
<td>0.9696</td>
<td>70.0</td>
</tr>
</tbody>
</table>

Figure 8-5 shows an increase in the flotation rate constant with increasing MIBC dosages. An increase in the flotation rate between 30 and 60 g t$^{-1}$ of MIBC can be explained by bubble size reduction occurring up to the CCC. Research by both Diaz-Penafiel and Dobby (1994) and Ek (1992) demonstrated that the probability of collision ($P_c$) increases as bubble size decreases, leading to higher flotation rates. The bubble size was reduced as the frother was added up to the CCC, leading to increased bubble surface area and bubble–particle attachment effect.

Figure 8-5. Flotation rate constant change against MIBC dosage: kerosene dosage, 500 g t$^{-1}$; agitation speed, 1,200 rpm.
At 60 g t\(^{-1}\), the MIBC dosage exceeded the CCC, yet the flotation rate constant continued to increase. Beyond the CCC, the increase in the rate constant was probably caused by a reduced induction time. The probability of adhesion (\(P_a\)) can be explained in terms of the induction time, which relates to the critical film thickness (\(H_C\)) (i.e., a thin film of water ruptures spontaneously at this thickness) (Yoon & Yordan, 1991). As the critical film thickness increases, the induction time decreases. The interaction between the collector and the frother—the collector adsorbed at the mineral surface and the frother at the gas/water interface—increases with the reagent concentration, increasing the critical film thickness and decreasing the induction time (Lekki & Laskowski, 1971; Laskowski 1993; Zhou et al., 1993). Thus, the higher the concentration of MIBC, the stronger its interaction with kerosene, resulting in faster flotation rates.

In summary, it is proposed that below the CCC, as the MIBC dosage increased, bubble size decreased, increasing the probability of collision (\(P_c\)). Beyond CCC, it is possible that the probability of adhesion (\(P_a\)) continued to increase as more MIBC was added, explaining the sustained increase in flotation rate. This increase in \(P_a\) may be attributed to the increased interaction effect between the collector and the frother described above, resulting in increased critical thickness (\(H_C\)) and a reduced induction time.

**8.4 Conclusion**

As a means to design an effective C-matter flotation strategy, the effect of the MIBC dosage on flotation performance was investigated using 500 g t\(^{-1}\) of kerosene as a collector. The role of MIBC in C-matter flotation was described and explained considering the effect of the frother on bubble size and froth stability. The major findings of this study are:

(1) Recovery: Higher dosages of MIBC resulted in higher C-matter recovery, regardless of flotation time. However, above 60 g t\(^{-1}\) of MIBC, after 6.5 min of flotation, the ultimate recovery converged, independent of the frother dosage. Between 30 and 60 g t\(^{-1}\) of MIBC, the difference in ultimate recovery
was attributed to bubble size reduction, as the CCC was between 30 and 60 g t\(^{-1}\) of MIBC. Decreasing bubble size led to more collisions and attachment, resulting in higher C-matter recovery.

(2) Selectivity: Increased MIBC dosage exhibited an advantage in terms of C-matter selectivity, resulting in the best performance with 150 g t\(^{-1}\) of MIBC. Improved selectivity resulted from decreasing entrainment and increasing flotation rate. As bubble size decreased between 30 and 60 g t\(^{-1}\) of MIBC, water recovery also increased, but the C-matter recovery rate increase was faster than that of water, resulting in better selectivity at 60 g t\(^{-1}\) of MIBC. Above 60 g t\(^{-1}\) of MIBC, water recovery was slightly reduced due to changes in the froth structure and increased retention time. These changes led to better water drainage and less entrainment at higher MIBC dosages. Further, C-matter recovery was higher with higher MIBC dosages, resulting in an overall increase in selectivity.

(3) Kinetics: All four flotation kinetics models fit well, but the improved gas/solid adsorption model had the best fit. The rate constant showed a positive correlation with the MIBC dosage. Below the CCC (30-60 g t\(^{-1}\) of MIBC), this correlation was attributed to the bubble size reduction, which increased collision probability between bubbles and particles. Above the CCC (60-150 g t\(^{-1}\) of MIBC), bubble size was constant, suggesting that the flotation rate increased due to a strong interaction between the frother and collector, which strengthened with increasing MIBC dosages. This interaction led to an increasing critical film thickness and decreasing induction time, ultimately increasing the flotation rate.

To conclude, this study described the effect of MIBC dosage on C-matter flotation performance. The frother addition was shown to influence bubble size and froth stability during flotation, resulting in changes to recovery, selectivity, and kinetics. Overall, the study showed the potential to integrate C-matter flotation into existing gold processing flowsheets, with the objective to produce tailored feed material for different downstream processing options (i.e., roasting and POX thiosulfate leaching), ultimately improving overall gold recovery.
Chapter 9

Investigation into selective collectors for C-matter flotation from a double refractory gold ore: transformer oil vs. kerosene

9.1 Introduction

At Barrick Gold Corp.’s Goldstrike Mine in Nevada, USA, pressure oxidation (POX) is used as a pretreatment for double refractory gold ores, followed by thiosulfate gold leaching (Baron et al., 2016); however, the process suffers from insufficient gold recovery from the alkaline POX discharge (59% at lab-scale without resin) (Lee et al., 2022, chapter 4&5). Goldstrike’s ore contains both sulfides and C-matter. The contained C-matter has been described as highly amorphous with a small crystalline component – similar to anthracite or higher-grade coal (Deal et al., 2020). C-matter is not decomposed by the POX process, leading to poor liberation of encapsulated gold in C-matter and insufficient gold recovery (Xu et al., 2016). To improve gold recovery, flotation was evaluated as a means to separate C-matter from the ore prior to POX, allowing the flotation concentrate and tailings to be treated by different processes: The C-matter concentrate could be sent to the Goldstrike roaster to decompose the C-matter, and the tailings (relatively free of C-matter) could be processed in the autoclave to oxidize sulfide minerals. If successful, the proposed process could potentially achieve higher overall gold recovery, as the gold recovery in the roasting circuit is higher than in the alkaline POX circuit (Cox et al., 2019). The Goldstrike roaster has limited capacity, and therefore flotation must be selective in order to limit the amount of feed to the roaster. In previous studies, to investigate the potential for flotation as means to improve overall gold recovery, different flotation circuits were evaluated, with a resulting recovery of 70% of the C-matter to a flotation concentrate at a grade of 4%, in 33% of the mass recovery (Lee et al., 2021b, chapter 7). This result was
achieved through multiple stages of flotation (rougher-scavenger-cleaner), and reagent consumption was high (total 970 g t$^{-1}$ kerosene and 160 g t$^{-1}$ MIBC for rougher-scavenger-cleaner), as reagents were added in each flotation stage. The limited flotation result with high reagent consumptions was primarily due to the fine-grained, highly disseminated nature of the ore, which required fine grinding to achieve adequate C-matter liberation.

In some cases, the flotation of C-matter is performed without collector due to its natural hydrophobicity, but it has also been reported that collector-less flotation leads to low selectivity, insufficient recovery, and high frother consumption (Leja, 1982; Gredelj et al., 2009). The application of a collector improves the flotation performance by increasing both recovery and flotation kinetics, and reducing frother consumption (Gredelj et al., 2009; Zhang & Honaker, 2015). However, an overdose collector can reduce selectivity, due to increased gangue recovery (ash, in the case of coal flotation), either through the collection of middling particles or hydraulic entrainment (Polat et al., 2003; Naik et al., 2005). Therefore, to achieve the best performance in C-matter flotation, careful investigation of collector type, dosage, and addition method (i.e., emulsified or not) is required.

An emulsion is one of the metastable colloids and generally consists of two immiscible fluids, which disperse through dispersion of one phase into the other (Leal-Calderon et al., 2007). Collector emulsion has been widely used in different types of C-matter flotation. In graphite flotation, finer and more stable oil droplets in collector emulsions (diesel and kerosene) were shown to increase recovery for different ores (Sahinoglu & Uslu, 2013; Shi et al., 2015; Peng et al., 2017). Zhou et al. (2020) investigated the effect of nano-size kerosene droplets on graphite flotation and found that finer droplets lead to a higher selectivity index by producing coarser bubbles, lower froth height, and less entrainment. A larger number of droplets and finer droplets increase the probability of contact with graphite particles, increasing the flotation rate. In the flotation of a fine coal, coal recovery increased when alkane oil was emulsified with a non-ionic surfactant, compared with an anionic or cationic surfactant; the result is attributed to stronger adhesion and spreading of the collector at the coal/water interface (Yu et al., 1990). Cheng et al. (2019) demonstrated
that in lignite (coal) flotation, emulsification of kerosene and diesel resulted in a shorter induction time, leading to better flotation performance and reduced collector consumption. Similarly, Sahinoglu and Uslu (2013) investigated the emulsification of sunflower oil, resulting in better ash and sulfide rejection during coal flotation. The reported benefits of oil emulsions in the flotation of graphite and coal warrant investigation into the effect of collector emulsification on recovery, entrainment, and reagent consumption in the flotation of C-matter from Goldstrike’s ore. Previous flotation studies on Goldstrike’s ore (Lee et al., 2021b, chapter 7) concluded that C-matter recovery and selectivity were limited by the mineralogy of the ore; C-matter was very finely disseminated, even after grinding to the 80% passing size of 37 µm. This led to a search for collectors with a similar function to typical fuel oils (i.e., diesel and kerosene) that perform well for the flotation of fine particles.

A few studies have investigated the use of ‘transformer oil’ as an alternative collector to kerosene in the flotation of fine particles, mainly for molybdenite ores (Xiao et al., 1987; Jiangang et al., 2012; Lin et al., 2017 & 2018). Transformer oil (also referred to as insulating oil) is used to insulate electrical power transformers and is categorized as paraffin-rich oil or naphthene-rich oil (Kaplan et al., 2010). From an environmental perspective, as an effort to treat the degraded transformer oil, recycling of the waste transformer oil has been already investigated (Belkhode et al., 2022). If the recycled transformer oil can be repurposed for use as a flotation reagent, it may offer some environmental benefits. However, in this study the use of new transformer oil as a novel collector in C-matter flotation was investigated. The use of transformer oil as a collector was first reported by Xiao et al., (1987) in the flotation of antimony oxide. In this study, transformer oil was emulsified with octyl hydroxamic acid (OHA) and sulfated coconut oil (Syntex), significantly improving antimony recovery from 60% to 97.5%. The authors showed that the transformer oil emulsion droplets react with the surfactants produce larger flocs (10 times that without emulsification) by the aggregation of fine particles, improving flotation performance. More recently, Jiangang et al. (2012) studied oil agglomerate flotation of molybdenite, showing that transformer oil collected more fine particles at a higher overall recovery than other oil collectors (kerosene, diesel, and rapeseed oil). As transformer oil
dosage increased from 2.0 to 13.8 kg t⁻¹, the agglomerate size increased from 0.15 to 0.68 mm, while the P50 size of the molybdenite particles recovered decreased from 9.1 to 2.1 µm. This result was supported by additional molybdenite flotation studies by Lin et al. (2017 & 2018) comparing transformer oil, kerosene, and diesel. Transformer oil consistently out-performed kerosene and diesel in both micro-flotation and bench-scale flotation tests. Transformer oil was readily dispersed and showed better selectivity than other collectors (Lin et al., 2017 & 2018). In addition, after emulsification, transformer oil produced more uniform and finer oil droplets than other collectors under the same emulsification conditions (Lin et al., 2018). While researchers have demonstrated that transformer oil collects more fine particles with better selectivity than conventional oil collectors (e.g., kerosene and diesel) in antimony oxide and molybdenite flotation, it has yet to be investigated as a collector in finely disseminated C-matter flotation (or similar ores containing graphite/coal).

This study evaluated the potential of transformer oil as a novel collector for selective C-matter flotation, with the ultimate objective of improving gold recovery from Goldstrike’s double refractory gold ore. Transformer oil was compared with kerosene in terms of flotation performance (grade and recovery) in a single rougher flotation stage. Transformer oil and kerosene were tested at varying dosages, with and without emulsification, using a 2-level full factorial Design of Experiments. As the final step, the overall gold recoveries obtained with flotation were estimated using Barrick’s a recovery estimation models and lab-scale testing.

9.2 Experimental

9.2.1 Materials

Kerosene (> 99%, Fisher Chemical™, Hampton, USA; C9-16 of carbon chain) and transformer oil (Analytical standard, PCB free, Sigma-Aldrich, Saint Louis, USA) were used as collectors, and MIBC (4-Methyl-2-Pentanol, 98%, Sigma-Aldrich, Saint Louis, USA) was added as a frother. The collector was
applied in either emulsified (called as “emulsion”) or non-emulsified (called as “normal”) form. The purchased transformer oil was a mixture of three components: 1) hydrotreated middle distillates (petroleum) (CAS-No. 64742-46-7), 2) base oil (CAS-No. 64742-53-6), and 3) butyl hydroxytoluene (BHT) (CAS-No. 128-37-0). Hydrotreated middle distillates (petroleum) consisted of C13-15 alkane and base oil in the C15-30 range of light naphthenic.

For the emulsification process, the collector solution (5 wt.%, made using de-ionized water) was treated with an ultrasonic homogenizer (UP400S, Hielscher Ultrasound Technology, Germany) at 45% amplitude for 2 min without the addition of any emulsifier. Under the selected conditions, no visible separation of the emulsion was shown even without the emulsifier (longer emulsification times were also tested with no observable difference in emulsion stability; the shorter emulsification time was selected to reduce energy consumption). The emulsification was performed immediately before each flotation test to maintain consistency between tests. For the observation of the droplets in the emulsion, a microscope (Discover Echo Inc., CA, USA) was used.

9.2.2 Test design by DOE

A 2-level full factorial design of experiments (DOE) was used to investigate collector type, the effect of emulsification, and collector dosage. The collector dosage (100-500 g t⁻¹) was investigated as a numerical factor, and collector type (kerosene/transformer oil) and emulsification were considered as a categorical factor (Table 9-1). The test design and data processing were performed by Design-Expert Software ver. 13 (Stat-Ease Inc., MN, USA). The selected test design included 8 tests with an additional 4 tests at the center point, for a total of 12 flotation tests (Table 9-2).

<table>
<thead>
<tr>
<th>Table 9-1. The selected test factors for the DOE study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
</tr>
<tr>
<td>A  Collector dosage, g t⁻¹</td>
</tr>
<tr>
<td>B  Collector type</td>
</tr>
<tr>
<td>C  Emulsification</td>
</tr>
</tbody>
</table>
9.2.3 Flotation procedure

The sample was split into 500 g charges using a rotary splitter followed by a riffle sample splitter. After grinding, the sample was added into a 2.5 L of flotation cell at 20 wt.% solids (Denver flotation machine). First, the sample was mixed with tap water for 3 min at 1,500 rpm, then collector and frother were added at 1 min and 0.5 min of conditioning time, respectively. The collector dosage and the emulsification varied according to the conditions outlined in Table 3. The MIBC dosage was held constant at 150 g t\(^{-1}\) for all tests, which was determined to be sufficient for flotation with 500 g t\(^{-1}\) of the normal kerosene without a detrimental effect on the flotation performance (Lee et al., 2021a, chapter 8). After conditioning with collector and frother, flotation was carried out and separate concentrate products were collected after 1, 2, 4, and 7 min to obtain kinetics samples. The weight of the collection pan was recorded before and after concentrate collection to obtain the water recovery to each product.

9.2.4 Analysis

After flotation, all test products were filtered, dried, and weighed. A 3 g representative sub sample was riffle split from each product and dissolved in 20% HCl solution (Certified ACS Plus, 36.5 to 38.0%, Fisher Chemical) at 80°C to remove all carbonate minerals. After HCl dissolution, each sample was dried
and weighed. All samples were analyzed by a carbon and sulfur analyzer (ELTRA, CS 2000) both before and after HCl dissolution to determine C-matter content. For the flotation kinetics analysis, a 1st order classical model (Equation 1) was selected and fit using MATLAB R2020a (MathWorks, Inc., MA, USA).

\[ R = R_\infty (1 - e^{-kt}) \]  

(9-1)

Where \( R \) is recovery, \( R_\infty \) is the ultimate recovery after infinite flotation time, \( t \) is the flotation time (min), and \( k \) is the rate constant (min\(^{-1}\)).

To assess the effect of flotation on overall gold recovery obtained from the commercial plant, the gold recovery was estimated based on the recovery equations outlined in Barrick’s technical report (Cox et al., 2019).

9.3 Results and discussion

9.3.1 The test results

For all flotation tests, the final cumulative C-matter recovery after 7 min was considered as the response (Table 9-3). 7 min of flotation time was enough time to collect floatable concentrate. The final grade, yield, and water recovery were also evaluated as a response, but the model obtained was not statistically significant. This can be attributed to the weak (< 80%) power (“the probability of finding a difference in population characteristics when such differences actually exist” (Ledolter & Kardon, 2020)) of the model due to the consideration of two categorical factors (collector type and emulsification) in the test design (Ortiz, 2012; Ledolter & Kardon, 2020). The results for C-matter recovery indicated that the single factors had a major effect, while the interaction effects of the factors tested only had a minor influence (not statistically significant, contributing less than 1% to the predicted recovery). Again, this may be the result of the weak power of the model, which was not enough to detect the effect of the interaction. With the elimination of the statistically insignificant parameters, the model consisted of only single factors as
described in equation 9-2 (coded factors, A: the collector dosage; B: the collector type; C: the emulsification). The collector dosage had the greatest effect on recovery response. The model had a $R^2$ of 0.9425, a $F$-value of 38.27, and a $p$-value of 0.0001, demonstrating that the model predicted the actual value well and was statistically significant at a 95% confidence interval (Figure 9-1).

\[
(C\text{-matter recovery,}\%) = 58.69 + 5.45A - 2.05B + 1.24C \tag{9-2}
\]

Table 9-3. The C-matter recovery results after 7 min of flotation under different test conditions

<table>
<thead>
<tr>
<th>Test</th>
<th>C-matter recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60.68</td>
</tr>
<tr>
<td>2</td>
<td>59.68</td>
</tr>
<tr>
<td>3</td>
<td>65.22</td>
</tr>
<tr>
<td>4</td>
<td>64.96</td>
</tr>
<tr>
<td>5</td>
<td>60.53</td>
</tr>
<tr>
<td>6</td>
<td>53.01</td>
</tr>
<tr>
<td>7</td>
<td>58.01</td>
</tr>
<tr>
<td>8</td>
<td>49.49</td>
</tr>
<tr>
<td>9</td>
<td>52.47</td>
</tr>
<tr>
<td>10</td>
<td>66.10</td>
</tr>
<tr>
<td>11</td>
<td>66.30</td>
</tr>
<tr>
<td>12</td>
<td>64.83</td>
</tr>
</tbody>
</table>

Figure 9-1. Predicted vs. Actual recovery as the response
To validate the model and determine if it was overfit to the data set, an additional test was performed outside of the original design space (A: 600 g t\(^{-1}\) (+1.5); B: Kerosene (-1); C: Emulsion (+1)), resulting in only a 0.78 % difference from the predicted value. This further confirmed that the model predicted the test results (no overfit) with a high degree of accuracy.

Considering both the recovery and the grade, 500 g t\(^{-1}\) of the kerosene emulsion was selected as the most promising condition for flotation. Two more tests were repeated with the selected conditions and without kinetics sampling, resulting in recoveries of 71.48% and 70.14%, and grade of 3.72% and 3.80% (A test from the main DOE tests was performed with the kinetics samples; two repeated tests were performed continuously without the kinetics sampling), respectively. The difference in the results (recovery: 66.10%; grade: 4.38%) was attributed to the collected sample with/without the kinetics sampling: With the kinetics sampling, the aeration was turned off and water was sprayed between concentrates to change the concentrate tray and wash the particles on the top of the cell. This reduced entrainment and the recovery of middlings, resulting in lower recovery (66.10%), but higher grade (4.38%). The results for the two tests conducted without kinetics sampling (Difference of C-matter recovery: 1.3%; C-matter grade: 0.1%) indicated that the tests exhibited a good repeatability.

9.3.2 Comparison between transformer oil and kerosene

9.3.2.1 Effect on C-matter recovery

There were differences in the relationship between collector dosage, emulsification, and flotation performance when transformer oil was used as a collector, as compared with kerosene. With kerosene, C-matter recovery increased up to 66% as the dosage increased to 300 g t\(^{-1}\), then there was no further increase at 500 g t\(^{-1}\), independent of emulsification (Figure 9-2). 300 g t\(^{-1}\) of kerosene could be enough to collect the available C-matter and the limited C-matter recovery at around 66% resulted in no more increase in C-
matter recovery at 500 g t\(^{-1}\) because of the ore properties. Transformer oil exhibited a different behavior regarding C-matter recovery and emulsification (Figure 9-2). At 500 g t\(^{-1}\), the emulsion demonstrated a higher C-matter recovery than the normal transformer oil. With the transformer oil, the collectable C-matter was still remaining (C-matter recovery: 60%) after flotation at 300 g t\(^{-1}\), and 500 g t\(^{-1}\) of transformer oil emulsion had a better collecting ability than the normal one, collecting more C-matter which cannot be collected by the normal transformer oil.

Figure 9-2 also indicated that the emulsion resulted in slightly higher recoveries across all dosages tested as compared with the normal collector. This can be attributed to the increased probability of collision between oil droplets and particles and the shorter induction time of the emulsion (Peng et al., 2017; Cheng et al., 2019). It was reported that finer droplets in the emulsion have a larger surface area, leading to more collision between the particles and the collector, and the induction time between the bubbles and the particles is reduced with the emulsification. Additionally, better flotation performance is achieved with the shorter induction time.

![Figure 9-2. The final C-matter recovery as a function of collector dosage](image-url)
Higher C-matter recovery with the emulsion could also be explained by a finer droplet size and the relative size difference between the particles and the oil droplet. As shown in Figure 9-3, the particles with a passing size of 36.5 µm contained ultrafine particles with a size of -10 µm. The detected C-matter which was expected to highly liberated has around 3 µm of fine size (Figure 9-4). The oil droplets were observed by the microscope (Figure 9-5). Both kerosene and transformer oil produced coarse (< 50 µm) and only a few numbers of droplets with agitation at 1,500 rpm (same speed with the flotation) (Figure 9-5 (a) & (b)). Through the emulsification, both finer and a larger number of oil droplets were produced (Figure 9-5 (c) & (d)) than for normal agitation. In the emulsion, the coarse droplet size (10-20 µm) was contained, and it also possessed a significant number of finer size droplets (< 10 µm). These fine size droplets can help to collect the fine particles through more collision and attachment with the fine particles, resulting in higher C-matter recovery. In addition, it was reported that the added oil droplets are instantly covered by ultra-fine particles, losing its collecting ability (Polat et al., 2003). However, the oil droplets of the emulsion which are finer than the particles could prevent the coverage of the collector by the particles, resulting in a higher recovery, which can be attributed to maintain the ability of the collector.

![Cumulative volume vs. Particle size graph](image)

*Figure 9-3. Particle size analysis result after rod mill grinding (20 min, 33 wt.%)*
Figure 9-4. TEM and mapping analysis results of the ore (Yellow box: highly liberated C-matter)
Figure 9-5. Microscope images of (a) normal kerosene (b) normal transformer oil (at 1,500 rpm for 3 min) (c) kerosene emulsion (d) transformer oil emulsion (same operating conditions as described in 2.1)

9.3.2.2 Effect on the flotation kinetics

The flotation rate with transformer oil was noticeably slower than with kerosene and only marginally changed as the transformer oil dosage changed (Figure 9-6). This observation differs from other studies on molybdenite flotation (Jiangang et al., 2012; Lin et al., 2017 & 2018), which reported that transformer oil resulted in faster kinetics and collected more fine particles than kerosene, with better selectivity. Researchers have credited this improved performance to transformer oil’s higher dispersion ability (despite a higher adsorption intensity of kerosene on hydrophobic particles) and its naphthenic
structure which forms more compact aggregates of fine molybdenite (Smit & Bhasin, 1985). It is likely that the opposite behavior observed with transformer oil in the flotation of C-matter from Goldstrike’s ore, is related to the selective behavior of the transformer oil coupled with the complex ore properties. Lin et al. (2017) suggested that transformer oil has good selectivity due to a strong repulsive force between the transformer oil and quartz. In Goldstrike’s ore, C-matter is highly disseminated in all minerals including quartz and dolomite (Figure 3-6) which are the main mineral constituents of the sample (Figure 3-5). Thus, it is likely that poor C-matter liberation inhibited the recovery of the middling particles due to their limited interaction with transformer oil, resulting in lower C-matter recovery (Figure 9-6) and slower flotation kinetics than was observed with kerosene.

![Figure 9-6. The rate constant (obtained by the classical 1st order model ($R^2 > 0.99$ for all test conditions)) as a function of collector dosage](image)

9.3.2.3 Effect on the C-matter grade and gangue recovery

The effect of collector type and preparation method on C-matter grade and gangue recovery was investigated. In this study, the gangue consisted of all minerals except for C-matter. Thus, the gangue recovery was calculated with the gangue mass which subtracted C-matter mass from the total mass. The C-
matter grade with normal collector was compared first (Figure 9-7 (a)). In all ranges of dosage, C-matter recovery with normal kerosene was higher than the normal transformer oil (Figure 9-2) and at 100 g t\(^{-1}\), the gangue recovery was the same for normal kerosene and transformer oil (Figure 9-7 (b)). This resulted in higher C-matter grade with the normal kerosene at 100 g t\(^{-1}\) (Figure 9-7 (a)). However, as the dosage increased, the gangue recovery increased for both cases, but it was more noticeable for normal kerosene. An overdose of kerosene can lead to a loss of selectivity, resulting from the collection of more middlings or entrainment (Naik et al., 2003). In the case of transformer oil, as explained above, the increased repulsive effect between transformer oil and quartz prevented a significant increase in gangue recovery (Lin et al., 2017). With the emulsion, C-matter grade was highly influenced by the gangue recovery; as the gangue recovery increased, C-matter grade was reduced (Figure 9-7). At 100 g t\(^{-1}\), the kerosene emulsion had a higher C-matter grade, attributed to higher C-matter recovery (Figure 9-2). This trend was also shown for the normal collector. At low dosage, the transformer oil had a weak repulsive force compared with kerosene, thus low dosage of transformer oil showed no advantage in terms of both selectivity and collecting ability. At 300 g t\(^{-1}\), the kerosene emulsion significantly increased the gangue recovery, resulting in a lower C-matter grade than for the transformer oil emulsion. However, at 500 g t\(^{-1}\), the gangue recovery with the kerosene emulsion was reduced, while the gangue recovery increased with the transformer oil emulsion. The increase in gangue recovery with the transformer oil emulsion was due to the collection of more middlings, containing C-matter. As discussed, 500 g t\(^{-1}\) transformer oil emulsion collected more C-matter than the normal transformer oil. However, the additional material collected was low grade.
9.3.3 The limitation of flotation performance

The discussed results indicated that the flotation performance was limited; the increase in C-matter recovery and the selective flotation performance were restricted at some point. Figure 9-8 describes the relationship between water recovery and C-matter/gangue recovery. The gangue recovery exhibited a linear relationship with the water recovery and the slope was less than 1, indicating that the gangue recovery was mostly a function of hydraulic entrainment (Zheng et al., 2006). The relationship between C-matter and water recovery was non-linear, demonstrating that the C-matter collection mechanism changed. The observed curvature in the relationship between C-matter recovery and water recovery suggests that the C-matter was initially collected by true flotation as the main mechanism, but entrainment became influential in collecting C-matter as the flotation progressed. Thus, there was a limitation to selective flotation in the system; only 40-50% of the C-matter was collected mainly through true flotation (i.e., the linear portion of the recovery curve) corresponding to the recovery of well-liberated particles with sufficient hydrophobicity. The recovery of the remaining C-matter (low grade/middling) was, at least in part, a function of hydraulic entrainment.
Figure 9-8. The relationship between water recovery and C-matter/gangue recovery with different dosages and the emulsification of (a) Transformer oil (b) Kerosene

Overall, in contrast to other studies, the capability of the transformer oil as a collector was limited. (Jiangang et al., 2012; Lin et al., 2017; Lin et al., 2018). However, the majority of the C-matter was finely disseminated in other minerals, including silicates. Thus, it can be concluded that the poorly liberated C-matter in the ore limited the flotation performance, regardless of collector type, preparation method and dosage. XRD analysis of the concentrate and the tailings also confirmed the presence of gangue minerals in the flotation concentrate, which was expected based on the limitation of the flotation performance (Figure 9-9). Most peaks in the XRD patterns were in the same position with a similar height for both concentrate and tailings. Only the peak height for quartz exhibited a change (marginally lower in the concentrate compared with the tailings), meaning that there was no major difference in the mineral distribution of the two flotation products. Therefore, the C-matter recovered to the concentrate was mostly related to complex, poorly liberated C-matter, not free C-matter. However, it is likely that the middlings contained a higher proportion of C-matter, and therefore exhibited a higher degree of hydrophobicity, reporting to the concentrate.
9.3.4 The overall gold recovery estimation

The gold assays of the concentrate and the tailings were 2.88 g t\(^{-1}\) and 1.66 g t\(^{-1}\), respectively; 51% of the gold reported to the concentrate and 49% of the gold remained in the tailings. The expected gold recovery in the commercial plant was calculated using Barrick’s reported gold recovery estimation models; the gold grade from the current process and the proposed process were used as inputs for comparative calculations (Cox et al., 2019). Equation 9-3 is for the gold recovery through the alkaline POX process followed by the resin-in-leach (RIL) process and equation 9-4 is used to calculate the gold recovery through roasting with cyanidation. HG indicates the head grade of gold in the ores (oz st\(^{-1}\) gold).

\[
(\text{Recovery, } \%) = 16.41 \ln(\text{HG})+103.58-14.0 \quad (\text{HG} \leq 0.28 \text{ oz st}^{-1})
\]

\[
(\text{Recovery, } \%) = 92.03-37.36 \exp(-12.94\text{HG}) \quad (\text{HG: all range})
\]
For the current process in the commercial plant, it was assumed that all the feed material grading 2.14 g t\(^{-1}\) was treated by the alkaline POX process and the recovery was calculated according to equation 9-3. For the proposed process, 51% of the gold in the concentrate may be processed in the roaster and the recovery can be calculated from equation 9-4. Then, 49% of the gold in tailings may be treated by the alkaline POX process at a recovery from equation 9-3. As shown in Table 9-4, the overall gold recovery in the commercial plant with the addition of flotation has the potential to increase gold recovery to 60.01% compared with 44.06% for the current process based on the models in Barrick’s report.

### Table 9-4. Gold recovery comparison between the current process and the proposed process in the commercial plant based on the models in Barrick’s report (Current process: alkaline POX; proposed process: concentrate -roasting and tailings – alkaline POX)

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<th>(Gold recovery, %)</th>
<th>Roasting</th>
<th>Alkaline POX</th>
<th>Overall</th>
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<td>Current process</td>
<td>-</td>
<td>44.06</td>
<td>44.06</td>
</tr>
<tr>
<td>Proposed process</td>
<td>79.43</td>
<td>39.89</td>
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</table>

The overall gold recovery estimation indicated that the proposed process with flotation has a potential to improve the overall gold recovery. The reduced amount of feed due to the flotation adds an advantage that it can be treated by the limited capacity of the roaster in Barrick’s plant; however, the additional operating cost of the flotation also needs to be considered for the application of the flotation process in Barrick’s commercial plant.

### 9.4 Conclusion

The flotation of C-matter from a refractory gold ore was investigated under different collector conditions (type, dosage, and emulsification). Both kerosene and transformer oil emulsions produced finer and a larger number of droplets than normal oil collector. In C-matter flotation, especially with poorly liberated ore, kerosene resulted in a higher recovery and faster flotation rate than transformer oil. In addition,
kerosene emulsion improved the selectivity compared with normal kerosene. The use of transformer oil resulted in lower recovery and slower kinetics than kerosene in this study, a result that was attributed to the complex mineralogy and finely disseminated C-matter in the ore tested. However, the results indicated the potential of transformer oil as a selective collector in C-matter flotation from a well liberated ore, which may offer improved performance compared with conventional collectors. Taking both C-matter recovery and grade into account, the optimum conditions were selected as 500 g t⁻¹ of kerosene emulsion, with 51% of gold from the feed reporting to the flotation concentrate. Based on Barrick’s gold recovery models, overall gold recovery was improved from 44% to 60% (for the feed material tested) by adding a flotation circuit into the existing process flowsheet.

This study successfully demonstrated the role of transformer oil as a collector in C-matter flotation, suggesting that transformer oil may be applicable in other flotation systems, outside of the gold industry. As mining and metallurgy begin to shift the focus from raw material extraction to recycling, transformer oil may find application as a collector in the flotation of battery materials such as graphite, from both primary and secondary resources.
Chapter 10

Conclusion

10.1 Summary

This study aimed at addressing the issue of low gold leaching recovery from the alkaline POX discharge of Barrick’s Goldstrike leaching plant. A thorough investigation was performed on the alkaline POX discharge and the alkaline POX feed, which were produced in Barrick’s plant and mined from Barrick’s Goldstrike mine, respectively. First, part I was undertaken to determine the maximum gold recovery from the alkaline POX discharge at the lab-scale, applying the leaching conditions being performed at Barrick’s current process and figure out the causes of low gold recovery. Then, the proper treatment methods were suggested, and their efficacy on the gold recovery from thiosulfate leaching process was studied. The conclusion derived from the results achieved in part I was that with the current process, the low gold recovery problem cannot be fully resolved; therefore, part II started to address the problem from a different approach. In part II, the flotation study was mainly investigated to determine the potential of the suggested new process.

10.1.1 Summary of part I

Part I consisted of three studies to investigate the reasons for low gold recovery from alkaline POX discharge leaching process, followed by exploring different pretreatment techniques to enhance gold recovery from the leaching process. The main outcomes of each study are summarized here under:

An investigation of the limited gold recovery from the alkaline POX discharge
1. Optimization investigation was conducted to reach the maximum recoverable gold from the alkaline POX discharge under the current performing process at Barrick’s Goldstrike leaching plant. Gold recovery of 59% was registered as the highest value after 24 h leaching at thiosulfate (TS) concentration of 0.14 M, cupric ion (Cu) concentration of 0.78 mM, and temperature of 50°C.

2. TEM investigation revealed that fine gold particles were scattered throughout all host minerals and high gold contents were also detected in the locked pyritic materials, uncovering the cause of low gold recovery from the alkaline POX discharge. A diagnostic test method demonstrated that the complex mineralogy and poor gold liberation of the original ores were the major issues associated with low gold recovery in the alkaline POX circuit.

3. Insufficient pyrite oxidation rate and poor liberation of gold in the alkaline POX process prevents higher gold recovery. Hence, this study suggests that an increase in the gold liberation is the key factor to enhance its leaching recovery from alkaline POX discharge.

**Mechanical treatment study through MA by the laboratory stirred media mill**

1. In Chapter 5, MA was explored as a pretreatment technique to liberate gold particle. MA was applied to alkaline POX discharge by ultrafine grinding in the laboratory stirred media mill. Increasing the ball to powder ratio and decreasing the pulp density increased grinding efficiency and reduced particle size.

2. The optimal MA conditions to maximize gold thiosulfate leaching recovery (72.1%) were grinding duration of 60 min at a ball to powder ratio of 5:1 and pulp density of 50 wt.%, which decreased the 80% passing size from 56.5 to 8.54 μm.
3. The enhanced recovery was attributed to the removal of the passivation layer from mineral surfaces and amorphization of gold-bearing minerals. The gold remaining in the leach residue was likely finely disseminated and/or locked in the sulfide matrix.

**Chemical treatment study by acid dissolution**

1. Chapter 6 examined acid dissolution of the alkaline POX discharge to improve the gold recovery. Acid treatment was performed with the selected acid concentrations (HCl: 1.0/3.0 M and H$_2$SO$_4$: 0.5/1.5 M) at 20 wt.% solids followed by thiosulfate gold leaching.

2. The leaching results indicated that HCl treatment under higher concentration and longer dissolution time reduced gold recovery to 40%, while H$_2$SO$_4$ dissolution improved gold recovery up to 67%. Acid treatment liberated a portion of the locked gold particles under the passive layers formed in the POX process; however, HCl dissolution led to the adhesion of finer particles on the surface of coarser ones, leading to reduced gold recovery.

Overall, the acid treatment showed the maximum gold recovery of 67%, lower than that achieved in mechanical treatment by ultrafine grinding (72%). This study once more confirmed that the gold remaining in the leach residue was finely disseminated and could not be liberated by the proposed pretreatment techniques, resulting in a maximum possible gold recovery of approximately 70% from the alkaline POX discharge.

**10.1.2 Summary of part II**

To improve the overall gold recovery, an alternative process with flotation was suggested in this study. This part contained three studies on the multi-stage flotation, frother, and collector.
Multi-stage flotation study

1. As the first step of the flotation study, the multi-stage flotation was performed with the different flotation circuit designs: 1) single stage rougher flotation, 2) rougher and scavenger flotation, c) rougher, scavenger, and scavenger cleaner flotation, and 4) rougher, rougher cleaner, scavenger, and scavenger cleaner flotation. In each process, kerosene and MIBC dosages were changed, which were used as collector and frother, respectively. Additionally, in rougher flotation, the input particle size was also investigated.

2. The selected conditions for the rougher flotation were 500 g t\textsuperscript{-1} of kerosene dosage, and 120 g t\textsuperscript{-1} of MIBC dosage with 36.5 µm of the 80% passing size, resulting in 70% with 3.42% of C-matter grade. However, for collecting more C-matter, the rougher flotation time was cut to 2.5 min, then the scavenger flotation was performed. The scavenger flotation increased C-matter recovery more than the single rougher flotation, while it was also accompanied by the reduction of C-matter grade with 350 g t\textsuperscript{-1} of kerosene and 21 g t\textsuperscript{-1} of MIBC as the optimum conditions. Under the optimum conditions, the rougher cleaner flotation increased the grade of the rougher concentrate to 5.18% and the scavenger cleaner flotation improved the grade to 2.87%.

3. The proposed flotation circuit was compared to determine the best flotation operating conditions. The results indicated that the scavenger flotation brought a high reduction of C-matter grade but significantly increased the C-matter recovery. As the cleaner flotation was performed, the C-matter grade was highly improved, indicating that the flotation circuit with rougher, scavenger, and cleaner flotations for both concentrates was the best circuit design. However, the maximum C-matter recovery was around 70% and the higher recovery was accompanied by a reduction in the grade. The additional selective flotation test (purposed the true flotation) showed that the locked C-matter in the ore resulted in the limited flotation performance.
Reagent study I: The role of MIBC on the flotation

1. The increase in MIBC dosage increased the cumulative C-matter recovery, while MIBC dosage at above 60 g t⁻¹ only had a minor effect on the improvement of C-matter recovery. The effect on the selectivity showed that the addition of more MIBC assisted with improving the flotation selectivity. It was attributed to the reduction of the entrainment by adding more MIBC.

2. The kinetics results indicated that the flotation kinetics increased with a higher dosage of MIBC from 30 to 150 g t⁻¹. The increase in the flotation kinetics was attributed to the reduction of bubble size at the beginning. Then, with the MIBC dosage above the CCC, the reduction of the induction time led to faster flotation kinetics.

Reagent study II: comparison between transformer oil and kerosene

1. For the achievement of the selective flotation, a novel collector of transformer oil and emulsification were investigated with a conventional oil collector of kerosene and a non-emulsified collector. The collector dosage (100-500 g t⁻¹), collector type, and emulsification were selected as the test factors. The repetitive test and the addition test at the deviated conditions proved again that the obtained model well described the actual value. The optimum conditions were selected as 500 g t⁻¹ of the kerosene emulsion.

2. The use of transformer oil as collector resulted in selective flotation, while the C-matter recovery was lower than the tests with kerosene. Additionally, the normal transformer oil at 500 g t⁻¹ showed the most selective results. Kerosene results showed higher C-matter recovery, but the selectivity was not tangibly changed under different test conditions.
3. The obtained C-matter concentrate, and tailings were applied to the new process and the overall gold recovery was estimated based on the lab-scale test results and the predicted model from Barrick’s report. Flotation resulted in 51% gold recovery from the concentrate containing 2.88 g t\(^{-1}\) gold, and 49% of gold remained in the tailings with 1.66 g t\(^{-1}\) gold. The overall gold recovery was estimated to enhance from 44% to 60% by the proposed process.

10.2 Significant contributions

This study was carried out to resolve the issue of low gold recovery from double refractory gold ores and ultimately improve gold dissolution in the leaching step. Various attempts have been made to deal with these problematic materials.

1. Chapter 4 dealt with a diagnostic investigation to demonstrate the causes for low gold recovery. This diagnostic test procedure was previously carried out along with cyanidation, but it has not been attempted with thiosulfate leaching. Chapter 4 reported the gold recovery from target minerals after each treatment. Hence, the diagnostic test procedure is effective in demonstrating the recoverable gold percentage with non-cyanide leaching.

2. The acidulation process (usually with H\(_2\)SO\(_4\)) has been used to treat the acidic POX feed prior to the POX process to remove the remaining carbonate minerals. In Chapter 6, HCl was considered as well as H\(_2\)SO\(_4\) to treat the sample to remove the carbonates. HCl dissolution showed a detrimental effect on gold recovery, which has not been reported in other literature. Hence, this study can help other researchers to avoid HCl pretreatment of carbonate-containing ore.

3. Chapter 9 introduced the use of transformer oil as a novel collector in C-matter flotation, which has not been previously investigated in C-matter flotation. Only a few studies of molybdenite flotation studied the use of transformer oil as a collector. In Chapter 10 it was demonstrated that
transformer oil had a potential to act as a collector in C-matter flotation and it could exhibit better selectivity than a conventional oil collector (e.g., kerosene and diesel). Thus, the study of the transformer oil as a novel collector is expected to increase interest in the transformer oil as a flotation collector for C-matter and other carbonaceous minerals.

10.3 Recommendation

Goldstrike’s double refractory gold ore proved to be a challenging complex ore-bearing mineral to work with, and effective improvements in gold recovery were limited. However, from another point of view, the complexity of the ore means that various challenges remain to be investigated. Based on the results obtained in these studies and the experience with the ores, the following future research is recommended:

1. The first suggestion is the application of additives in the thiosulfate gold leaching procedure. As described in the literature review of chapter 2.3.6, studies of additives in thiosulfate gold leaching have been performed by many researchers and some additives provided benefits. The main cause of poor recovery in the ore was identified as the poor liberation of gold; however, additives may help to increase the leaching kinetics or reduce the reagent consumption, leading to lower costs for the process at current recovery levels.

2. The second suggestion is a combination of the oxidation process with grinding (a similar successful process was investigated as the “Albion process”). One of the causes of low gold recovery was insufficient sulfide oxidation rate and passivation, resulting from the products of the alkaline POX process. Thus, the process of combined oxidation and grinding may help to increase the gold recovery by increasing gold liberation. This process could be applied to non-oxidized gold ores (i.e., the alkaline POX feed). The grinding action during oxidation may prevent passivation, leading to higher sulfide oxidation and liberating more gold particles.
3. The roaster has a much higher gold recovery than the alkaline POX discharge; however, the limited capacity of the roaster in Barrick’s plant restricts the amount of feed for the roaster as a little mass as possible. The C-matter concentrate produced using flotation possessed more gold with a lower mass recovery than the tailings, meaning that the gold is preferentially associated with C-matter. This association might be attributed to the higher gold concentrations in the C-matter, but also a close relationship between C-matter and sulfide minerals. The sulfide minerals in the ore are known for having a high concentration of gold. Thus, the flotation of C-matter followed by sulfide flotation might increase the gold recovery with a reduced operating cost. Through the flotation of both C-matter and sulfides, it is expected that very little gold would remain in the tailings, eliminating the need for gold extraction. The flotation concentrate could be sent to the roaster with less mass and higher gold recovery values. In addition, the operating cost of the alkaline POX process could be eliminated. C-matter flotation with the same test conditions used in this study can be performed first, followed by sulfide mineral flotation with xanthate reagents as a collector. However, the environmental issue of roasting must be considered in parallel with the feasibility and economic assessments.

4. Transformer oil was first introduced as a novel collector for C-matter flotation in this study. Due to the ore properties, the efficacy of transformer oil was also limited; however, the results obtained clearly showed its potential in C-matter flotation, especially in selective C-matter flotation. Therefore, the application of transformer oil in C-matter flotation can be suggested for future studies on other double refractory ores, and on other types of C-matter. One potential application is the use of transformer oil to recover graphite from a recycled lithium-ion battery (LIB) by flotation. As the price of lithium has soared, the treatment of the used LIB is becoming more important. The successful separation of C-matter from the LIB is one of an important research area and has been widely investigated. Thus, the potential of transformer oil as a selective collector in
C-matter flotation means that it can also be expected to be suitable collector for recovering C-matter from recycled LIBs.

The recovery of gold from this challenging ore was investigated using diverse treatments to determine the cause of low gold recovery from Barrick’s alkaline POX discharge and to achieve better gold production results. This study described the cause of insufficient gold recovery and the primary issues with the current process, then suggested feasible treatments to overcome these issues. The results and conclusions from the study will provide background information and fundamental knowledge on gold processing and be used by future researchers investigating the recovery of gold and other materials from increasingly complex ores.
References


Ortiz, F. (2012). Dealing with categorical data types in a designed experiment part i: Why you should avoiding using categorical data types. *STAT T&E Center of Excellence.*


Appendix A

Supplementary information: Chapter 3

Table A-1. Element contents in old alkaline POX discharge analyzed by ICP-OES

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Table A-2. Element contents in new alkaline POX discharge analyzed by ICP-OES

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<td>9.20</td>
<td>16.50</td>
<td>316.00</td>
<td>46.10</td>
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</table>
Figure A-1. TEM image of the alkaline POX discharge (green box: expected as the locked sulfide and iron oxide, which covered the gold)
Figure A-2. TEM image of the alkaline POX discharge (orange box: expected as the dolomite minerals and related gold)
Figure A-3. TEM image of the alkaline POX discharge (green box: expected as the complicated mineralogy and related gold)
Table A-3. Element contents in alkaline POX feed analyzed by ICP-OES

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Ag</th>
<th>Al</th>
<th>As</th>
<th>Ba</th>
<th>Be</th>
<th>Ca</th>
<th>Cd</th>
<th>Ce</th>
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<tbody>
<tr>
<td>Unit</td>
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<td>%</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>%</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>Content</td>
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<td>7.92</td>
<td>4.5</td>
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<table>
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<th>Cu</th>
<th>Fe</th>
<th>K</th>
<th>La</th>
<th>Li</th>
<th>Mg</th>
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</thead>
<tbody>
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<td>ppm</td>
<td>%</td>
<td>%</td>
<td>ppm</td>
<td>ppm</td>
<td>%</td>
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<tr>
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<td>347</td>
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<td>30</td>
<td>3.96</td>
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<table>
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<th>Na</th>
<th>Ni</th>
<th>P</th>
<th>Pb</th>
<th>Rb</th>
<th>S</th>
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<td>%</td>
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<table>
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<tr>
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<th>Sr</th>
<th>Ti</th>
<th>U</th>
<th>V</th>
<th>Y</th>
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<td>ppm</td>
<td>%</td>
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<td>ppm</td>
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<td>ppm</td>
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<tr>
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<td>447</td>
<td>20</td>
<td>340</td>
<td>44</td>
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</table>
Figure A-4. TEM image of the alkaline POX feed - 1 (yellow box: expected as the locked C-matter)
Figure A-5. TEM image of the alkaline POX feed - 2 (yellow box: expected as the locked C-matter)
Figure A-6. TEM image of the alkaline POX feed - 3 (yellow box: expected as the locked C-matter)
Appendix B

Supplementary information: Chapter 5

**Figure B-1.** EDS analysis of spectrum 1 in Figure 5-10

**Table B-1.** Element contents of spectrum 1 in Figure 5-10

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass Norm. (%)</th>
<th>Atom (%)</th>
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<tbody>
<tr>
<td>Ca</td>
<td>1.31</td>
<td>0.90</td>
</tr>
<tr>
<td>Fe</td>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
<td>O</td>
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<td>4.89</td>
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<tr>
<td>S</td>
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<td>0.18</td>
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<tr>
<td>Si</td>
<td>95.56</td>
<td>93.98</td>
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<tr>
<td>Total</td>
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</table>
Figure B-2. EDS analysis of spectrum 2 in Figure 5-10

Table B-2. EDS analysis of spectrum 2 in Figure 5-10

<table>
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<th>Element</th>
<th>Mass Norm. (%)</th>
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</tr>
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<tbody>
<tr>
<td>Ca</td>
<td>55.56</td>
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<td>Fe</td>
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<td>4.98</td>
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<tr>
<td>S</td>
<td>0.19</td>
<td>0.18</td>
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<tr>
<td>Si</td>
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<tr>
<td>Total</td>
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<td>100.00</td>
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</table>
Figure B-3. EDS analysis of spectrum 4 in Figure 5-10

Table B-3. EDS analysis of spectrum 4 in Figure 5-10

<table>
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<th>Element</th>
<th>Mass Norm. (%)</th>
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</tr>
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<tbody>
<tr>
<td>Ca</td>
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<td>Fe</td>
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<td>Mg</td>
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<tr>
<td>O</td>
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<tr>
<td>S</td>
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<tr>
<td>Si</td>
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<td>Total</td>
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</table>
Appendix C

Supplementary information: Chapter 7

Table C-1. Test 1 flotation conditions

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<th>Kerosene (g t⁻¹)</th>
<th>MIBC (g t⁻¹)</th>
<th>Collecting time (min)</th>
<th>Cond. Speed (rpm)</th>
<th>Collect. Speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rougher</td>
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<td>1,200</td>
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<tr>
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<td>350</td>
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<td>11</td>
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Table C-2. Test 1 flotation results

<table>
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<th>Cum. Yield (%)</th>
<th>Cum. C-matter (%)</th>
<th>Cum. S (%)</th>
<th>Cum. C as CO₃ (%)</th>
<th>C-matter grade (%)</th>
<th>S grade (%)</th>
<th>C as CO₃ grade (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rougher</td>
<td>9.84</td>
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<tr>
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Table C-3. Test 2 flotation conditions

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<th>MIBC (g t⁻¹)</th>
<th>Collecting time (min)</th>
<th>Cond. Speed (rpm)</th>
<th>Collect. Speed (rpm)</th>
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</thead>
<tbody>
<tr>
<td>Rougher</td>
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<td>22</td>
<td>3</td>
<td>1,200</td>
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</tr>
<tr>
<td>Scavenger 2</td>
<td>-</td>
<td>11</td>
<td>3</td>
<td>1,200</td>
<td>1,500</td>
</tr>
<tr>
<td>Scavenger 3</td>
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</table>

Table C-4. Test 2 flotation results

<table>
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<th></th>
<th>Cum. Yield (%)</th>
<th>Cum. C-matter (%)</th>
<th>Cum. S (%)</th>
<th>Cum. C as CO₃ (%)</th>
<th>C-matter grade (%)</th>
<th>S grade (%)</th>
<th>C as CO₃ grade (%)</th>
</tr>
</thead>
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## Table C-5. Test 3 flotation conditions

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<th>MIBC (g t⁻¹)</th>
<th>Collecting time (min)</th>
<th>Cond. Speed (rpm)</th>
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<td>1,200</td>
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## Table C-6. Test 3 flotation results

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<th>Cum. C as CO₃ (%)</th>
<th>C-matter grade (%)</th>
<th>S grade (%)</th>
<th>C as CO₃ grade (%)</th>
</tr>
</thead>
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<td>4.46</td>
<td>12.59</td>
<td>1.97</td>
<td>2.79</td>
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<td>8.76</td>
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