# MEMBRANE CONTACTORS FOR CYANIDE TREATMENT AND RECOVERY: IMPLEMENTATION AND EVALUATION AT GOLD PROCESSING FACILITIES IN AREQUIPA, PERU

by

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# ABSTRACT

Cyanide is widely used in the gold extraction industry but poses environmental and human health hazards due to its acute toxicity. The first objective of this thesis was to characterize gold processing facilities in the Arequipa region of Peru and evaluate current cyanide usage and management approaches. Through the analysis of six different gold processing facilities, volatilization of free cyanide during processing and accumulation of metals, cyanide and metal-cyanide complexes, through zero effluent discharge policies were identified as key issues. Analysis of tailings revealed higher levels of cyanide and metals than previously reported in literature, indicating cyanide retention in tailings storage facilities, even after months of inactivity. Findings from this study highlighted the need for cyanide treatment and/or recovery and reuse at these facilities.

The core component of this thesis was to develop and apply a novel membrane contactor system to evaluate the feasibility of recovering cyanide at gold extraction facilities. A lab-scale membrane contactor system was constructed that allowed evaluation of different membranes (polypropylene (PP) and polytetrafluoroethylene (PTFE)) for recovering cyanide from synthetic effluent solution and an effluent from a US-based gold processing plant. The effects of variables including distillate pH, temperature, and feed cyanide concentration on cyanide recovery efficiency were examined. The results showed that PTFE and PP membranes could be used to effectively recover cyanide, and that membrane contactors are cost-competitive with current recovery methods.

Based off the lab-scale research, a pilot-scale membrane contactor was built and tested with effluents from gold processing plants in the US and Arequipa. Although treatment of US effluents was similar to results generated from lab-scale experiments, Arequipan effluents presented more challenges as mineral precipitation affected system performance. A stepwise pH adjustment of the feed solution improved cyanide recovery for one Arequipan facility. Despite these additional challenges, economic analysis suggested that cyanide recovery via membrane contactors is more cost-effective than purchasing new cyanide. Results from this thesis underscore the potential of membrane contactors as a sustainable and scalable solution for cyanide recovery in gold processing and are expected to contribute to the further development and implementation of this technology.

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| | |
|---|---|
| American Society for Testing and Materials | ASTM |
| Adenosine triphosphate | ATP |
| Acidification, volatilization, and reutilization | AVR |
| Below detection limit | BDL |
| Capital expenditures | CAPEX |
| Carbon in pulp | CIP |
| Deionized | DI |
| Energy dispersive X-ray spectroscopy | EDS |
| High-density polyethylene | HDPE |
| International Cyanide Management Code | ICMC |
| Ion Chromatography | IC |
| Inductively Coupled Plasma Spectroscopy | ICP |
| Inductively coupled plasma-optical emission spectroscopy | ICP-OES |
| Life cycle assessment | LCA |
| Lethal dose 50 | $LD_{50}$ |
| Ministry of Environment (Peru) | MINAM |
| Ministry Of Energy and Mines (Peru) | MINEM |
| Not available | NA |
| Net present value | NPV |
| Operating expense | OPEX |
| Peruvian Sol | PEN |
| Polypropylene | PP |
| Polytetrafluoroethylene | PTFE |
| Polyvinylidene fluoride | PVDF |
| Strong acid dissociable cyanide complex | SAD |
| Supervisory control and data acquisition | SCADA |
| Severe acute respiratory syndrome coronavirus 2 | SARS-CoV-2 |
| Sulfidization, acidification, recycling and thickening | SART |
| Scanning electron microscope | SEM |

| | |
|---|---|
| Test ‘N Tube | TNT |
| Total organic carbon | TOC |
| Tailings storage facility | TSF |
| United States | US |
| United States Environmental Protection Agency | US EPA |
| Ultraviolet | UV |
| Weak acid dissociable cyanide complex | WAD |

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# CHAPTER 1 INTRODUCTION

## 1.1 Background

### 1.1.1 Gold Cyanidation and Cyanide Usage in Arequipa, Peru's Gold Processing Industry

The process of gold production has changed substantially over the past several hundred years transitioning from placer, or alluvial-based, mining, to gold amalgamation with mercury, and after the 19th century to the use of gold cyanidation (Verbrugge et al., 2021). The transition of gold processing to gold cyanidation has increased the efficiency of gold extraction, enabling the extraction of gold from low-grade ores, further boosting the gold mining industry (Verbrugge et al., 2021). Gold cyanidation, also known as the cyanide process or the MacArthur-Forrest process, is a hydrometallurgical technique used to extract gold from ore by dissolving it in a high pH cyanide solution (Kondos et al., 1995). Gold will form water soluble complexes with free cyanide which are easily recoverable. To achieve this, gold ore is crushed in ball mills to increase the surface area of the ore particles. The crushed ore is mixed with water, sodium cyanide, and base solution to form a high pH slurry which is then mixed to ensure maximum contact between the cyanide and gold containing ore. During this process free cyanide will leach gold out of the ore by forming complexes in the following reaction:

$$4\,Au + 8\,NaCN + O_2 + 2H_2O \rightarrow 4\,Na[Au(CN)_2] + 4\,NaOH \quad (1.1)$$

For low-grade ores with limited silver content and at smaller scales, adsorption to activated carbon suspended in the solution, a process known as carbon-in-pulp (CIP), is generally considered the most cost-effective method for separating dissolved gold complexes from the slurry (Staunton, 2016). The gold-loaded carbon is subsequently filtered out by a wire mesh with the remaining slurry being discharged into tailings storage facilities TSFs. The gold is lastly recovered from the carbon by washing off the gold-cyanide complexes after which the solutions pass through an electrowinning cell to extract the gold. Gold cyanidation is used in Peru for nearly all sizes of gold mines and processing plants ranging from production capacities of 1000 to 918,000 ounces of gold per year (Newmont Mining Corporation, 2016; Veiga et al., 2015). Despite its own toxicity, gold cyanidation has largely replaced mercury amalgamation due to its higher gold extraction efficiency and imposition of stricter environmental regulations on mercury-based methods (Gonçalves et al., 2017).

Gold mining has been an important part of the history and economy of the Arequipa region in Peru for centuries and has been practiced for thousands of years (Eerkens et al., 2009; Lothrop, 1937). After Peru gained its independence from Spain in 1821, gold mining continued to be an important industry in the region, and in the 20th century, large-scale mining operations began to be established in the area, with the

introduction of more advanced technologies (such as gold cyanidation) and equipment (Beal et al., 2013). As one of the largest gold producers in the world, Peru's mining industry is vital for the country's economy and has played a major role for Peru's economic recovery following the SARS-CoV-2 pandemic (Herrera Jara et al., 2022). The Arequipa region has the third largest mining industry in Peru, producing 19.5% of the country's annual gold in 2022 (Herrera Jara et al., 2022). Small-scale gold processing facilities (ore capacities up to 350 metric tons per day) play a large role in the industry, accounting for 40% of the Arequipa region's gold production, with medium- (ore capacities of 350-5,000 metric tons per day) and large-scale processing facilities (>5000 metric tons of ore capacity) responsible for the remaining 60% (Dammert Lira and Molinelli Aristondo, 2007; MINEM, 2022). Today, gold cyanidation is the preferred method of gold extraction in Peru (Vera Gargurevich et al., 2023) as efforts have been undertaken to reduce mercury pollution from artisanal and small-scale gold mining (Veiga et al., 2015). Peru has strict limits on the discharge of cyanide from gold processing facilities. However, many of Arequipa's processing facilities do not discharge water because the decanted tailings storage facility (TSF) pond water is typically recycled to reduce water consumption. There is little regulation on cyanide limits in tailings and during gold cyanidation itself, which impacts process water quality which in turn can affect cyanide use and accumulation of undesirable constituents. More information on the role of cyanide in the gold processing industry of Arequipa is provided in Chapter 2 and in a manuscript titled "The History and Future of Gold Mining in Peru", submitted to the journal of The Extractive Industries and Societies by the author Julia Zea and co-authors Carlos A. Zevallos-Rojas, Pablo Garcia-Chevesich, Francisco D. Alejo-Zapata, Eliseo Zeballos, Johan Vanneste, Vincent Hammer, Henry G. Polanco-Cornejo, Christopher Bellona, and David C. Vuono.

### 1.1.2 Cyanide in the Environment

The toxicity of cyanide arises from its propensity to bind to the ferric iron (III) of the mitochondrial cytochrome oxidase, inhibiting ATP production which leads to rapid cell death (Hall and Rumack, 1986). Due to its high bioavailability, free cyanide (HCN and $CN^-$) is regarded as the most toxic cyanide species (Dzombak et al., 2006). Wildlife can be exposed to free cyanide through various means, including inhaling HCN, and consuming contaminated water and animals (Eisler and Wiemeyer, 2004). Freshwater fish are especially sensitive to cyanide, experiencing adverse effects after continuous exposure to 5 µg/L of free cyanide and high mortality occurring at 20 µg/L of free cyanide (Eisler and Wiemeyer, 2004). Mammals and birds have similar oral $LD_{50}$, ranging from 1.4 mg $CN^-$/kg body weight to 14.8 mg $CN^-$/kg body weight depending on species (Eisler and Wiemeyer, 2004).

The environmental fate of cyanide compounds is influenced by their properties, as well as physical, chemical, and biological processes already present in the environment (Dzombak et al., 2006). The natural

cyanide cycle can degrade anthropogenic cyanide as many plants, bacteria, fungi species possess the ability to metabolize cyanide species (Yarar, 2001). However, mining wastewater often contains especially high concentrations of cyanide, metal-cyanide compounds, and heavy metals which inhibit bacterial growth and biodegradation. As a result, it has been reported that the most prominent form of natural attenuation in cyanide tailings is volatilization (Brüger et al., 2018) where free cyanide volatilizes as gaseous HCN to the atmosphere. Volatilized HCN is transported in the atmosphere though air movement and is eventually absorbed into moisture droplets and reenters surface water and soil though precipitation. Cyanide that volatilizes from storage ponds is incorporated into the natural cyanide cycle where it is degraded by hydrolysis, biological processes, or plant and animal metabolism. Metal cyanide complexes, with the exception of mercury cyanide, are considered less toxic, as the primary toxic agent, free cyanide, is only released through dissociation (Eisler and Wiemeyer, 2004). These complexes are more persistent than free cyanide and pose long-term environmental risks as they can release free cyanide over longer periods of time under low pH conditions (Eisler and Wiemeyer, 2004). During gold cyanidation processes, heavy metals are leached from the ore through the formation of metal cyanide complexes and retained in processing solutions and the TSF. The mobility of metals such as copper, iron, zinc, arsenic and mercury are greatly increased and pose an additional hazard when discharged to the environment. Past accidents involving the release of cyanide, cyanide complexes, and heavy metals have been environmentally devastating. The 2000 Baia Mare cyanide spill catalyzed the founding of the International Cyanide Management Code, a voluntary program to improve the best practice for the use of cyanide in gold mining, processing, and waste management. The prime concern of regulatory agencies and gold processing facility operators is the contamination of surface and ground waters with cyanide.

### 1.1.3 Cyanide Treatment Technologies

Cyanide treatment processes are applied to reduce residual cyanide concentrations in contaminated waste streams to levels that comply with storage regulations, as outlined in the international cyanide management code or by local regulations (Akcil, 2010). Common industrial cyanide treatment methods involve degradation processes such as alkaline chlorination, sulfur oxidation, and photolysis coupled with hydrogen peroxide (Kuyucak and Akcil, 2013). Although effective in reducing cyanide concentrations to acceptable levels, degradation processes result in the formation of cyanate and thiocyanate ammonia, leading to a degradation of water quality (Kuyucak and Akcil, 2013). Oxidation methods such as alkaline chlorination may also introduce secondary contaminations such as chloramine and excess chlorine, which may require additional treatment (Norman and Raforth, 1994). Furthermore, these cyanide detoxification approaches can be costly due to the expense of chemical reagents and offer no direct return on investment (Demopoulus and Cheng, 2004; Mosher and Figueroa, 1996). This economic burden can be especially

challenging for small- and medium-scale gold processing facilities, potentially discouraging voluntary adoption of best-practice cyanide handling protocol, such as the International Cyanide Management Code.

### 1.1.4 Cyanide Reuse Technologies

Cyanide recovery and reuse technologies have been proposed to reduce cyanide consumption and reduce cyanide treatment costs. The most commonly used cyanide recovery technology is acidification, volatilization, and reutilization (AVR) in which hydrogen cyanide is volatilized and the air/HCN mixture is then moved through a column containing a strong alkaline solution that will strip the HCN from the air into the solution as cyanide anions (Dai et al., 2012; US EPA, 1994). The main disadvantages of AVR are high capital and high operating and maintenance costs associated with the corrosiveness of the low-pH process fluid and acid gas (Estay et al., 2014; Fleming, 2016). The sulfidization, acidification, recycling and thickening process (SART) has also seen commercial application at gold processing facilities worldwide (Estay, 2018; Estay et al., 2020). The main advantage of this process is the additional recovery of copper that precipitates along with free cyanide. This not only reduces cyanide consumption but also allows for the processing of high copper ores through the generation of copper as a byproduct. More recently, Green Gold proposed the ReCyn process using a strong base resin to immobilize cyanide for reuse. Green Gold claims that this approach is used in 30 projects and that the cost of the recycled cyanide is approximately half of the cost of new cyanide (Whittle and Pan, 2020).

The focus of this thesis lies in the application of membrane contactors for efficient and economic cyanide recovery. Membrane contactors allow for the transfer of gases through a porous hydrophobic membrane, which separates the liquid feed (i.e., cyanide laden effluent) from the liquid distillate phase. This approach has been successfully demonstrated through desalination efforts (membrane distillation) and the recovery of ammonia (pKa = 9.25) from aqueous solutions under an alkaline feed and acidic distillate solution (Hasanoğlu et al., 2010; Huo et al., 2020; Lawson and Lloyd, 1997; Zhu et al., 2005). Past studies (Estay et al., 2021, 2013; Han et al., 2005; Shen et al., 1997; Wu et al., 2011) have shown that membrane contactors can be used to recover cyanide (pKa = 9.21) from synthetic cyanide solutions and pesticide manufacturing wasteater utilizing acidic feed and alkaline distillate solutions, allowing for the transfer of HCN gas through the membrane due to a difference in vapor pressure.

Membrane contactors can be constructed from relatively inexpensive and corrosion-resistant materials and offer high membrane packing densities (Huo et al., 2020). Subsequently, they are expected to be more compact, scalable, and cost-effective than the large stainless steel absorption columns used in AVR. Membrane contactors only require acid and base chemicals for operation, which are often less expensive than chemicals used in common oxidation treatment methods such as alkaline chlorination and sulfur oxidation. Furthermore, by removing cyanide from the effluent, no degradation products are formed that

would need to be addressed through further treatment. The flexibility and adaptability of membrane contactors make them a promising technology for the treatment of complex gold cyanidation effluents.

## 1.2 Research Motivation and Thesis Chapter

The main goal of this thesis was to characterize gold cyanidation effluents in the Arequipa region and develop and evaluate a cost-efficient cyanide recovery method. Membrane contactors were evaluated for cyanide recovery as they offer several apparent advantages over competing cyanide recovery technologies and traditional cyanide treatment methods. Membrane contactors were first studied at the lab-scale using synthetic wastewaters and US-based gold mining processing effluents, the findings of which were then applied to construct and test a pilot-scale system for the treatment of more complex effluents originating from Arequipan facilities. Chapters 2 and 3 of this thesis consist of manuscripts published in peer reviewed journals, whereas Chapter 4 consists of a manuscript submitted to a peer reviewed journal.

### 1.2.1 Chapter 2: Characterization of Medium and Small-Scale Gold Processing Operations, Wastewaters, and Tailings in the Arequipa Region of Peru

The second chapter focuses on the operational landscape of gold cyanidation in the Arequipa region of Peru. The objectives of this work were to characterize process waters and tailings of gold processing facilities under the specific conditions found in Arequipa and determine the fate of cyanide in the effluents of these sites. For this, six gold cyanidation facilities with ore capacities of 10-430 $m^3$/day were visited and characterized. Grab samples of barren water, decant water, and tailings were taken and analyzed for pH, cyanide speciation and concentration, and metals concentrations. Using measured data and information obtained through interviews, a cyanide mass balance was created to better understand the fate and losses of cyanide throughout the gold cyanidation process. The resulting data provides a snapshot of conditions commonly found in the gold processing industry of Arequipa, highlighting opportunities and challenges in the treatment of these complex effluents. Work detailed in this chapter is drawn from a journal publication titled “Characterization of medium and small-scale gold processing operations, wastewaters, and tailings in the Arequipa region of Peru” published in Science of the Total Environment with co-authors Johan Vanneste, Francisco D. Alejo-Zapata, Julia Zea, Héctor G. Bolaños-Sosa, Carlos A. Zevallos Rojas, Linda A. Figueroa, Aaron Malone, Christopher Bellona, David C. Vuono (Hammer et al., 2024).

### 1.2.2 Chapter 3: Membrane Contactors as a Cost-Effective Cyanide Recovery Technology for Sustainable Gold Mining

The third chapter focuses on the evaluation of membrane contactors as a cyanide recovery and treatment option to reduce cyanide concentrations of effluents discharged into tailings storage facilities. A

lab-scale membrane contactor was used to determine the viability of two membrane materials (polypropylene and polytetrafluoroethylene) in two different configurations (hollow fiber module and flat sheet). Experiments were conducted using synthetic cyanide solutions and the effluents of a US based mine and gold processing facility. Various parameters were altered including pH, feed cyanide concentration, distillate cyanide concentration, cross membrane pH differential, and temperature to determine optimal operating conditions. The cost effectiveness of this technology was evaluated for a small-scale (effluent flow of 10 m3/h) and a large-scale (200 m3/h) cyanide recovery scenario using a techno-economic analysis. Work from this chapter has been published in ACS ES&T Water under the title of "Membrane Contactors as a Cost-Effective Cyanide Recovery Technology for Sustainable Gold Mining" with the co-authors Johan Vanneste, David C. Vuono, Francisco D. Alejo-Zapata, Henry G. Polanco-Cornejo, Julia Zea, Carlos Zevallas Rojas, Linda A. Figueroa, and Christopher Bellona (Hammer et al., 2023)

### 1.2.3 Chapter 4: Pilot-Scale Assessment of a Mobile Off-Grid Membrane Contactor System for the Treatment of Cyanide in Gold Processing Wastewater in Arequipa

The research conducted in the fourth chapter builds off of the work conducted during completion of Chapter 3 for the development and deployment of a pilot-scale membrane contactor in Arequipa, Peru. The pilot-scale membrane contactor was developed to operate on solar power to consider off-grid gold processing locations. Experiments using synthetic water and real mining wastewater (from the same US-based facility as in Chapter 3) were conducted in Colorado to confirm the functionality of the system. The system was then shipped to Arequipa for further testing using gold mining effluents from the region. The work of this chapter has been submitted for publication as a manuscript titled "Pilot-scale assessment of a mobile off-grid membrane contactor system for the treatment of cyanide in gold processing wastewater in Arequipa" to the journal ACS ES&T Water with co-authors David C. Vuono, Francisco D. Alejo-Zapata, Julia Zea, Héctor G. Bolaños-Sosa, Carlos A. Zevallos Rojas, Linda A. Figueroa, Christopher Bellona, and Johan Vanneste.

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# CHAPTER 2 CHARACTERIZATION OF MEDIUM AND SMALL-SCALE GOLD PROCESSING OPERATIONS, WASTEWATERS, AND TAILINGS IN THE AREQUIPA REGION OF PERU

Modified from a paper published in Science of The Total Environment[1]

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## 2.1 Abstract

Gold cyanidation facilities in the Arequipa Region of Peru are challenged by the availability and quality of water for processing in an arid environment. The facilities reuse decant water which recycles residual cyanide but also undesirable constituents. To understand the impact of intensive recycling, we collected barren water, decant water, and tailings samples from six gold cyanidation facilities with ore capacities of 10-430 tons per day. Processing facilities in Arequipa recycle all effluents, with decant waters making up 58±11% of process waters. Decant water contained non-target metals: copper (394±161mg/L), iron (59±34 mg/L), and zinc (74±42 mg/L). In addition, decant water mean free and complexed cyanide concentrations were 534±129 mg/L and 805±297 mg/L, respectively. Complexed cyanide concentrations remained more constant than free cyanide concentrations with 786±299 mg/L for

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barren water and 805±297 mg/L for decant water. Cyanide mass balances showed between 21% and 42% of unaccounted free cyanide from the start of gold cyanidation and discharge to the tailings storage facility (TSF). Free cyanide estimated losses due to volatilization were 0.8 kg and 2.5 kg of hydrogen cyanide per ton of ore processed at barren water pH of 10.1 and 9.7. Together these results indicate two acute hazards: 1) volatilization of free cyanide during processing and 2) loading and retention of cyanides and metals into TSFs. This study elucidates the extent of uncontrolled vapor phase cyanide release during gold processing operation and contaminant concentrations in the tailings facilities. The data highlights the need for improvement oversight, accountability, and regulation of gold processing facilities practicing intensive recycling and zero discharge.

## 2.2 Introduction

The Arequipa region has the third largest mining industry in Peru, producing 19.5% of the country's annual gold in 2022 (Vera Gargurevich et al., 2023). Small-scale gold processing facilities (ore capacities up to 350 metric tons per day) play a large role in the industry, accounting for 40% of the Arequipa region's gold production, with medium- (ore capacities of 350-5,000 metric tons per day) and large-scale processing facilities (>5000 metric tons of ore capacity) responsible for the remaining 60% (Dammert Lira and Molinelli Aristondo, 2007; "Producción metálica Enero-Diciembre 2022," 2022). The process of gold extraction has changed substantially over the past several centuries evolving from placer, or alluvial-based, mining, to gold amalgamation with mercury, and starting in the 19th century, to the use of gold cyanidation (Verbrugge et al., 2021). Adoption of gold cyanidation has increased the efficiency of gold extraction, enabling the extraction of gold from low-grade ores, further expanding the gold mining industry (Verbrugge et al., 2021). Today, gold cyanidation is the preferred method of gold extraction in Peru (Vera Gargurevich et al., 2023) as efforts have been undertaken to reduce mercury pollution from artisanal and small-scale gold mining (Veiga et al., 2015). However, the growing gold mining industry in Arequipa raises concerns about the environmental impact of gold cyanidation (Roca Servat, 2012), because the processing facilities in the region face significant water challenges, resulting in conflicts on water rights, usage, and pollution (Demopoulus and Cheng, 2004; Mosher and Figueroa, 1996). Contamination of scarce water sources through mining is a major point of concern for agriculture, fish and crayfish populations in (Bebbington and Williams, 2008; Triscritti, 2013) gold processing locations, where the gold industry and communities coexist in proximity (Malone et al., 2021; Orellana Mendoza et al., 2021; Santi et al., 2021). Although previous literature has focused on the environmental impacts of mercury usage in artisanal and small-scale gold processing facilities, the potential impacts of the cyanidation process used at small-scale and medium scale gold cyanidation facilities have largely remained unstudied.

Gold cyanidation comes with its own challenges: cyanide is acutely toxic, volatile under low pH conditions, and complexes with heavy metals (Dzombak et al., 2006). Wildlife can be exposed to free cyanide through various means, including inhaling HCN, consuming contaminated water and animals (Eisler and Wiemeyer, 2004). Freshwater fish are especially sensitive to cyanide, experiencing adverse effects after continuous exposure to 5 µg/L of free cyanide and high mortality occurring at 20 µg/L of free cyanide (Eisler and Wiemeyer, 2004). Mammals and birds have similar oral $LD_{50}$, ranging from 1.4 mg $CN^-$/kg body weight to 14.8 mg $CN^-$/kg body weight depending on species (Eisler and Wiemeyer, 2004). Metal cyanide complexes, with the exception of mercury cyanide complexes, are considered less toxic, as the primary toxic agent, free cyanide, is only released through dissociation, however they still pose considerable hazards (Alencar Meira Da Silva and Davée Guimarães, 2024; Eisler and Wiemeyer, 2004; Manar et al., 2011). These complexes are more persistent than free cyanide and pose long-term environmental risks as they can release free cyanide over longer periods of time as they naturally degrade (Eisler and Wiemeyer, 2004). In sites where mercury contaminated tailings are reprocessed with cyanide to recover additional gold, as is common in Arequipa's small and medium scale processing plants, formation of mercury cyanide complexes exacerbates environmental harm (Malone et al., 2023).

In gold cyanidation facilities, heavy metals are leached from the ore through the formation of metal cyanide complexes and retained in processing solutions and the tailings storage facility (TSF) (Karimi et al., 2010). The creation of these complexes increases the mobility of metals such as Fe, Cd, Zn, Ni, Cu, Co, and Hg and creates additional hazards in the event of TSF failure (Cánovas et al., 2023; Meeussen et al., 1995). This was exemplified in the 2000 Baia Mare cyanide spill, which catalyzed the founding of the International Cyanide Management Code (ICMC) (Akcil, 2010). While the aim of this code is to improve the best practice for the use of cyanide in gold mining, processing, and waste management, this is still a voluntary program that is not adopted by all processing facilities. Many small- and medium-scale gold processing facilities in Peru have little incentive to participate in the cyanide code. Furthermore, while there are strict regulations for cyanide discharge to surface and groundwater (MINAM, 2017), there are no cyanide limits for tailings. Considering many of Arequipa's processing facilities do not discharge water (e.g., all the decanted TSF pond water is recycled to reduce water consumption), this management practice impacts cyanide use and accumulation of undesirable constituents in process waters and tailings (Bahrami et al., 2007). Thus, there is a need to characterize the process and tailings water quality to understand the impact of recycled cyanide and other constituents on operations and gold processing residuals (e.g., tailings and process effluents).

The main objective of this study was to characterize the process water and tailings at a range of facilities to identify the effects of intensive recycling and zero discharge practices on cyanide and cyanide metal complexes in process water and tailings. For this study, six gold cyanidation facilities, from 10

metric tons/day to 430 metric tons/day, were evaluated based on interviews for operations information and grab samples process water and tailings composition.

## 2.3 Materials and Methods

### 2.3.1 Facilities Evaluated and Operational Characteristics

Operating parameters of visited facilities were obtained through interviews with the lead process engineers of the sites (Table 2.1). Sites 1, 2 and 5 are located within 50 km of Arequipa city. Sites 3, 4, and 6 are located within 45 km of Chala, a town that houses a large gold processing industry with 34 registered processing facilities in the surrounding area. All analyzed facilities utilized gold cyanidation in a carbon-in-pulp/electrowinning process. Operators and process engineers were interviewed to obtain operational parameters such as NaCN and NaOH consumption, water flows, water sources, and processing capacity. This information was used to calculate water flow balance, cyanide usage, and cyanide fate mass balances.

Table 2.1 Summary of gold processing facilities in this study. NA = not available. * = uncertain information

| Site # | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Location | Inland | Inland | Inland | Coastal | Inland | Coastal |
| Site type | Training | Processing | Mine and Processing | Processing | Processing | Processing |
| Estimated ore processing (metric tons/day) | 10 | 15 | 200 | 250 | 350 | 430 |
| NaCN consumption (kg/metric ton of ore) | 2 | 4 | 2.4-2.5 | NA | 6 | 6.5 |
| NaOH consumption (kg/metric ton of ore) | 3 | NA | 2.2 | NA | 2-3.5 | 2-3 |
| Process water flow (m3/day) | 12 | 18 | 230-240 | 85* | 420 | 462 |
| Source water consumption ($m^3$/day) | NA | NA | 150 | 30 | NA | 120 |
| TSF status | Active | Active | Active and inactive | Active and inactive | Active and inactive | Active |

### 2.3.2 Water and Tailings Samples

Three types of water samples were collected at the studied cyanidation facilities: source water, barren water, and decant water. Source water refers to well-water used to cover water consumption during the cyanidation process and storage in the TSF. Barren water refers to samples taken from the effluent of the last carbon adsorption tanks prior to being pumped into the TSF. Decant water refers to water from the active TSF reclaim pond that is reused in the cyanidation process and was sampled from a smaller storage pond prior to being returned to the processing facility. Sampling locations are depicted in Figure A.1 of Appendix A ion. pH and conductivity were measured immediately, after which grab samples were split into triplicates of 15 mL filtered (0.45 µm) and unfiltered water and stored in falcon tubes. To preserve cyanide concentrations of barren water and decant water samples, 1 ml of 1 M NaOH water was added to the falcon tube. The cyanide concentration was measured on the day of collection using a field spectrometer and Hach 862 test tubes and ICP, IC, and TOC analysis were carried out within 2 days. Overall storage times for samples ranged from 3 days to 10 days under the mentioned conditions.

Tailing samples were collected from inactive TSFs at sites 3 and 4, and from the beach of active TSFs at sites 1, 2, and 6. Each sample was taken in triplicates from surface and subsurface layers in random patterns over 12 m2 and stored in 50 ml polyethylene vials for further analysis. A list of collected samples is summarized in Table A.2.

### 2.3.3 Sample Analysis

Conductivity and pH were measured using an Apera Instruments SX823-B multi parameter meter and probe. Free cyanide was measured manually with Hach Test ‘N Tube (TNT) 862 using the colorimetric pyridine barbituric acid method. The tubes were then analyzed using a Hach DR 1900 field spectrometer. Total cyanide and weak acid dissociable cyanide complex (WAD) concentrations were determined using an OI Analytical Flow Water FS3700 Automated Chemistry Analyzer with 330092CT and 330090CT cartridges. The methods used for the analysis were ASTM D 7286-08 for total cyanide and ASTM 7511 for WAD. Elemental analysis of the waters was performed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Avio-500, PerkinElmer, Fremont, CA). Inorganic anions in the water samples were measured by ion chromatography (IC) (Dionex 1500, Sunnyvale, CA). Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, Columbia, MD).

The tailings samples were analyzed for pH by adding deionized water and a 0.01 M $CaCl_2$ water in a ratio of 1:2 as described in ASTM D4972-19. Water content and dry weight were determined using the ASTM D2216-92 standard methods by heating the soil sample to 110 °C for 24 hours. If applicable, the supernatant of the tailings samples was decanted and analyzed using Hach Test ‘N Tube (TNT) 862 test tubes, as well as ICP-OES, IC, and TOC. Metals within the tailing samples were extracted by US EPA

method 3051A and the extract analyzed using ICP-OES (Clesceri et al., 1998). The amount of water-soluble cyanide in the dry tailings was determined by leaching the tailings sample in a 10% NaOH water over a time period of 48 hours (Zagury et al., 2004). The leached water was then analyzed for free cyanide using Hach Test 'N Tube (TNT) 862 test kits.

## 2.4 Results and Discussions

### 2.4.1 Summary of the Gold Cyanidation Process in the Arequipa Region

Most commonly, gold processing facilities in the Arequipa region operate independently from mines, purchasing ore from multiple sources. Ores of varying grades are mixed to form a consistent gold grade and are crushed in ball mills (Figure A.2 A). Water, NaCN and NaOH are added in the appropriate quantity to the ball mills and conveyed to lixiviation tanks (Figure A.2 B). The heap leach process was not observed for any of the visited sites. Pregnant water from the lixiviation tanks is then pumped into a series of adsorption tanks containing activated carbon to extract the gold-cyanide complexes (Figure A.2 C). Gold loaded carbon is periodically removed from the adsorption tanks and eluted from the carbon with a concentrated sodium cyanide solution at 95-120°C for subsequent electrowinning. The remaining barren water is then pumped into the TSF which is lined with a high-density polyethylene (HDPE) liner to contain the tailings material and avoid seepage (Figure A.2 D). No thickening process was observed as water recycling from the TSF pond is common practice.

### 2.4.2 Barren and Decant Water Characterization

Gold cyanidation facilities target a pH of at least 10.5 to maximize cyanide leaching efficiency and balance cyanide addition with free cyanide losses through volatilization (Perky et al., 1999). A pH of 11.5 is required to limit the fraction of volatile HCN to 1% of free cyanide. Cyanide speciation based on a $pK_a$ of 9.48 at 15°C (Visual MINTEQ 3.1) and measured pH (Table A.2.), suggests that HCN/total free cyanide ranged from 5 to 40% in barren solutions and 10 to 60% in decant waters (Figure 2.1). Volatilization is responsible for 90% of natural cyanide removal from gold cyanidation effluents and tailings and has been the most common method of reducing cyanide concentrations (Kuyucak and Akcil, 2013). However, recent research indicates that volatilized HCN does not undergo significant natural degradation and contaminates air in the vicinity of gold cyanidation facilities, presenting considerable health and environment hazards (Brüger et al., 2018). Studies have even documented HCN emissions from gold processing facilities operating at high pH values (5 air/ppm of HCN at pH > 12 with ~ 1 g/L aqueous cyanide), suggesting our study locations likely have higher HCN releases due to lower operating pHs (Brüger et al., 2018). While HCN was detected at several sites through personal HCN detectors, precise air HCN concentrations were not directly measured.

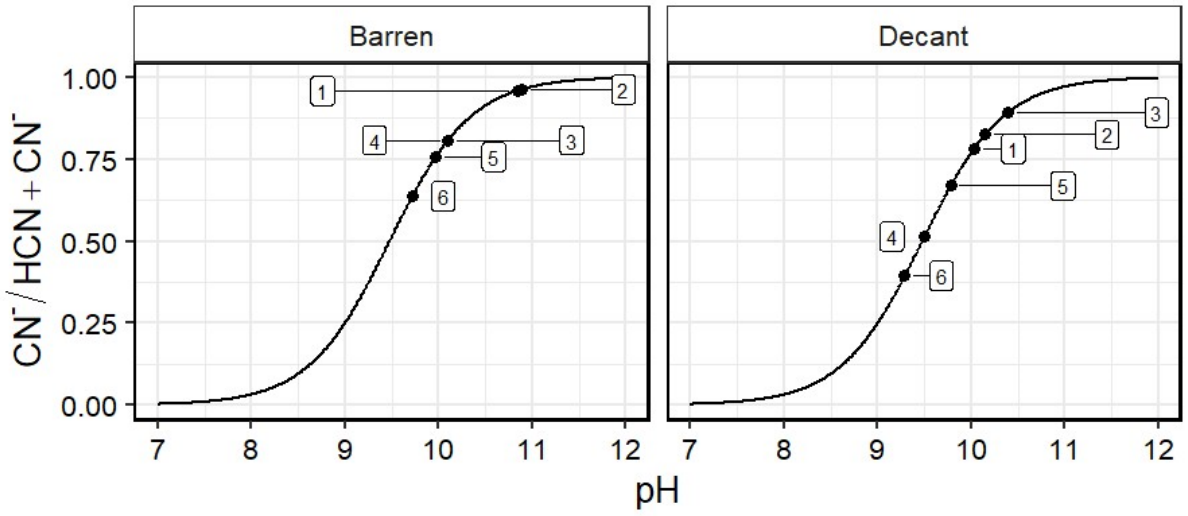


Figure 2.1 Distribution of CN- as a function of pH at 15 °C (pKa = 9.48) with corresponding measured pH from each site. The distribution curve of CN-/HCN was generated using Visual MINTEQ 3.1

The surface areas of TSF ponds were estimated to range from 20 $m^2$ at site 1 to 11,600 $m^2$ at site 6. Sites with larger TSF pond surface areas had lower measured pH values in the decant water. This observation is supported through a Pearson correlation with r = -0.804, and p = 0.05 values, suggesting a strong negative correlation between decant water pH and TSF pool sizes; as TSF surface area increases, pH in decant water decreases. $CO_2$ uptake from the atmosphere could be the main driver in pH reduction of gold cyanidation decant waters, which is expected to increase with higher TSF surface areas (Johnson, 2015). The pH of barren solutions also decreased at sites with larger TSF pond surface areas, this suggests the reuse of low pH decant water decreases the overall processing pH without adequate correction. Ore characteristics, water buffering capacity, and individual dosage control also impact the pH of the processing sites and are not captured by this correlation.

The speciation of cyanide and its concentrations greatly influence toxicological risks: high concentrations of free cyanide indicate high acute toxicity while high concentrations of metal-cyanide complexes suggest long term releases of cyanide and metal mobilization (Johnson, 2015). Samples obtained from the examined gold processing facilities were analyzed for cyanide speciation in both barren and decant waters (Figure 2.2). WAD and strong acid dissociable complex (SAD) concentrations were determined by subtracting measured free cyanide concentrations from measured WAD concentrations and measured WAD concentrations from measured total cyanide concentrations respectively. Previous studies have reported free cyanide concentrations in gold processing effluent between 11.2 to 530 mg/L, with

most concentrations reported at less than 100 mg/L (Mike A. Acheampong et al., 2013; Mike Agbesi Acheampong et al., 2013; Bakatula and Tutu, 2016; Johnson, 2015; Khamar et al., 2015; Leon et al., 1995; Zagury et al., 2004). Measured free cyanide concentrations at the six studied sites varied widely but were generally higher than literature reported values, ranging from 19.5 mg/L for the decant water of site 2, to 1375 mg/L for barren water of site 6 (average among the six sites was 753.8 mg/L). Low pH operating conditions require facilities to continuously add more cyanide to offset losses due to HCN volatilization.

High free cyanide concentrations are needed in gold cyanidation operations to overcome the demand created by presence of cyanide complexing metals (e.g., copper, iron, zinc) and to promote selective adsorption of gold-cyanide complexes onto activated carbon by shifting copper and other cyanide complexes to less adsorbable species (Dai et al., 2012; Larrabure and Rodríguez-Reyes, 2021). Copper specifically reduces the process efficiency by leaching faster than the targeted precious metals (Sceresini, 2005). Due to the elevated copper, iron and zinc levels reportedly observed in gold-bearing ores in the Arequipa region (De Haller and Fontbote, 2009), as well as the retention of metals in recycled process waters, we also observed high free cyanide concentrations at the six sites (Figure 2.2). Results of WAD and SAD cyanide complex analysis of barren and decant water samples are presented in Figure 2.2 and concentrations of copper, iron and zinc in Figure 2.3. The presence of copper- and zinc-cyanide complexes at sites 1, 4, 5, and 6 is indicated through relatively high concentrations of copper and zinc coinciding with high WAD concentrations. Sites 3, 5, and 6 had high SAD concentrations, with site 3 having the highest concentration of iron. However, barren and decant water from Sites 5 and 6 did not have high measured iron concentrations which may be due to complexed iron not being measured through ICP analysis. Positive correlations were found between free cyanide and sum of complexed cyanide ($r = 0.787$ and a $p = 0.063$ for the barren water and $r = 0.844$ with a $p = 0.035$ for the decant water), and between copper and zinc concentrations and WAD cyanide ($r = 0.751$ with a $p = 0.085$ for decant waters and $r = 0.978$ with a $p = 0.001$) in both barren and decant waters indicating increased free cyanide dosing to address cyanide complexation to non-target metals. Additional metals of interest including As, Cd, Ni and Pb also occur naturally in the ores and soil of the Arequipa region (Huerta Alata et al., 2023) and were measured in barren and decant waters (Figure A.3) at significantly greater concentrations than environmental quality standards for rivers established by the Peruvian Ministry of the Environment (MINAM) (MINAM, 2017).

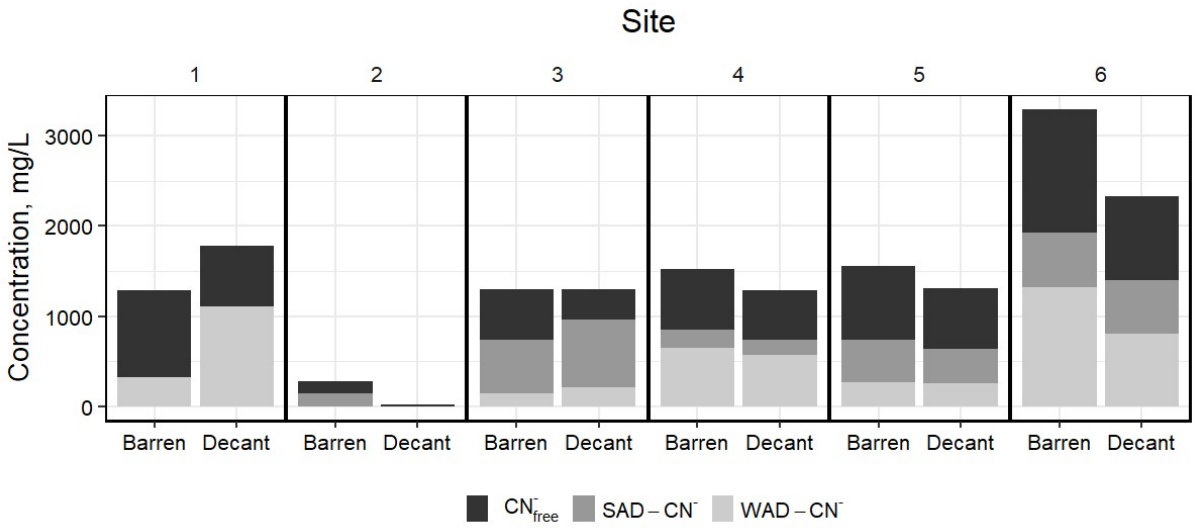


Figure 2.2 Concentration of free cyanide, WAD, and SAD cyanide forms in the barren and decant waters. Total cyanide concentrations are the sum of free cyanide, WAD, and SAD.

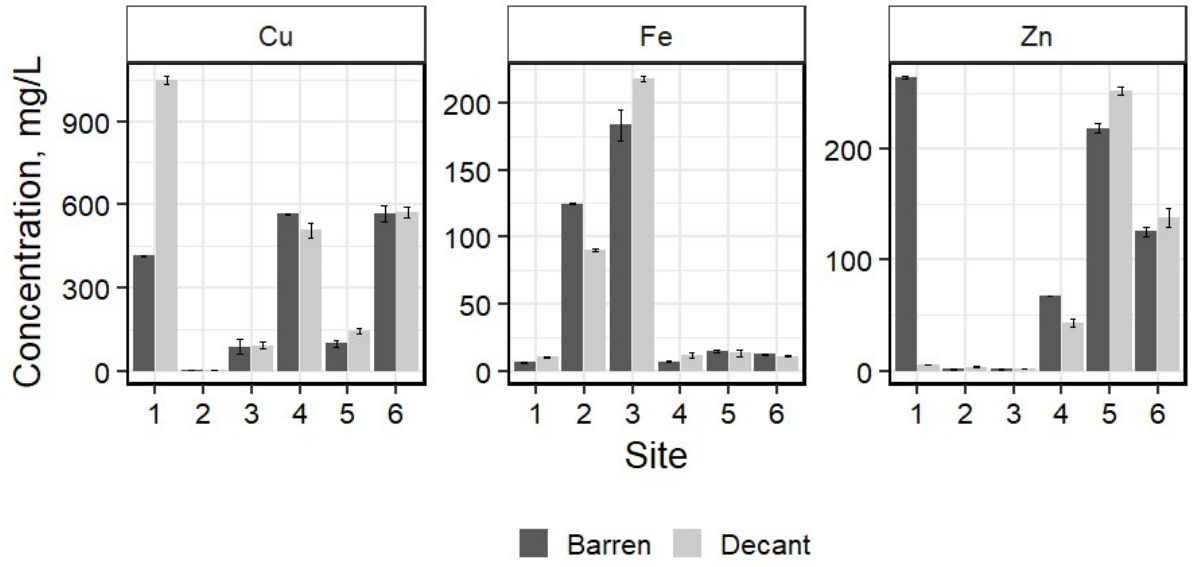


Figure 2.3 Concentrations of copper, iron, and zinc in barren waters and decant waters.

Due to the lack of surface water in the coastal areas of the Arequipa region, water demands of the processing facilities are met either using industrial water of uncertain origin or local groundwater. At sites 4 and 6, source water is primarily made up of locally sourced groundwater. We observed both the source water to have higher than expected conductivity (48,200 µS/cm and 39,100 µS/cm respectively) compared to their inland counterparts (1192 µS/cm and 1043 µS/cm for sites 3 and 5 respectively) (Figure A.4). Extraction of groundwater for industrial purposes likely causes saltwater intrusion into the aquifer (Sherif

and Singh, 2002), which causes high conductivities in gold cyanidation barren and decant waters and leaves Chala dependent on importing domestic water from surrounding areas.

In comparison to coastal facilities, inland facilities had significantly lower barren and decant water conductivities due to the usage of low conductivity source water (Figure A.4). Water samples from site 4 measured the highest conductivity in this study at 70,900 µS/cm for the decant, and 68,900 µS/cm for barren water, whereas site 2 measured the lowest conductivities at 4760 µS/cm for barren, and 5760 µS/cm for decant water. The reuse of decant water in the processing facilities also increases ion concentrations due to evaporative water losses (15 m3/day from site 3 and 60 m3/day from site 6, discussed in section 3.3). The salinity and composition of source water is important for processing facilities as the water quality directly influences the efficiency of gold cyanidation and was reported to be one of the major challenges coastal processing facilities face (Adams, 2001; Perky et al., 1999). Very alkaline saline conditions may further promote co-precipitation of metal hydroxides which results in acidic products that drive the pH down (Perky et al., 1999; Van Vuuren et al., 2000). Precipitation of metal hydroxides and diminishing gold dissolution rate at pH > 9.5 may be a contributing factor in gold cyanidation facilities to operate at pH < 11.5 (Marsden and House, 2006).

### 2.4.3 Water Balance and Fate of Cyanide

The overall water budget of a gold cyanidation facility can significantly influence the management of process waters and other operations such as water treatment processes and chemical dosing. For facilities with negative water balances and no wastewater discharge (this study), operators estimated that 35-80% of barren water was recovered as decant water for reuse. With no processes for removal of constituents including cyanide and cyanide complexes (WAD and SAD), metals, and other anions and cations, water recycling can result in accumulation of these constituents within unit processes and tailings and also negatively impact cyanidation efficiency (Bahrami et al., 2007). Information gained through site visits was used to develop a water usage model for sites 3 and 6 which is presented in Figure 2.4. These sites have two contrasting operational water schemes: site 3 uses more source water at the start of the process (62.5%) compared to site 6, which uses more recycled water (71.5%). These differences are likely based on economic reasons. Site 3 opts for higher overall water consumption at a lower source water cost (4.4 PEN/m3) in favor of higher process water quality. Conversely, site 6 pays 12 PEN/m3 for their source water and to offset this higher cost, they recycle more of their decant water (water costs obtained through personal correspondence). Detailed water consumption and water usage profiles hold important information to optimize decant water recycling, which impacts economic considerations, process water quality, TSF contaminant loading, and effluent water discharges (if applicable).

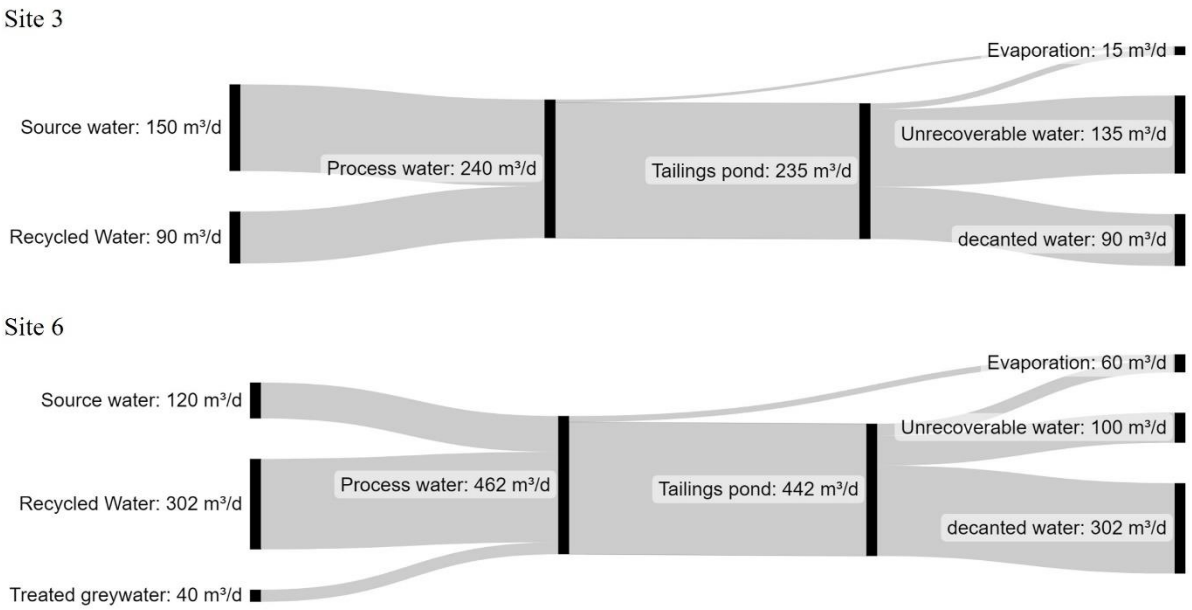


Figure 2.4 Water flows and consumption of sites 3 and 6

Next, we aimed to characterize the fate of cyanide throughout the cyanidation process, including loss from volatilization, degradation, or accumulation in TSFs. Cyanide consumption at all sites ranges from 2-6.5 kg NaCN/metric ton of ore (Table 2.1), with sites 2, 5, and 6 being on the high end of reported average consumptions (1-6 kg NaCN/metric ton of ore) (Kianinia et al., 2018; Kondos et al., 1995). Sites 3 and 6 were chosen for a more in-depth analysis (Figure 2.5). The percentage of new free cyanide to total free cyanide (recycled free cyanide + new free cyanide) at the start of the gold cyanidation process is similar between sites 3 and 6 (88.8% and 82.3%, respectively). Most of the free cyanide consumption occurs during the lixiviation process when cyanide complexes with metals. Low Cu and Zn concentrations (WAD forming metals) and high Fe (SAD forming metal) concentrations at site 3 (Figure 2.2) result in more CN- being bound to SADs than WADs. Conversely, high Cu and Zn, and low Fe concentrations at site 6 result in more CN- being bound to WADs than SADs.

The gold-cyanide binding efficiency is comparable between the facilities, measuring both at 0.15% demonstrating factors such as pH and conductivity do not appear to influence cyanide efficiency. Gold-cyanide binding efficiency was calculated with the following equation:

$$Gold - cyanide\ binding\ efficiency = 2 * \frac{gold\ grade * plant\ capacity}{M_{Au}} * \frac{M_{NaCN}}{NaCN\ consumption} \quad (2.1)$$

Contrary to concerns brought up by process engineers at the study locations and La Brooy and Muir, 1993, extensive decant water reuse does not appear to impact cyanide binding efficiency. This finding may enable the use of saline source waters, potentially relaxing the demand on groundwater wells and decreasing the amount of saltwater intrusion into the aquifer. However, more research is recommended to definitively ascertain co-variation and interdependence of operational parameters from saline water within the gold cyanidation process.

Unaccounted cyanide values, shown in Figure 2.5 (middle section) encompass free cyanide lost to natural degradation and volatilization during the gold cyanidation process. Site 6 had a higher unaccounted for free cyanide percentage (41.6%) compared to site 3 (20.6%). As reported in section 3.2, the pH of site 6 is lower than site 3, which increases HCN volatilization and causes higher unaccounted cyanide losses of site 6. Free cyanide remaining in the barren water is pumped into the TSF where it is either recycled through the decant water or settles in the TSF. Cyanide that remains in the TSF volatilizes, degrades naturally, persists in the porewater of the tailings, or dries out as NaCN (Johnson, 2015). The amount of free cyanide recycled through decant water is highly dependent on the amount of decanted water recycled. Site 6 recycles over twice the cyanide (50.1%) compared to Site 3 (23.5%) due to its higher decant water reuse.

At the time of the field sampling, none of the cyanidation facilities in this study participated in the ICMC and consequently, no additional treatment methods were used to reduce TSF cyanide concentrations to the recommended standard of 50 mg/L total cyanide. High cyanide concentrations in the TSF ponds are desirable for processing facilities with no effluent discharge as cyanide from decant waters can supplement overall cyanide consumption. However, volatilization of free cyanide is a major cyanide sink within the gold cyanidation process and an environmental concern. Processing water pH and TSF pond pH could be increased to avoid cyanide losses through volatilization and improve cyanide recycling through decant water. This would decrease the amount of new cyanide needed to maintain free cyanide levels while also mitigating the environmental and health hazard of HCN volatilization but could also lead to unwanted precipitation in high conductivity waters. Conversely, increasing free cyanide concentrations in the TSF poses an increased risk to wildlife, especially birds, with several facilities using bird deterrents such as speakers and shooting of blanks. The recovery of cyanide through novel technologies such as AVR, SART, and membrane contactors could provide a more direct pathway for cyanide reuse in the cyanidation process, greatly limiting cyanide discharge to the TSF altogether (Dai et al., 2012; Hammer et al., 2023; Kuyucak and Akcil, 2013; Whittle and Pan, 2020).

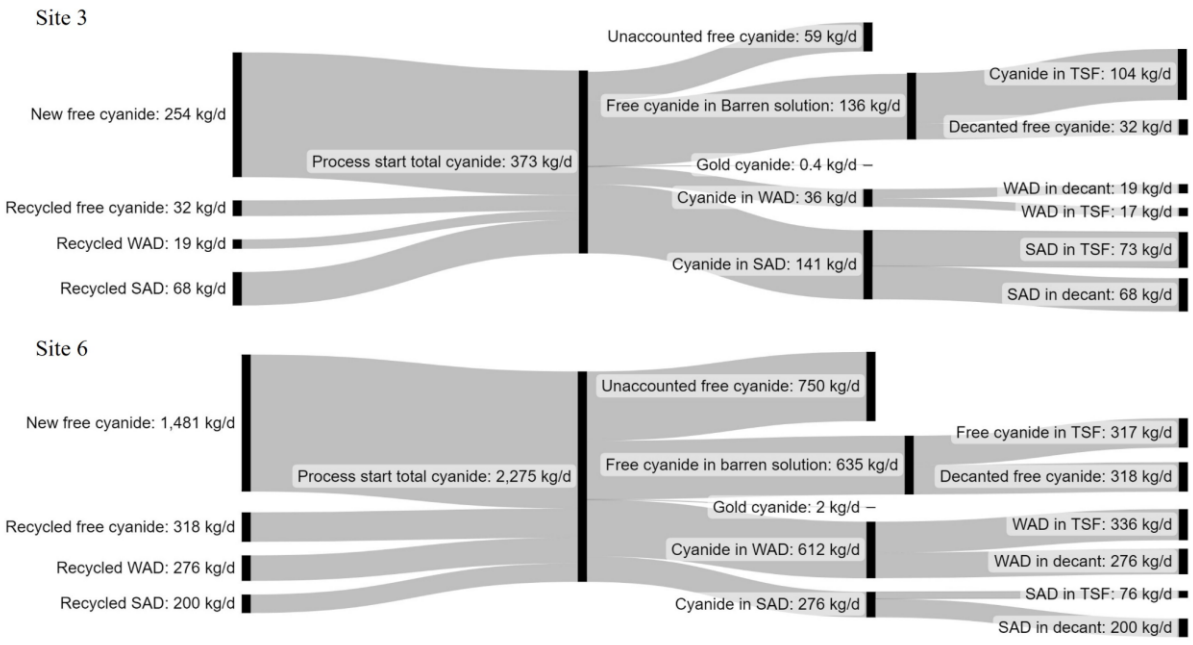


Figure 2.5 Process flow of Cyanide at Sites 3 and 6.

### 2.4.4 Tailings Solids Characteristics

Tailings solids samples were analyzed for water content, pH, cyanide, and metals (Tables 2.2 and 2.3). The inactive TSF surface and subsurface samples retained an average of 11% and 28% water content, respectively, and the active TSF surface and subsurface layers retained an average of 24% and 31% water content, respectively. These data demonstrate that in subsurface layers of inactive TSF, minimal water loss is observed, even after 1 year of inactivation (timeline provided through communication with process engineers). Finely milled tailings and the formation of crusts caused by high salinity (Figure A.5) facilitate water retention at inactive facilities. To accurately determine the influence of water retention on TSF safety, an assessment of tailings shear strength and tailings liquefaction throughout the depth of the TSF is needed.

Next, we compared the free cyanide concentrations in the surface layer of the inactive TSF at sites 3 (38,589 mg/kg) and the active TSF at site 6 (731 mg/kg) (Table 2.2). Both concentrations were higher than previously reported values of 3-53 mg of $CN^-$ per kg of tailings (Bakatula and Tutu, 2016; Fourie et al., 2008; Lemos et al., 2020; Zagury et al., 2004). The presence of high free cyanide concentrations in the inactive TSF of site 3 further indicates that the retention of free cyanide in TSFs might be greater than previously expected, increasing the potential environmental harm and impact of inactive TSFs. Free cyanide was also measured on the surface layer of the active TSF of site 1 (19.6 mg/kg), however, no free cyanide was found on the surface layer of sites 2 (active) and 4 (inactive). The tailings of site 2 likely

exhibit lower cyanide concentrations due to low effluent flow and low effluent cyanide concentrations. In contrast, site 4 with its comparatively low tailings solids pH promotes cyanide mobility, potentially contributing to its lower cyanide content. For sites 1, 3, and 6 it was further found that the surface layers contained more free cyanide than the subsurface layers, suggesting that free cyanide is migrating and accumulating at the surface of the TSF. The retention of free cyanide in TSFs is influenced by a variety of factors such as volatilization, complexation, precipitation, adsorption, biological transformation, and sulfurization (Johnson, 2015). While the retention of free cyanide in TSFs is often low due to these processes, some TSFs like site 3 may retain dangerous concentrations of free cyanide even after months of inactivation.

As metal-cyanide complexes are less susceptible to mechanisms governing the removal of free cyanide, we expected WAD and SAD concentrations in the TSFs to be higher than free cyanide concentrations. Indeed, at all sites WAD and SAD metal-cyanide concentrations exceeded free cyanide concentrations (Table 2.2). Notably high concentrations of WADs were found in the surface layers of sites 3 (78,614 mg/kg) and 6 (1,483 mg/kg). Similarly, SADs analysis revealed elevated concentrations at all TSFs with the surface layer of site 1 (6,807 mg/kg) and site 3 (14,552 mg/kg) exhibiting the highest concentrations. Elevated concentrations of WADs and SADs generally coincided with higher copper, zinc, and iron concentrations in the TSF (Table 2.3). High iron concentrations in samples with low SAD concentrations suggest incomplete leaching of iron during gold cyanidation or natural degradation of the release of iron through natural degradation of iron-cyanide complexes in the TSF. High concentrations of metal cyanide complexes highlight potential long-term environmental concerns through the gradual release of free cyanide and mobilization of metals from the TSF (Johnson, 2015). Tailings with total cyanide concentrations above 5,900 mg/kg and leachate (barren water) with total cyanide concentrations greater than 64 mg/L are classified very dangerous tailings by Arequipa's environmental authority (Eppers, 2014). All sites in this study complied with the recommended standards for the deposition of very dangerous tailings into a TSF with leachate control and both chemical and physical stabilization. However, monitoring programs of inactive and abandoned TSFs, overseen by the Peruvian Ministry of Mining (MINEM, 2001), could be significantly strengthened by incorporating cyanide assessments to a more comprehensive risk assessment of TSFs in this region.

Capillary action is likely transporting cyanides and salts to the TSF surface and water evaporation deposits free cyanide and cyanide complexes in the remaining pore water and tailings solids (Shehong et al., 2005). High cyanide concentrations in the surface layer of TSFs increase exposure potential for wildlife and enhance the susceptibility of cyanide contamination through eolian mobilization. Dust and aerosol transport in arid environments like the Atacama Desert are well studied and show insoluble dust deposition originating from local soil environments (Li et al., 2019). The TSFs in this study, located in the

outskirts of the Atacama Desert, likely experience similar erosion and aerosolization of cyanide laden dust from the dried-out surfaces of TSFs. This potentially contributes to the low cyanide concentrations found in the inactive TSF of site 4, compared to the active TSF of site 6. Chronic cyanide exposure, even in low concentrations, is known to cause adverse health effects observed in humans and animals (Cliff et al., 2015; Okolie and Osagie, 1999). Knowledge gaps exist regarding potential exposure pathways and the health consequences of inhaling cyanide-laden dust originating from TSFs deserves further investigation. To mitigate the risk of cyanide-laden dust contamination, we recommend the implementation of dust control and cover designs after TSF inactivation and prior to TSF closure.

Table 2.2 Water content, tailings solids pH, and cyanide concentrations of analyzed tailings. Numbers represent the sample site; S represents surface samples and U represents subsurface samples. Standard errors are shown in Table A.3.

| | 1S | 1U | 2S | 3S | 3U | 4S | 4U | 6S | 6U |
|---|---|---|---|---|---|---|---|---|---|
| TSF status | Active | Active | Active | Inactive | Inactive | Inactive | Inactive | Active | Active |
| Gravimetric water content (%) | 19% | 35% | 29% | 12% | 35% | 9% | 20% | 24% | 24% |
| pH, DI-water | 11.15 | 10.63 | 9.78 | 10.43 | 10.36 | 8.03 | 8.28 | 9.2 | 8.96 |
| pH 0.01M $CaCl_2$ | 11.2 | 10.38 | 9.15 | 10.27 | 9.55 | 7.86 | 8.07 | 8.97 | 8.68 |
| $CN^-$ (mg/kg – tailings) | 19.6 | 0.5 | 0 | 38,589 | 1,130 | 0 | 0 | 731 | 349 |
| WAD – $CN^-$ (mg/kg – tailings) | 357 | 17.5 | 1.9 | 78,614 | 4,234 | 0.28 | 2.9 | 1,483 | 852 |
| SAD – $CN^-$ (mg/kg – tailings) | 6,807 | 910 | 89.3 | 14,552 | 2,485 | 96.3 | 283 | 637 | 383 |

Gold cyanidation leaves behind large amounts of mobilized heavy metals which are of high-risk for the sensitive water systems of southern Peru (Karimi et al., 2010). Arsenic occurs naturally in rock and soil throughout the Arequipa region and is present in the tailings at concentrations up to 6,653 mg/kg (Table 2.3), 1000 times higher than typical As soil concentrations (6.5 mg/kg) (Huerta Alata et al., 2023). Other metals of concern, including Cd (930.0 mg/kg), Pb (11,250 mg/kg), Zn (6,604 mg/kg), and Co (84.5 mg/kg), are present at concentrations exceeding regular soil levels (Cd = 0.18 mg/kg; Pb = 9 mg/kg; Zn = 30 mg/kg; and Co = 4 mg/kg) by more than 200, 1000, 200, and 200 times respectively (Huerta Alata et al., 2023). Generally, metals were found in higher concentrations on the TSF surface than the subsurface, indicating mobilization of metals through cyanide complexation plays a major role in the heterogenous

distribution of metals. Sulfite weathering and metals depletion further increase tailings metal heterogeneity, creating enrichment and depletion potentially not fully captured by our samples (Blight and Bentel, 1983; Nikonow et al., 2019). Metal buildup and surface enrichment heighten environmental exposure risks through runoff and aerosolization, further highlighting the need for dust control or cover strategies.

Table 2.3 Concentration of metals in tailings. Standard errors are shown in Table A.4.

| Metal, mg/kg | 1S | 1U | 2S | 3S | 3U | 4S | 4U | 6S | 6U |
|---|---|---|---|---|---|---|---|---|---|
| Al | 3,647 | 2,771 | 22,389 | 5,464 | 15,981 | 5,152 | 7,718 | 5,007 | 6,452 |
| As | 239.1 | 155.6 | 109.5 | 240.1 | 131.1 | 4,611 | 3,506 | 6,653 | 5,547 |
| Cd | 22.3 | 5.2 | 4.2 | 19.1 | 45.2 | 346.0 | 708.6 | 558.5 | 930.0 |
| Cu | 3,272 | 7,054 | 139.0 | 107,243 | 3,469 | 3,169 | 1,987 | 4,205 | 3,861 |
| Fe | 210,058 | 14,078 | 49,136 | 19,808 | 30,476 | 75,798 | 69,704 | 147,015 | 122,698 |
| Ni | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Pb | 1,403 | 294.2 | 68.3 | 441.8 | 51.1 | 3,777 | 3,129 | 11,250 | 8,424 |
| Zn | 568.1 | 313.0 | 41.2 | 156.7 | 34.8 | 3,966 | 4,347 | 6,739 | 6,904 |
| Co | 53.7 | 14.0 | 29.9 | 84.5 | 25.2 | 62.9 | 58.4 | 63.5 | 49.8 |

Site visits highlighted tailings dam failures as a major concern of residents near TSFs. This concern is especially pronounced in Chala as many TSFs are located upslope from residential areas, potentially putting them into the spill zone of a potential dam breach. Historical data reveals that earthquakes are a major contributing factor in causing tailings dam failures, with 17% of incidents over the last 100 years being caused by earthquakes (Lyu et al., 2019). The Arequipa region of Peru exhibits a high frequency of seismic events, with 53 earthquakes recorded within the last year alone (U.S. Geological Survey, 2024). The 2001 southern Peru earthquake with a magnitude of 8.4 highlighted the susceptibility of TSFs to seismic activity by causing liquefications and partial damage to multiple TSFs (Rodriguez-Marek et al., n.d.). The Medium- and small-scale processing facilities are estimated to operate TSFs containing up to 500,000 m3 of tailings, a volume 5 times greater than the material released during the Baia Mare disaster. Consequently, the release of such quantities of tailings in the event of TSF failures would cause widespread cyanide and heavy metal contamination.

## 2.5 Conclusions

Extensive decant water recycling was found to be a major factor in the high concentrations of cyanide, cyanide complexes, and metals in both gold cyanidation effluents and tailings. The accumulation of these constituents is further increased by the absence of active effluent treatment at the visited sites. Decant

water recycling was further found to increase the conductivity of process waters. The potential presence and accumulation of mercury cyanide complexes in process water and tailings through the reprocessing of mercury amalgamation tailings deserves further investigation as these complexes are persistent and pose harm through bioaccumulation.

This study reveals high amounts of unaccounted free cyanide throughout the gold cyanidation process. Analysis through the mass balance of the measured cyanide concentrations and the reported dosing of sodium cyanide indicated substantial losses of free cyanide attributed to volatilization of HCN. The presence of vapor phase cyanide in the ambient air within the processing facilities poses considerable health risks to workers.

TSF were found to retain cyanide, even after being inactive for several months. Surface layers appeared to have higher cyanide concentrations than lower depths. Elevated surface cyanide concentrations in TSFs heighten the potential for the dispersion of cyanide-laden dust with wind events as the sites studied did not implement dust mitigation on inactive TSFs. Metal cyanide complexes (WAD and SAD) were found to be a significant contributor to the total cyanide remaining in TSFs. Exposure pathways and health effects of cyanide-laden dust are unknown and warrant further investigation.

A more extensive study of TSF surfaces is needed to evaluate the heterogeneity of cyanide and metals concentrations found in the tailings. Samples taken over a wider area would give a better understanding of metal enrichment- and depletion zones. Deeper subsurface samples along a depth gradient would also help better understand the transport and mobility of metals and cyanide within the TSF and give a more representative view of the TSF's overall metals concentration.

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# CHAPTER 3 MEMBRANE CONTACTORS AS A COST-EFFECTIVE CYANIDE RECOVERY TECHNOLOGY FOR SUSTAINABLE GOLD MINING

Modified from a paper published in ACS ES&T Water[12]

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## 3.1 Abstract

Cyanide is the ligand of choice for large-scale gold extraction plants and is increasingly replacing amalgamation for small-scale gold extraction processes. Although cyanide is less recalcitrant than mercury, it is still acutely toxic. Current absorption-column-based recovery and oxidation processes have high capital and chemical costs respectively and are therefore rarely implemented and only at large-scale operations. Membrane contactors with a pH gradient can be used for selective separation of cyanide into a distillate solution. This study evaluated cyanide recovery using polypropylene (PP) and polytetrafluoroethylene (PTFE) membranes and the impact of operating conditions with synthetic and real mining wastewater. Results show successful recovery of cyanide from both the PTFE and the PP

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membrane, as well as a significant impact of distillate pH, temperature, and feed cyanide concentration on process efficiency. Conversely, distillate cyanide concentrations showed very limited impact on process performance suggesting limited freshwater resources are required for cyanide recovery. Results of a techno-economic analysis indicate that membrane contactors are cost-effective both on large- and small-scale. While the PTFE membrane system exhibits a slightly lower cost at the small-scale and the PP membrane system is more advantageous at a large-scale, both membrane systems can be considered cost-competitive with current cyanide recovery methods.

## 3.2 Introduction

Gold mining has been identified as a significant source of negative environmental impacts including destruction of ecosystems and long-lasting issues such as waste tailings, chemical releases and contamination (Swenson et al., 2011). Mercury has historically been used to recover gold, but the cyanidation process is increasingly being used with the highly toxic, but less recalcitrant cyanide anion (Verbrugge et al., 2021). Currently, cyanide is used in approximately 80% of gold extraction activities with approximately 15% of total cyanide usage coming from the mining industry (du Plessis et al., 2021; Kuyucak and Akcil, 2013). Approximately 1.3-2.7 kgs of free cyanide are used per ton of ore to achieve optimal leaching of gold, (Muir, 2011; Órdenes et al., 2021) and cyanide in typical gold processing effluents reportedly range anywhere from 100-500 mg/L (Muir, 2011). As large amounts of cyanide are present in gold mining and refining operation effluent, treatment of these wastewaters is a major concern.

Cyanide treatment (detoxification) is most commonly achieved through a degradation process such as alkaline chlorination, sulfur oxidation, and photolysis coupled with hydrogen peroxide (Kuyucak and Akcil, 2013). In general, cyanide treatment approaches have high chemical, operation, and maintenance costs, as well as challenges associated with treating high solids, metals, and cyanide concentrations (Demopoulus and Cheng, 2004; Mosher and Figueroa, 1996) Additionally, during oxidation processes cyanide is converted to cyanate or thiocyanate, which are less toxic than cyanide, and eventually ammonium (Dai et al., 2012; EPA, 1994), which may lead to water quality degradation.

Existing cyanide detoxification approaches are costly with no direct return on investment (Demopoulus and Cheng, 2004; Mosher and Figueroa, 1996). Cyanide recovery and reuse may reduce substantial cyanide procurement and eliminate treatment costs and has been the focus of past research with several large-scale applications reported. (Kuyucak and Akcil, 2013) Currently, acidification, volatilization and reutilization (AVR) appears to be the only cyanide recycling technology operated commercially (Dai et al., 2012; EPA, 1994) in which hydrogen cyanide (HCN) is volatilized and the air/HCN mixture is then moved through a column containing a strong alkaline solution that will strip the

HCN from the air into the solution as cyanide anions ($CN^-$). The main disadvantages of AVR are high capital and high operating and maintenance costs associated with the high corrosiveness of the low pH process fluid and acid gas (Estay et al., 2014; Fleming, 2016). More recently, Green Gold proposed the Recyn process using a strong base resin to immobilize cyanide for reuse. Green Gold claims that this approach is used in 30 projects and that the cost of the recycled cyanide is about half the cost of new cyanide (Whittle and Pan, 2020).

An additional method for cyanide recovery uses membrane contactors to facilitate transfer of cyanide from acidified process water to an alkaline capture solution. A porous hydrophobic membrane separates the liquid feed (i.e., process water) from the liquid distillate phase allowing for HCN gas transfer through the membrane due to a difference in vapor pressure. Membrane contactors are generally made out of relatively inexpensive and corrosion-resistant materials and have high membrane packing densities (Huo et al., 2020). As a result, they are expected to be more compact, easier to scale and more cost-effective than the large stainless-steel absorption columns used in AVR. Moreover, only acid and base chemicals are required for operation, which are often less expensive than chemicals used in common oxidation treatment methods such as alkaline chlorination and sulfur oxidation.

Past studies have demonstrated that membrane contactors operating under an alkaline feed and acidic distillate solution can be used to successfully recover ammonia ($pK_a$ of 9.25) from aqueous solutions (Hasanoğlu et al., 2010; Huo et al., 2020; Zhu et al., 2005). Estay et al. and others (Estay et al., 2021, 2013; Han et al., 2005; Quilaqueo et al., 2020; Wu et al., 2011) have shown that this method is also able to recover cyanide (with a $pK_a$ of 9.21, similar to ammonia) from synthetic cyanide solutions utilizing the opposite pH differential used for ammonia. The studies of Estay et al. (Estay et al., 2021, 2013) and Quilaqueo et al., 2020 have evaluated systems similar to the one proposed in this study. Estay et al. (Estay et al., 2013) determined the influence of feed solution pH, flow rate, temperature, and feed solution zinc and copper content. Quilaqueo et al., 2020 focused on the evaluation of several hollow fiber polypropylene (PP) membranes of different sizes and configurations at different flow rates.

The purpose of this study was to evaluate and optimize cyanide recovery using a membrane contactor system on real mining wastewater. To further broaden the scope of applicable membrane materials, two different membrane contactors: a flat sheet polytetrafluoroethylene (PTFE) and a hollow fiber polypropylene (PP) membrane module were evaluated. As far as the authors are aware, no previous evaluations of membrane materials other than PP have been carried out. Operating parameters were studied to characterize the performance of the PTFE and PP membranes and evaluate parameters controlling process efficiency. This study expands on known parameters and evaluates the effect of distillate water recycling on the performance of both membranes. A techno-economic model was developed to elucidate the most cost-effective membrane module and operating conditions. Lastly, the

economic viability of this technology was evaluated for a small- and large-scale gold mining operation and compared to previous economic analysis of this technology and competing cyanide recovery and destruction methods (Adams and Lloyd, 2008; Estay et al., 2021, 2014; Fleming, 2016; Mosher and Figueroa, 1996).

## 3.3 Materials and Methods

### 3.3.1 Water Types Evaluated

Two different source waters were utilized in this study to evaluate cyanide recovery including model water, and process water obtained from an ore processing facility. Model water solutions were prepared using Type 2 deionized water and spiked with sodium cyanide (NaCN) at a nominal concentration of 195 mg/L to achieve a free cyanide concentration of ~100 mg/L. Model water was used to validate cyanide recovery efficiency observed in this study relative to preexisting research. Prior to NaCN addition, the pH of the model water was adjusted to 11.5 with a 0.1 M sodium hydroxide (NaOH) solution to avoid cyanide volatilization. All chemicals were obtained from Sigma Aldrich (St. Louis, MO).

Barren gold cyanidation heap leaching effluent (henceforth termed 'process water') was obtained from a US gold mine for experiments to evaluate cyanide recovery. The initial composition (upon receiving) of the process water is summarized in Table 3.1. Standard deviations were obtained by analysis of three samples with the methods described in section 2.2. Prior to experimentation, the pH of the gold processing effluent was adjusted to 11.5 and filtered with a 0.2-micron cartridge filter. The original cyanide concentration of the process water was reportedly close to 100 mg/L, however initial cyanide measurements showed approximately 44 mg/L, which continued to decrease during storage. Therefore, NaCN was added to achieve a nominal free cyanide concentration of 100 and 1000 mg/L prior to experiments. This range of cyanide concentrations reflects common concentrations found in gold mining process water effluents (Vuono et al., 2021).

Table 3.1 Process water composition

| Component | Concentration (mg/L) | Standard deviation |
|---|---|---|
| pH | 9.56 | - |
| $CN^-$ | 44.4 | - |
| Total inorganic C | 4.25 | 0.14 |
| Total organic C | 95.8 | 3.76 |
| $Cl^-$ | 121.8 | 2.94 |
| $NO_3^-$ | 863.7 | 66.46 |
| $NO_2^-$ | 32.5 | 2.41 |
| $NH_3$ | 22.5 | 0.77 |
| $SO_4^{2-}$ | 698.1 | 38.85 |

Table 3.1 Continued

| | | |
|---|---|---|
| $PO_4^{3-}$ | BDL | - |
| Ca | 179.7 | 0.74 |
| S | 107.2 | 2.62 |
| Na | 86.9 | 0.67 |
| Sr | 10.6 | 0.16 |
| K | 9.3 | 0.47 |
| Si | 4.1 | 0.16 |
| Mo | 2.6 | 0.05 |
| Mg | 1.2 | 0.02 |
| Fe | 0.15 | 0 |
| Cu | 0.14 | 0 |
| Al | 0.1 | 0 |
| As | 0.064 | 0 |

BDL = Below detection Limit

### 3.3.2 Sample Analysis

Cyanide concentrations for all waters were measured manually with Hach Test N' Tube (TNT) 862 using the pyridine barbituric acid method. Elemental analysis on real mining wastewater was performed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Avio-500, Perkin-Elmer, Fremont, CA, USA). Inorganic anions in the wastewater were measured by ion chromatography (Dionex 1500, Sunnyvale, CA, USA). Total organic carbon TOC was measured using a TOC analyzer (Shimadzu, Columbia, MD, USA). Nitrate and ammonia were measured using sensors (YSI, IQ SensorNet VARiON Plus Sensors) and Hach Test N' Tube (TNT) 836 and 832 respectively.

### 3.3.3 Experimental System

A small-scale membrane contactor system was used to test the recovery of free cyanide in real and synthetic gold mining processing effluents (Figure 3.1). The system consisted of two tanks, the feed and distillate tank, with the feed tank having a total volume of 4.4L and a distillate tank of 3.3L. Both tanks were connected with an interchangeable membrane module with solutions in the tanks circulated on each side with a pump. The system was equipped with pH sensors and pumps for dosing 0.2 M sulfuric acid and 2 M NaOH to control pH in both tanks using a supervisory control and data acquisition (SCADA) system. Constant system temperature during was maintained using a thermocycler (IsoTemp 3006, Fischer Scientific, Waltham, MA, USA).

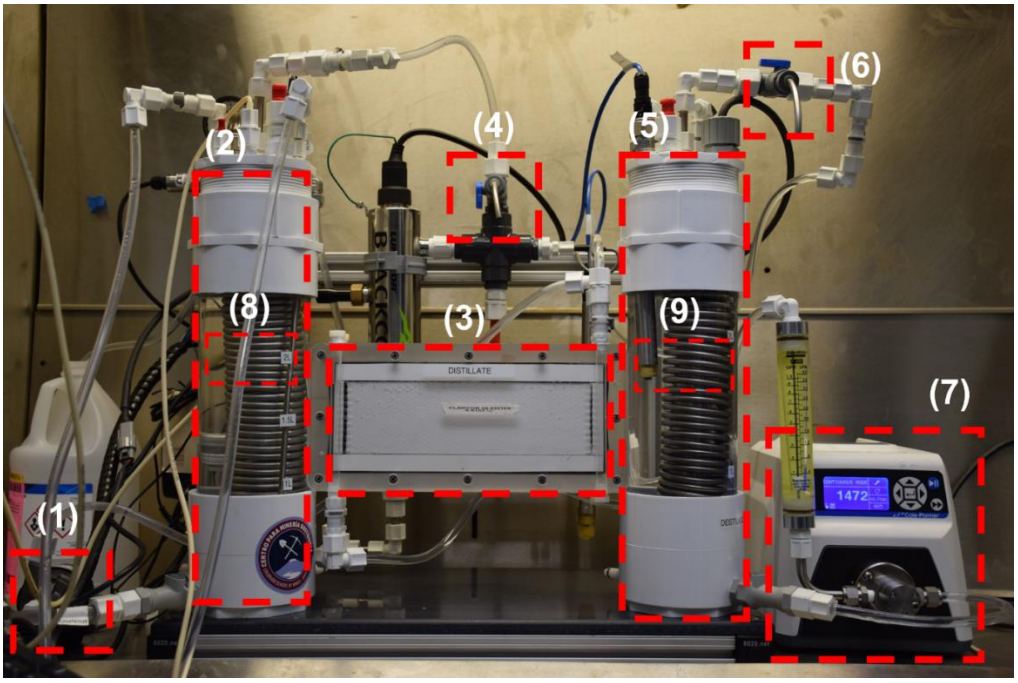


Figure 3.1 Bench scale system for cyanide treatment with membrane contactors. 1: feed solution pump, 2: feed solution tank, 3: membrane module, 4: feed sampling port, 5: distillate tank, 6: distillate sampling port, 7 distillate solution pump, 8: feed temperature control, 9: distillate temperature control

### 3.3.4 Membranes

Two examples of commercially available porous hydrophobic membranes were used in this study: BHA Altair, LLC QL822 and 3M Liqui-Cel hollow fiber module. QL822 is a PTFE membrane that was used in flat sheet modules with a measured membrane area of 0.0195 m2. Polypropylene diamond spacers were used on each side of the flat sheet membrane to fill the channel with dimensions of 2 mm high, 10 cm wide and 19.5 cm long. The Liqui-Cel module uses PP hollow fibers that were contained in a membrane cartridge. Relevant properties of the employed membranes are provided by the manufacturers in Table 3.2. After successful demonstration of cyanide transfer using a PTFE membrane, a second module was added to increase the membrane size to 0.039 m2.

Table 3.2 Membrane properties

| **Membrane** | **QL822** | **Liqui-Cel** |
|---|---|---|
| Material | PTFE | PP |
| Type | Flat sheet | Hollow fiber |
| Area per module ($m^2$) | 0.0195 | 1.5 |
| Thickness µm | 127-203 | 40 |
| Porosity (%) | 70-85 | 40 |
| Pore size (µm) | 0.45 | 0.04 |

### 3.3.5 Data Analysis and Modelling

An overall mass transfer coefficient (*K*) was used as a metric to compare the performance of the two membranes evaluated in this study. K was also used to calculate cyanide flux and the required membrane size for a full-scale system for the economic analysis. *K* (m/h) was obtained from the slope of the natural logarithm of the normalized feed concentration versus a membrane area- and feed volume-normalized time axis using Eqn. (3.1):

$$\mathrm{K} = \frac{\mathrm{V}}{\mathrm{At}} \ln\left(\frac{[\mathrm{HCN}]_{\mathrm{f},0}}{[\mathrm{HCN}]_{\mathrm{f}}}\right) \tag{3.1}$$

where V is the volume of the feed ($m^3$), A is the membrane area ($m^2$), t is time (h), $[HCN]_{f,0}$ is the initial feed hydrogen cyanide concentration and $[HCN]_f$ is the feed hydrogen cyanide concentration in mg/L at time t (Huo et al., 2020). An example of the linear fitting is presented in Figure B.2 B of Appendix B. Because cyanide concentrations can vary between waters, cyanide flux values were used as a measurement of mass transfer. Cyanide flux ($g/m^2h$) is calculated as

$$J_{CN^-} = K([HCN]_f - [HCN]_d) \tag{3.2}$$

where $[HCN]_f$ and $[HCN]_d$ are the concentration of volatile hydrogen cyanide ($g/m^3$) in the feed and distillate, respectively (Huo et al., 2020). Because HACH TNT vials only measure dissolved cyanide [$CN^-$], the total concentration of free cyanide ($CN_{tot}$) was derived from the measured cyanide ion ($CN^-$) concentration and the measured pH using the Henderson-Hasselbach equation:

$$[HCN] = \frac{[CN^-]}{10^{pH-pK_a}} \tag{3.3}$$

For calculations using Eqn. (3.3), the $pK_a$ of hydrogen cyanide ranged from 9.21 at 20°C to 8.8 at 35°C, shifting the dominance of $CN^-$ to lower pH levels at higher temperatures (Dzombak et al., 2006).

To model cyanide concentrations in the system, a sequential mass balance was performed using the calculated K and measured pH values. Initial cyanide flux was calculated based on starting feed concentration and pH using Eqns. (3.1), (3.2) and (3.3). In the subsequent time step, the concentrations were calculated based on measured cyanide removal and the assumption that it was transferred to the distillate. From these concentrations a new flux was calculated and so forth. Results were used for the development of the cost model which is dependent on calculated flux and *K* values.

### 3.3.6 Economic Analysis

Various sources of information were used to obtain parameter values needed for the economic model. Two cases were considered for the economic analysis including a large-scale and a small-scale cyanide gold processing operation. Case 1 (large-scale processing facility) assumed a 200 $m^3$/h effluent flow rate of barren process water. The cyanide concentration of Case 1 process water was assumed to be 0.25 g/L (free cyanide) which is supported by current literature (Muir, 2011; Órdenes et al., 2021). Case 2 is based off Perez (2016) (Perez Quiroz, 2016), who describes a small-scale processing plant capable of processing 10 $m^3$ of ore per day and a 0.132 $m^3$/h effluent flow rate. Cyanide consumption in small-scale processing plants is usually higher than large-scale processing plants resulting in the process water to contain higher free cyanide concentrations (Verbrugge et al., 2021). Free cyanide concentration for Case 2 (small-scale) was set at 0.84 g/L based on measurements taken from mines of similar processing capacities. Both theoretical treatment systems are modeled after a batch style system to match the cyanide output from the process water flow of case 1 and 2 with the treatment capacity. Retention times in this scenario are dependent on the capacity of the feed tank as the system is designed to keep up with the process water flow. Other parameters such as chemical costs, electrical costs, and membrane costs were obtained through direct communication with manufacturers or industry partners. Relevant formulas for the cost model are shown in section B.1 of Appendix B.

Parameter values used in the economic analysis are summarized in Table B.2. in Appendix B. Assumed cyanidation effluent flow rates were used to calculate the annual avoidable cyanide consumption assuming 100% cyanide recovery. Total system cost was assumed to be double that of the membrane modules (both PTFE and PP) for case 1 and four times for case 2 with requisite membrane area calculated using the average cyanide flux for optimal conditions measured during cyanide recovery experiments (Eqn. (B.1)) (Woods, 2007). Chemical costs were based on required acid (sulfuric acid) and base (%CaO; %NaOH) dosing to continuously achieve feed and distillate pH of 7 and 11.5 (equation (B.13-20)), respectively, and energy costs assumed to be due to pumping according to equations (B.11) and (B.12).

## 3.4 Results and Discussion

Experimental data from cyanide recovery experiments were fit with equation 3.1 (see Figure 3.2 for example model fits) for calculation of the overall mass transfer coefficient ($K$) to evaluate the impact of system and process parameters on cyanide recovery efficiency and allow comparison between this work and previous studies. Furthermore, cyanide recovery experiments yielded necessary process information to develop an economic analysis and comparison between alternate cyanide recovery methods. Prior to this work, the reproducibility of the cyanide recovery process was confirmed by replicating experimental

conditions of Estay et al. (Estay et al., 2013) using the same membrane. This experiment resulted in a *K* value of 0.024 m/h, identical to that found by Estay et al. (Estay et al., 2013) (see section B.3 of Appendix B).

### 3.4.1 Controlling Parameter Evaluation

Past research has focused on cyanide recovery using PP hollow fiber membranes of varying sizes (Estay et al., 2013; Han et al., 2005; Quilaqueo et al., 2020; Wu et al., 2011). Other membrane materials (such as PTFE) and configurations have been used to successfully recover ammonia from synthetic and wastewater solutions (EL-Bourawi et al., 2007; Huo et al., 2020). Due to the similarities between ammonia and cyanide, PTFE membranes should therefore be an effective membrane material for the recovery of cyanide. Thus, experiments were conducted with a single flat sheet PTFE membrane module (0.0195 $m^2$) using process water spiked with 100 mg/L of free cyanide (Figure B.3).

The relationship of measured and modeled feed and distillate cyanide concentrations (and subsequent cyanide recovery) when treating process water for the two membranes evaluated is presented in Figure 3.2. For the flat-sheet PTFE membrane, and over the 4-hour runtime, the initial feed cyanide concentration was reduced by 99% with approximately 91% cyanide recovered in the distillate solution (Figure 3.2 A). Data for the 1.5 $m^2$ PP hollow fiber membrane are shown in Figure 3.2 B in which the initial cyanide concentration was reduced by 99%, and 94% of the total cyanide was recovered in the distillate solution after 20 minutes of runtime. Losses of total cyanide during the experiments are likely attributed to HCN volatilizing in the headspace of the feed tank and samples. Figure 3.2 experimental results were replicated through triplicate experiments and used as a baseline to compare results from optimization experiments.

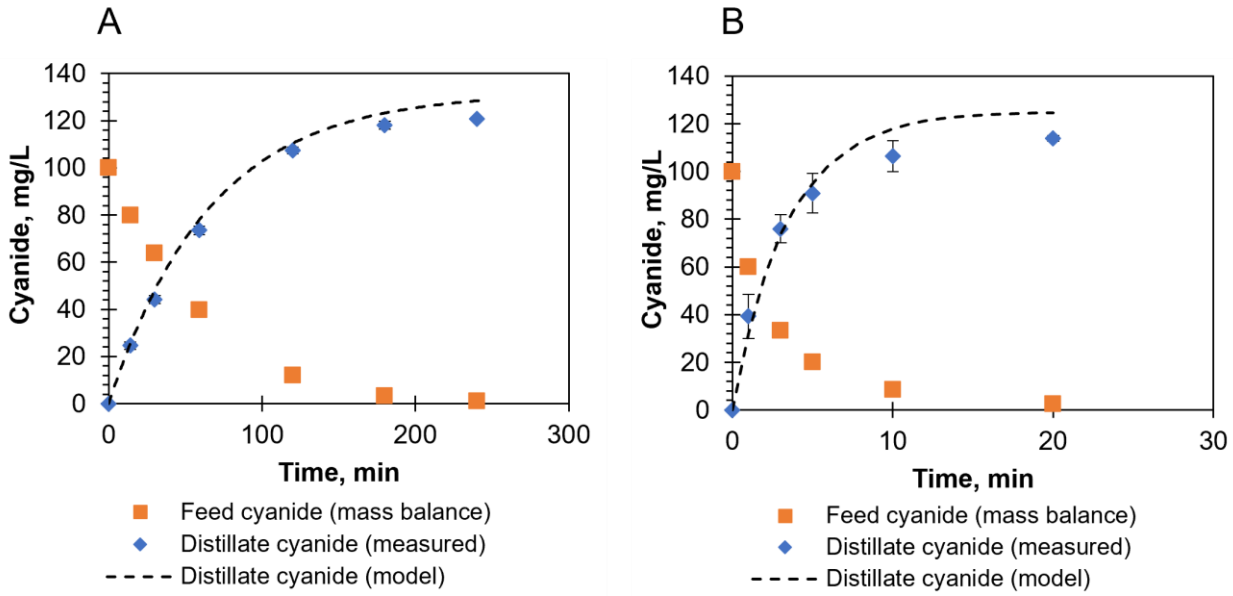


Figure 3.2 Cyanide reduction in the feed solution and recovery in the distillate solution using the flat sheet PTFE membrane (A) and the hollow fiber membrane (B). Sodium cyanide amended to total cyanide concentration of 100 mg/L. Feed pH maintained at 7 and distillate pH at 11.5, temperature at 20°C, flow velocity was 0.167 m/s for A and 0.02 m/s for B. Error bars represent the standard deviation obtained from triplicates.

The impact of evaluated system flow rates (1 and 2 L/min) and resulting flow velocity (0.083 m/s and 0.167 m/s for PTFE and 0.01 m/s and 0.02 m/s for PP) on calculated *K* values is illustrated in Figure 3.3 (A). Due to the vastly different area of the membrane modules and limitations of the system pumps, similar flow velocities could not be achieved for both membrane modules. Differences in membrane parameters (see Table 3.2) and module configuration (hollow fiber vs flat sheet) also play a significant influence which can vary membrane performance of the same material. Experiments were thus forced to be operated at significantly differing flow velocities. Results show that higher flow velocity and liquid turbulence improves mass transfer and *K*, resulting in subsequently faster treatment times, particularly for the PTFE membrane. Estay et al., 2013 also reported increases in mass transfer at higher flow rates using synthetic cyanide solutions. Our findings with real process water show that flow rate had a much higher impact on the PTFE membrane (*K* increased by 89.5%) compared to the PP membrane (*K* increased by 10.2%) which is due to the relative increase in flow rate and flow velocity compared to the membrane area.

To evaluate the influence of feed cyanide concentrations, experiments were performed using process water with total cyanide concentrations of 100 and 1000 mg/L which were chosen to represent conditions of small- and large-scale gold processing operations as identified through industry collaborators and past studies (Acheampong et al., 2013; Johnson, 2015). *K* values and fluxes obtained at the different cyanide

concentrations are presented in Figure 3.3 (B). A decreased *K* value was observed with increasing cyanide concentration, and treatment took significantly longer with runtimes increasing from 4 to 7 hours with the PTFE membrane and 20 minutes to 45 minutes for the PP membrane. However, the cyanide flux for the PTFE membrane (as calculated using Eqn. (3.3)) was 11.4 $g/m^2h$ at 100 mg/L and 59.6 $g/m^2h$ at 1000 mg/L. For the polypropylene membrane, cyanide flux was 3.58 $g/m^2h$ at 100 mg/L and 17.3 $g/m^2h$ at 1000 mg/L. Although *K* decreased with increasing concentration, flux increased, which increases the efficiency of the process and is beneficial for cyanide recovery.

For effective cyanide recovery, feed side pH should be low enough to volatilize HCN with distillate pH high enough to continuously absorb HCN from the pores of the membrane. Estay et al. (2013) evaluated a pH of 4, 5 and 7 on the feed side and 11 on the distillate side of the membrane and reported little difference in *K* for pH values between 4 and 5, and a slight decrease in performance at pH 7. In this study, four experiments were run for each membrane using distillate pHs of 10.5 and 11.5 and feed pHs of 8 and 7, respectively. As shown in Figure 3.3 (C), membrane performance (*K*) decreases with lower distillate pH values, which also impacts the overall treatment time resulting in incomplete recovery of cyanide (~95% compared to 99%). Higher *K* values at greater distillate pH were likely due to increased capacity of the distillate to dissociate HCN back into $CN^-$. Furthermore, lower distillate pH values result in conversion of $CN^-$ into HCN which is a potential safety issue.

The influence of temperature on cyanide recovery was evaluated although a stable temperature differential could not be maintained as heat exchange occurred across the membrane. However, an increase in *K* could be observed (Figure B.4) at temperatures of 31°C and 29°C in the feed and distillate solution over previous experiments at room temperature (20°C). At 35°C in both feed and distillate solutions, *K* increased significantly (Figure 3.3 (D)) especially for the PTFE membrane compared to 20°C. The increase of cyanide volatility and mass transfer with temperature could be implemented through heat exchangers (recovered waste heat) or solar thermal collectors thereby reducing the membrane area needed to effectively recover cyanide. Increasing temperature also decreases the $pK_a$ of HCN which would increase acid and decrease base consumption.

The overall difference in membrane performance between the PTFE and PP membranes is due to the specific membrane properties of the evaluated membranes (see Table 3.2). Although the PTFE membrane is thicker than the PP membrane its higher porosity and pore size allows for a higher overall mass transfer coefficient and cyanide flux. As these membrane properties are not intrinsic to the membrane material, experimentation with membranes of similar properties would be necessary to draw direct comparisons between the two membrane materials.

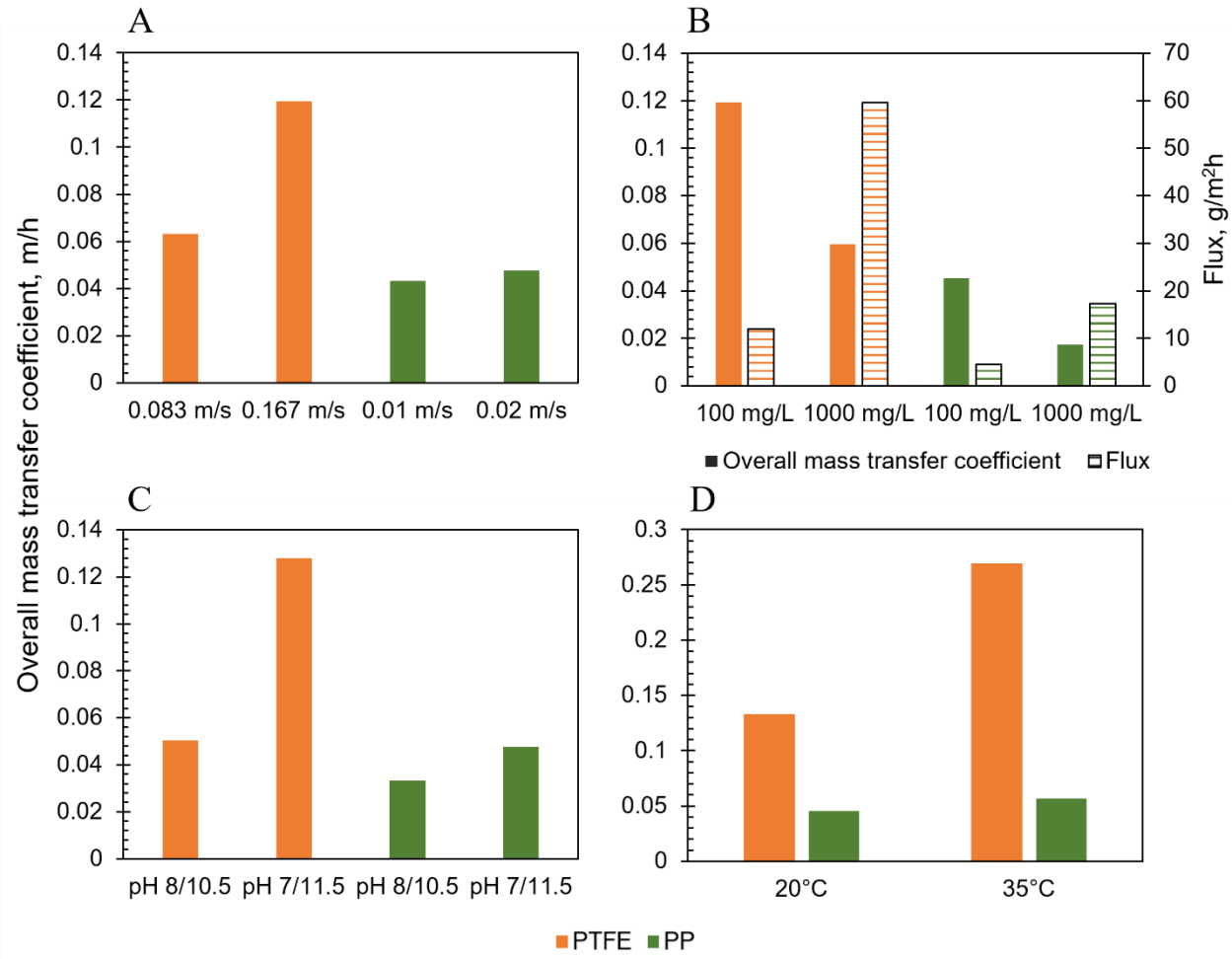


Figure 3.3 Influence of system parameters on *K* for the PTFE and PP membranes. (A) Influence of flow velocity at 100 mg/L total cyanide, pH 7 feed solution and 11.5 distillate solution, and 20°C. (B) Influence of total cyanide concentration on *K* and flux at total cyanide concentrations of 100 and 1000 mg/L, pH 7 feed solution and 11.5 distillate solution at 20°C and flow velocities of 0.167 m/s and 0.02 m/s for PTFE and PP respectively. (C) Influence of pH on *K* at a total cyanide concentration of 100 mg/L at 20°C and the highest tested flow velocities. (D) Influence of temperature on *K* at 100 mg/L of cyanide, feed pH 7, distillate pH 11.5 and the highest tested flow velocities.

### 3.4.2 Distillate Recycle

Reduction of water usage is an important factor influencing sustainability of gold production (Meißner, 2021; Stoltenborg and Boelens, 2016) and maximizing the cyanide concentration in the membrane distillate is needed for subsequent reuse. A potential solution is the reuse of the distillate to treat multiple batches of process water thereby increasing the concentration of recovered cyanide and minimizing water and storage volumes (Muir, 2011; Órdenes et al., 2021). Experiments were performed over four recovery cycles with the 1.5 $m^2$ hollow fiber PP membrane with a cycle defined as the treatment

of the feed solution to less than 1 mg/L total cyanide after which the treated feed solution was replaced. For each cycle a new 100 mg/L free cyanide water solution was prepared and acidified to a pH level of 6. The pH of the distillate solution was maintained at pH of 11.5 for the total duration of the experiment. The free cyanide concentration in the feed solution decreased by 99% after each cycle and a recovery rate of 90% was measured (possibly due to HCN volatilization in the feed tank). A decrease in *K* was observed after the first cycle (0.0359 m/h to 0.0319 m/h) to the second cycle (Figure 3.4) after which *K* stayed relatively constant. If the pH of the distillate is high enough to assure 99% conversion of HCN to the $CN^-$ (pH of at least 11.5), the concentration of cyanide could likely be increased to its solubility limit with little impact on performance.

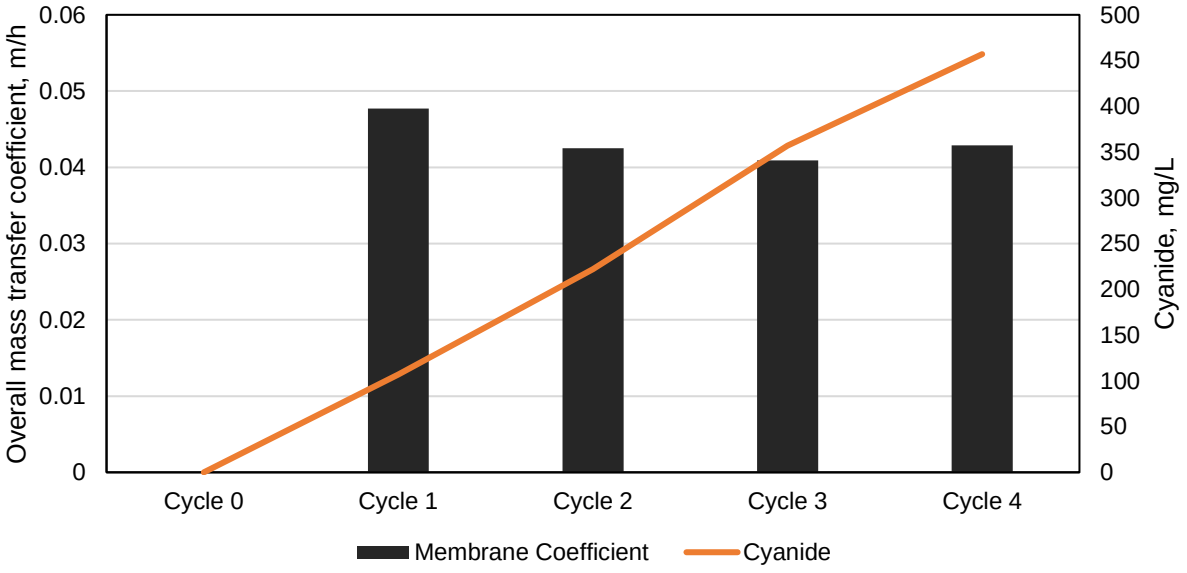


Figure 3.4 Changes in K after recycling of the distillate solution with a 1.5 $m^2$ hollow fiber PP membrane module. For each cycle, fresh process water was spiked with sodium cyanide to reach total cyanide concentrations of 100 mg/L. The distillate solution remained in the tank while the feed solution was replaced. Each cycle was operated under the same conditions: feed solution pH of 7, distillate solution pH of 11.5, 0.02 m/s flow velocity and 20°C.

### 3.4.3 Comparison with Previous Studies

The recovery of ammonia and cyanide through membrane contactors using pH differentials has been demonstrated in past studies (Estay et al., 2013; Huo et al., 2020). However, differences between studies including membrane types, water types, system parameters (e.g., pH, temperature, flow rate) and cyanide concentration make comparisons between studies difficult. A summary of *K* values obtained from literature and during this study are provided in Table 3.3. Overall, higher *K* values were observed in this study, especially when considering relatively low feed cyanide concentrations of 100 mg/L. Higher *K*

values were found for the high porosity and large pore size PTFE membrane compared to the PP membrane in this study, as well as previous studies. The type of wastewater also has significant influence; treatment of synthetic solutions of just DI-water and sodium cyanide have resulted in higher *K* values than treatment of real mining wastewater, industrial wastewater, and acrylonitrile wastewater.

Table 3.3 Current state of cyanide recovery research using membrane contactors

| | Membrane type | Membrane area ($m^2$) | Water type | Feed [$CN^-$] (mg/L) | Feed pH | Dist. pH | Flow rate (L/min) | System T (°C) | *K* (m/h) |
|---|---|---|---|---|---|---|---|---|---|
| This Study | PTFE | 0.039 | Synthetic | 100 | 6-7 | 11.5 | 2 | 20 | 0.221 |
| This Study | PP | 1.5 | Synthetic | 100 | 6-7 | 11.5 | 2 | 20 | 0.046 |
| This Study | PTFE | 0.039 | Process water | 1000 | 6-7 | 11.5 | 2 | 20 | 0.057 |
| This Study | PP | 1.5 | Process water | 1000 | 6-7 | 11.5 | 2 | 20 | 0.017 |
| Estay et al. (2013) | PP | 0.58 | Synthetic | 2000 | 5 | 11 | 2 | 15 | 0.024 |
| Quilaqueo et al. (2020) | PP | 0.5 | Synthetic | 2500 | 3.5 | 14 | 0.469 | 15 | 0.02 |
| Han et al. (2005 | PP | 0.052 | Industrial | 562 | 2-10 | 14 | 0.18 | 18 | 0.04 |
| Wu et al. (2011) | PP | 0.012 | Industrial | 817 | 5 | 14 | - | 18 | 0.0025 |

### 3.4.4 Economic Analysis

Optimal system parameters and chemical (acids and bases) usage rates for optimal *K* and $J_{CN^-}$ values identified through experiments (Section 3.1) were used to perform an economic assessment of cyanide recovery under the two scenarios (Case 1 – large-scale; Case 2 – small-scale). For this analysis, optimal conditions for both membrane products (i.e., PTFE, PP) were compared with overall mass transfer coefficients obtained at highest tested cross flow velocity, and a pH of 7 in the feed and 11.5 in the distillate. A breakdown of the costs required for the treatment of cyanide effluent streams for Case 1 and 2 is presented in Figure 3.5. For better comparison of the two cases, relevant costs have been expressed as \$/kg of recovered $CN^-$. Avoided costs of cyanide oxidation with $SO_2$ + air are also shown for comparison as that cost would be eliminated when implementing cyanide recovery. Prefiltration was not considered for this economic analysis as no prefiltration was necessary for the provided process water and previous studies also omitted the costs of prefiltration. The benefits of exothermic dissolution of lime (calcium oxide) have also not been considered since lime is only used by some mines for pH regulation over the more common NaOH. The specific avoided costs of traditional treatment were given by an industry partner and are provided in table B.3. of the SI. Chemical costs were provided by vendor quotes or industry partners. The cost of free cyanide as $CN^-$ was assumed to be \$5.01/kg for Case 1 and \$7.34/kg for Case 2 according to current industry rates (September 2022). Recovered cyanide can be either directly recycled into the gold cyanidation process, stored at high pH until needed, or even sold to other plants or industries. As recovered cyanide is present in its dissolved form it facilitates the reutilization compared to

the commercially sold soldi sodium cyanide. Due to the recovery of cyanide in a clean water solution it is assumed that recovered cyanide has value equal to cyanide obtained from vendors.

The biggest cost for Case 1 is for chemicals with acid and base accounting for 73% of the costs for the PTFE membrane system and 80% for the PP membrane system. Due to the vast difference in flow velocities PTFE pumping costs play a significant role for the PTFE membrane, more so than for the PP membrane. Costs for both membranes are similar, with the evaluated type of PTFE membranes being a lower cost option over the evaluated type of PP membranes due to the smaller membrane size required. Overall, the costs required for a treatment system are 39% of the cost of new cyanide ($5.01/kg as $CN^-$) for a system using the PTFE membrane and 30% for a system using the PP membrane. This finding indicates that the evaluated PP membrane would be a better choice for a large-scale treatment system due to its slightly lower chemical consumption and pumping costs. If the avoidance of cyanide treatment costs is considered, an additional $5/kg of $CN^-$ can be saved. The pay-back period (PBP) for case 1 is 0.3 years for the PTFE membrane system and 0.2 years for the PP membrane system. Return of investment rates (ROI) are 428.9 %for the PTFE system and 624.7% for the PP system.

Case 2 resulted in a different cost profile compared to Case 1 with differences in chemical and specific membrane costs, and treatment system requirements playing a significant role. Base consumption is the highest cost for both membranes mainly because the specific base cost tripled compared to case 1. Due to economies of scale and much higher cyanide concentrations, membrane costs have a much higher relative cost compared to Case 1. The impact of acid dosing costs is significantly lower for Case 2 because of lower cost of sulfuric acid, as well as the impact of costs scaling with process water cyanide concentration and process water flow. Additional savings of $4.48/kg of $CN^-$ for case 1 and $4.40/kg of $CN^-$ for case 2 can be expected through the redundancy of traditional treatment systems. The total treatment costs for Case 2 are 49% of the price of new cyanide ($7.34/kg as $CN^-$) for the PTFE membrane and 51% of the price of new cyanide for the PP membrane. The evaluated type of PTFE membranes are a better choice for small-scale treatment systems as the overall treatment cost is lower compared to that of evaluated type of PP membranes. Due to the higher performance of the specific PTFE membrane, less surface area is required compared to the specific PP membrane which decreases the membrane costs. The PBP and ROI for case 2 is 2.3 years and 225.7% for the PTFE membrane system, and 4.0 years and 172.1% for the PP membrane system.

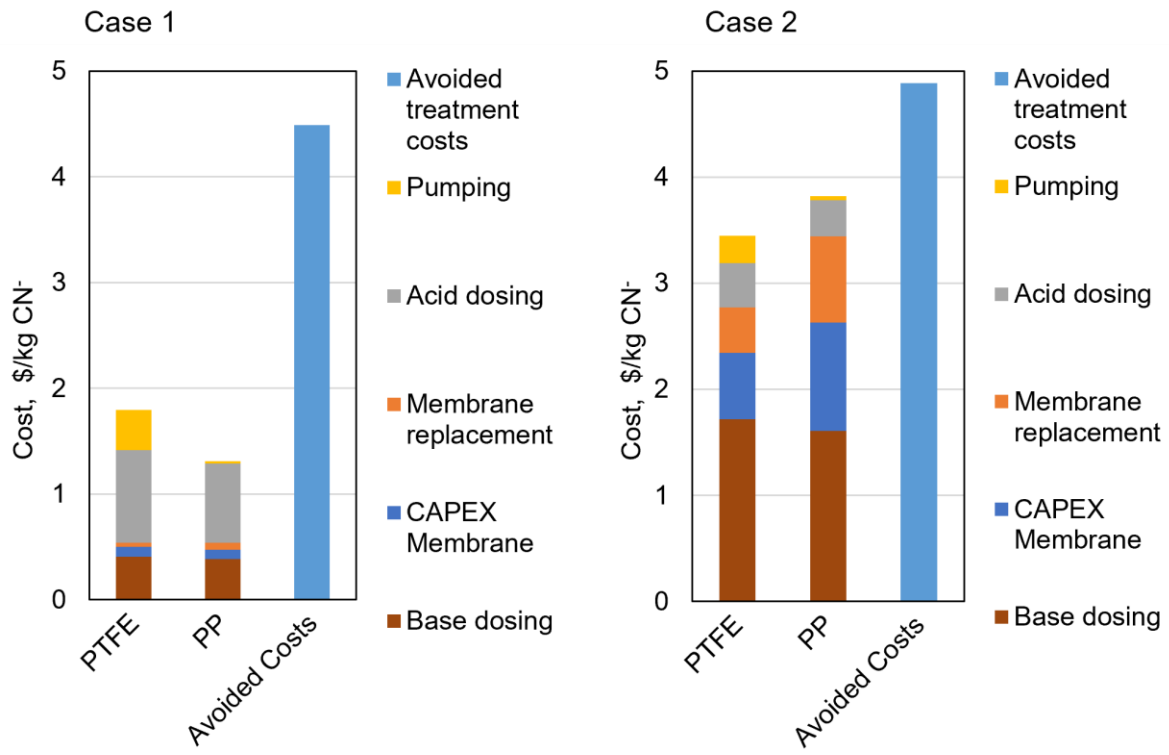


Figure 3.5 Cost distribution for a large-scale (Case 1) and small-scale gold cyanidation plant (Case 2) for the PTFE and PP membranes using assumptions from Table B.2. Avoided treatment costs are for an $SO_2$+air cyanide oxidation system. Procurement costs of new cyanide are \$5.01/kg $CN^-$ for Case 1 and \$7.34/kg $CN^-$ for Case 2.

A sensitivity analysis was performed to evaluate the impact of operating parameter changes on cost savings associated with recovered cyanide. Results are summarized in Table 3.4 as a percentage change to the economic predictions using optimal lab conditions and in Figures B.3 and B.4 of the SI. Increased flow rates (especially for the PTFE membrane) increase membrane performance ($K$) and cyanide flux ($J_{CN^-}$) allowing the use of smaller membranes. The sensitivity analysis shows that the reduction of membrane costs significantly offsets higher pumping costs for small-scale operations. However, for large-scale operations low flow velocity is preferable as pumping costs outweigh membrane costs. Higher cyanide concentrations mean more cyanide needs to be removed and hence a larger membrane area is required as well as higher chemical consumption costs. The increase of costs through larger membrane areas and higher chemicals consumption is offset by the higher amount of recovered cyanide, making process waters with high cyanide concentrations more attractive for cyanide recovery. However, the sensitivity analysis reveals savings tapering off at higher concentrations which suggests an optimal process water cyanide concentration. The sensitivity analysis also indicated that a distillate pH greater than 11.5 is optimal in all cases except for Case 1 when using the PP membrane. Using the PP membrane

at large-scale, the cost of chemicals to maintain a pH differential is greater than the cost of the membrane, thus using less chemicals and larger membranes in these scenarios is more economical. Although maintaining higher distillate pH requires more base dosing, the increase in *K* enables higher cyanide flux which decreases required membrane sizes. Although higher temperatures are beneficial, the cost of heating elements and energy is expected to be too high to be justified in large-scale operation. From the sensitivity analysis it is clear that cyanide concentration has the highest influence on savings followed by flow and lastly distillate pH.

Table 3.4 Summary possible savings as influenced by changes in parameters compared to optimal operating conditions (Case 1 (PTFE): 3.03 M$, Case 1 (PP): 3.23 M$, Case 2 (PTFE): 7509 $, Case 2 (PP): 6854 $)

| Case | Membrane | Parameter | Lowest Parameter Value | Highest Parameter Value | Optimal Parameter Value |
|---|---|---|---|---|---|
| 1 | PTFE | Flow | 100% | 97.0% | 1 L/min |
| 1 | PP | Flow | 100% | 99.9% | 1 L/min |
| 2 | PTFE | Flow | 96.1% | 100% | 2 L/min |
| 2 | PP | Flow | 98.4% | 100% | 2 L/min |
| 1 | PTFE | Distillate pH | 89.3% | 100% | 11.5 |
| 1 | PP | Distillate pH | 100% | 99.6% | 10.5 |
| 2 | PTFE | Distillate pH | 90.3% | 100% | 11.5 |
| 2 | PP | Distillate pH | 96.8% | 100% | 11.5 |
| 1 | PTFE | $[CN^-]$ | 33.1% | 406% | 1 g/L |
| 1 | PP | $[CN^-]$ | 36.1% | 396% | 1 g/L |
| 2 | PTFE | $[CN^-]$ | 0 | 120% | 1 g/L |
| 2 | PP | $[CN^-]$ | -0.06% | 114% | 1 g/L |

Although cyanide recovery systems are rarely implemented at large-scale gold mining operations and never at small-scale operations, several technologies are reportedly capable of economical cyanide recovery. Costs reported in the literature of different cyanide recovery technologies (AVR, SART (sulfidization, acidification, recycling and thickening), ion exchange, and ReCyn) are summarized in Table 3.5. Such comparisons can be difficult due to differing scope of the study or missing assumptions. For this study, chemical, system, membrane and membrane replacement, and pumping costs were considered. The costs of each cyanide recovery system were compared to the price of new cyanide, either as identified by the authors, or estimated according to the market price (obtained from vendors) at the time of the associated study. Adam and Lloyd (Adams and Lloyd, 2008) considered only chemical costs associated with AVR and SART. The direct costs of the ion exchange process as described by Fleming (Fleming, 2016) and the ReCyn process as described by Whittle and Pan (Whittle and Pan, 2020) are not completely defined with details either hidden by non-public reports or company confidentiality. Despite including more cost factors in this analysis, membrane contactors are competitive with other cyanide

recovery techniques with large-scale (Case 1) scenarios recovering cyanide at 26-36% of the cost of new sodium cyanide. Large-scale membrane contactors would stand in closest competition to AVR and ReCyn systems with membrane contactors performing slightly better. Although Estay et al. (Estay et al., 2014) also obtained promising economic results, membrane contactor and other capital cost assumptions were unfortunately not disclosed. Using experimental data generated through recovery of cyanide from synthetic process effluents and modelling they found a continuous operating system to perform the best at a net present value of 3.65 $/kg NaCN/year. This study has found net present value (NPV) to be significantly higher at 20.8$/kg NaCN/year for case 1 using the PP membrane and 21.0 $/kg NaCN/year for case 2 using the PTFE membrane. This difference in NPV is due to economic factors such as differences in chemical prices and membrane prices may have come down substantially in the last decade. Other factors that cause this difference are chosen operating parameters such as the process cyanide concentration, operating pH, and temperature. Furthermore, this study achieved higher K and JCN- values than Estay et al. (Estay et al., 2014) which are beneficial for the operation of the system and thus NPV. AVR and SART have been found to be 1.82 $/kg NaCN/year and 4.24 $/kg NaCN/year respectively, suggesting that membrane contactors are more economic than AVR and SART systems. Moreover, system complexity and higher initial capital costs disadvantage SART systems invoking additional hurdles for implementation (Estay et al., 2014). Membrane contactors could be a viable alternative due to lower capital costs (Estay et al., 2014) which is an advantage as small-scale ore processing plants would likely be hesitant to invest large upfront capital costs. The ease of operation relative to SART and AVR are also conducive to adoption at small-scale operations. Lastly, the confinement of volatile hydrogen cyanide to the membrane pores, which is a much smaller volume than AVR absorption columns, improves the safety of the recovery process.

Table 3.5 Comparison of cyanide recovery costs using different technologies.

| | Method | Cost of recycled cyanide ($/kg) | Cost of new cyanide ($/kg) | % Recovery cost to new cyanide |
|---|---|---|---|---|
| This Study (Case 1) | Membrane contactor | 1.31-1.80 | 5.01 | 26-36 |
| This Study (Case 2) | Membrane contactor | 3.60-4.31 | 7.34 | 49-59 |
| Adams and Lloyd (2008) | AVR | 1.02-1.39 | 2.64 | 39-53 |
| Adams and Lloyd (2008) | SART | 0.60-0.73 | 2.64 | 23-28 |
| Fleming (2016) | Ion exchange | 1.60-2.17 | 1.88-2.82 | 57-115 |
| Whittle and Pan (2020) | ReCyn | 2.50 | 5.01 | 50 |

## 3.5 Conclusions

Cyanide recovery provides a suitable alternative to cyanide destruction/detoxification processes as it does not generate byproducts like ammonia that could lead to eutrophication of receiving surface waters. Membrane contactors in particular offer a solution to this challenge due to their low capital costs, easy scalability, and safe operability relative to other cyanide recovery technologies like AVR that are seldomly implemented especially at small-scale operations. This work demonstrated using real mining wastewater that membrane contactors cannot only recover cyanide, but also concentrate it in the distillate, substantially limiting the amount of water required for recovery. Moreover, a new PTFE membrane was identified with more than double the mass transfer of previously proposed PP membrane contactors. A techno-economic analysis was performed for a typical large- and small-scale gold mining operation. Although large-scale operations will still have substantially lower membrane costs due to economies of scale, cyanide recovery at small-scale operations will be profitable too, as they typically operate at much higher cyanide concentrations which increases membrane fluxes as well as revenue from cyanide recovery. At smaller scales the PTFE membrane system showed a slightly lower total cost relative to the PP membrane system. Further research should evaluate membrane contactors on a pilot scale. Long-term cyanide recovery experimentation on process waters of varying quality and components is also needed for process validation.

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# CHAPTER 4 PILOT-SCALE ASSESSMENT OF A MOBILE OFF-GRID MEMBRANE CONTACTOR SYSTEM FOR THE TREATMENT OF CYANIDE IN GOLD PROCESSING WASTEWATER IN AREQUIPA

Modified from a paper published in ACS ES&T Water [23]

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## 4.1 Abstract

A pilot-scale membrane contactor was constructed to determine the effectiveness of cyanide recovery from real gold processing effluents from the US and the Arequipa region of Peru. The system was designed to operate off-grid using a mobile solar array to enable implementation independently of power-grid availability. Although 98% recovery of free cyanide was obtained during experiments with the US process effluents, effluents from the Arequipa region posed a larger challenge. Free cyanide recovery from the first Arequipan facility's effluent (Aq1) yielded only 45% cyanide recovery, while the effluent of the second Arequipan facility (Aq2) showed a free cyanide recovery of 81%. Precipitation of minerals was observed throughout experimentation with both effluents and likely contributed to the overall lower recovery. Maintaining a feed solution pH of > 7 limited precipitations, albeit at a lower mass transfer rate. However, a subsequent pH drop in the feed solution to 5 yielded an improved cyanide recovery rate of

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95% for the Aq2 effluent. Economic analysis revealed that operational and CAPEX costs for cyanide recovery in each case were lower than the purchase of new cyanide. However, pretreatment and staged pH adjustment may be required for the efficient recovery of cyanide using membrane contactors.

## 4.2 Introduction

The gold mining industry of Arequipa, Peru, is a significant economic contributor and has undergone many historical changes, evolving from placer mining and mercury amalgamation to gold cyanidation as the most common method in the present day (Veiga et al., 2015; Verbrugge et al., 2021). This shift facilitated the extraction of low-grade gold ores, expanding the gold industry and increasing its profitability (Verbrugge et al., 2021). While gold cyanidation offers efficiency advantages over historically employed practices, the production of cyanide laden effluents and tailings poses an environmental threat that needs to be addressed (Jaszczak et al., 2017; Johnson, 2015). Current cyanide treatment methods such as alkaline chlorination and UV enhanced oxidation are used by gold processing facilities to reduce cyanide concentrations in effluent waters to levels suitable for discharge or storage adhering to the international cyanide management code (Akcil, 2010; Kuyucak and Akcil, 2013). These commonly implemented cyanide treatment technologies are costly, offer no direct return on investment, and produce secondary contaminants such as cyanate, thiocyanate, and ammonia that may require further treatment (Dzombak et al., 2006; Kuyucak and Akcil, 2013). A more sustainable and cost-effective solution lies in cyanide recovery and reuse. Technologies such as acidification-volatilization-reabsorption (AVR), and the Green Gold ReCyn process have achieved large-scale adoptions, however, high capital, operating, and maintenance costs limit widespread utilization (Dai et al., 2012). Alternative cyanide recovery methods such as sulfidization-acidification-recycling-thickening (SART) and ion exchange demonstrate potential, however, have seen few large-scale implementations (Estay et al., 2020; Whittle and Pan, 2018). Membrane contactors for cyanide recovery have been successfully demonstrated for treating industrial wastewater and mining effluents at lab-scale (Estay et al., 2014; Han et al., 2005; Quilaqueo et al., 2020).

Membrane contactors utilize a porous and hydrophobic membrane to facilitate the transfer of HCN gas from acidified process water to an alkaline capture solution for subsequent reuse (Estay et al., 2014). This transfer is driven by the vapor pressure difference created between the two separated liquid phases. Membrane contactors demonstrate cost effectiveness through the use of low-cost materials and efficient usage of chemicals and past studies have shown the efficacy of membrane contactors for cyanide recovery at bench- and small-scale applications (Estay et al., 2014; Hammer et al., 2023). Additionally, the high packing density of membranes facilitate process capacity and scalability, compared to AVR and SART, and techno-economic analysis reveals that membrane contactors are competitive with other cyanide

recovery technologies (Estay et al., 2014; Hammer et al., 2023). Pilot-scale cyanide membrane contactor studies have only been conducted for pesticide manufacturing wastewaters but have not been implemented in any pilot- or large- scale study in the gold processing industry (Shen et al., 2004).

Volatilization has been identified as a major loss of cyanide in gold cyanidation facilities in South America, especially Arequipa (Brüger et al., 2018; Hammer et al., 2024). Cyanide recovery addresses both environmental concerns and economic losses of cyanide volatilization by effectively treating and reusing cyanide after gold extraction. Ideal application of a membrane contactor for cyanide recycling system would be immediately after the last adsorption tank to minimize cyanide volatilization in the tailings pond. However, due to the high solids content of the effluent, this is likely not possible. Another potential point of application is the recovery of free cyanide from the tailings pond after sedimentation has occurred. Lower amounts of solids in the tailings pond water would allow the use of filters to pre-treat the water. Losses due to volatilization and to tailings might still occur prior to treatment with a cyanide recycling system, but rapid treatment after sedimentation would keep these losses minimal. Implementation of such a system could decrease the amount of new cyanide that needs to be added during the milling step. Confirmation of an economic model predicting the profitability of the process using these types of mining water would solidify cyanide recovery as a viable alternative to regular cyanide treatment or non-treatment.

This study expands on successful bench-scale demonstrations of cyanide recovery from real mining effluents to evaluate and optimize cyanide recovery using a pilot-scale membrane contactor in the unique conditions encountered by Arequipa's gold processing operations (Estay et al., 2014; Hammer et al., 2023; Quilaqueo et al., 2020). Gold cyanidation effluents in Arequipa are generally not discharged because of extensive tailings storage facility (TSF) pond water reuse. Driven by extensive reuse practices, effluents experience a concentrating effect, increasing conductivities and constituent concentrations (Hammer et al., 2024). Notably, these effluents exhibit high concentrations of total cyanide (free cyanide, weak acid dissociable (WAD), and strong acid dissociable (SAD) cyanide complexes) due to high sodium cyanide dosing during gold cyanidation and absence of active cyanide treatment methods (Hammer et al., 2024). The presence of high WAD cyanide complexes, SAD cyanide complexes, and metals within the concentrated effluents might influence the performance of gold cyanidation when recycled (Bahrami et al., 2007). The removal of free cyanide from gold cyanidation effluents could benefit the reusability of cyanide by effectively removing undesirable constituents from the recycled solution. However, some metal-cyanide complexes and other constituents may precipitate under the low pH conditions ( <pH 7) required for cyanide volatilization potentially affecting cyanide mass transfer rates and recovery or creating operational challenges (Dzombak et al., 2006; Quilaqueo et al., 2020; Shen et al., 1997).

To comprehensively assess the applicability of membrane contactors for cyanide recovery under various operating conditions, this study employed a range of water sources. The investigation utilized synthetic water solutions formulated to represent ideal operating conditions. Additionally, real mining effluents were introduced to evaluate performance under more realistic conditions. The real effluents included one sample sourced from a mine in the United States (US) and two samples obtained from Arequipa, Peru. Operational parameters of flow rate and cyanide concentration for the US effluent were examined experimentally to identify process limitations. Experimental results were used for comparing the performance of the pilot-scale membrane contactor with that of a lab-scale system treating the same effluents (Hammer et al., 2023). Building upon these findings, a techno-economic model was developed to assess the economic viability of membrane contactors under the specific conditions of the analyzed effluents and operating conditions.

## 4.3 Materials and Methods

### 4.3.1 Evaluated Water Types

In total, five different waters, two synthetic and three mining effluents, were evaluated in this study. Synthetic water solutions were prepared in Colorado and Arequipa to create a performance baseline and validate membrane integrity between transport and experimentation. Synthetic water solutions were prepared using tap water with a pH of 11.5 (using NaOH) and spiked with 195 mg/L of NaCN to achieve nominal free cyanide concentrations of ~100 mg/L. Barren heap leaching solution (US) was obtained from a U.S. gold mine. Throughout storage, the concentration of free cyanide in the barren water was reduced to below detection levels. Therefore, NaCN was added to achieve nominal free cyanide concentrations of 100 and 1000 mg/L prior to experiments (US1 and US2 respectively). Barren solutions were obtained from two gold cyanidation plants in Arequipa, Peru. Site 1 (Aq1) is a medium-scale processing plant with an ore capacity of 350 metric tons/day which utilizes a carbon in pulp and electrowinning process, whereas Arequipa site 2 (Aq2) is a large-scale processing facility with an ore capacity of 1730 metric tons/day that uses the Merril-Crowe process. After arrival at the research facility, the pH of the waters was adjusted to 11.5 to avoid volatilization of free cyanide. Cyanide concentrations were measured prior to experimentation and no additional NaCN was added to adjust cyanide concentrations. Relevant water characteristics at the time of arrival are presented in Table 4.1.

Table 4.1 Composition of real mining wastewaters from the US and Arequipa

| | US | Aq1 | Aq2 |
|---|---|---|---|
| pH* | 9.56 | 9.34 | 11.34 |
| Component (mg/L) | | | |

| Table 4.1 Continued | | | |
|---|---|---|---|
| $CN^-$* | 44.4 | 863 | 1532 |
| WAD – $CN^-$ | - | 267.3±109.0 | 573.3±134.0 |
| SAD – $CN^-$ | - | 468.3±106.7 | 489.0±213.1 |
| Total organic C | 95.8±3.76 | 688.8±22.1 | 681.8±1.4 |
| $Cl^-$ | 121.8±2.94 | 277.6±4.6 | 68.3±0.9 |
| $NO_3^-$ | 863.7±66.46 | 168.3±2.7 | 35.3±0.6 |
| $NO_2^-$ | 32.5±2.41 | BDL[a] | 83.6±0.3 |
| $SO_4^{2-}$ | 698.1±38.85 | 4931.6±14.9 | 2537.4±14.0 |
| $PO_4^{2-}$ | BDL[a] | BDL[a] | BDL[a] |
| Ca | 197.7±0.74 | 53.6±1.4 | 626.0±2.4 |
| S | 107.2±2.62 | 1438.0±18.2 | 1602.6±16.2 |
| Na | 86.9±0.67 | 2085.5±8.8 | 2091.5±9.6 |
| Sr | 10.6±0.16 | 1.9±0.3 | 3.9±0 |
| K | 9.3±0.47 | 33.4±0.7 | 193.4±2.7 |
| Si | 4.1±0.16 | 5.0±0.2 | 11.0±0.2 |
| Mo | 2.6±0.05 | 0.7±0 | 7.6±0.1 |
| Mg | 1.2±0.02 | 0.8±0.1 | 0.5±0.0 |
| Fe | 0.15±0 | 76.0±0.5 | 0.1±0 |
| Cu | 0.14±0 | 252.8±3.1 | 119.8±0.6 |
| Al | 0.1±0 | BDL[a] | 0.2±0.0 |
| As | 0.064±0 | 13.3±0.2 | 0.3±0 |
| Zn | BDL[a] | 58.6±0.7 | 530.4±3.1 |

*measured pH before adjustment to 11.5, [a]below the detection limit

### 4.3.2 Sample Analysis

Free cyanide concentrations in the field were measured manually with Hach Test 'N Tube (TNT) 862 using the colorimetric pyridine barbituric acid method and a Hach DR 1900 field spectrometer. Total cyanide and weak acid dissociable cyanide complex (WAD) concentrations were determined using an OI Analytical Flow Water FS3700 Automated Chemistry Analyzer with 330092CT and 330090CT cartridges. The methods used for the analysis were ASTM D 7286-08 for total cyanide and ASTM 7511 for WAD. Elemental analysis of the waters was performed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Avio-500, PerkinElmer, Fremont, CA). Inorganic anions in the water samples were measured by ion chromatography (IC) (Dionex 1500, Sunnyvale, CA). Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, Columbia, MD). Precipitation samples were analyzed using a Hitachi TM-1000 Tabletop scanning electron microscope (SEM) using energy dispersive X-ray spectroscopy (EDS).

### 4.3.3 Pilot-Scale Treatment System

The pilot-scale membrane contactor consists of several components. It is powered by a 3300 W solar array to enable off-grid and sustainable operation. Lightweight aluminum construction allows for the

transportation of the solar array to remote locations. The solar system is further equipped with three 3.8 kWh lithium iron phosphate batteries to ensure treatment can continue when no sunlight is available.

The membrane contactor is designed to operate as a batch style treatment system with interchangeable feed and distillate tanks for more flexible field operations (Figure 4.1). For the experiments done with this system two 31 L tanks and two 220 L tanks were used. The feed tank was additionally connected to a 20 µm and 0.45 µm cartridge filter to stop any precipitants from entering the membrane module. Water from both tanks is circulated using rotary vane pumps. pH sensors and an automatic dosing system regulate and maintain the desired pH levels for cyanide transfer by dosing 5M NaOH and 3.6M sulfuric acid. Ultrafiltration was added as an optional pre-treatment method to remove solids from entering the membrane contactor.

All chemicals used during experimentation in Colorado were obtained from Sigma-Aldrich (St. Louis, MO) and Rocky Mountain Reagents Inc (Golden, CO). However, the chemicals used in Arequipa were of an unknown manufacturer and purity grade.

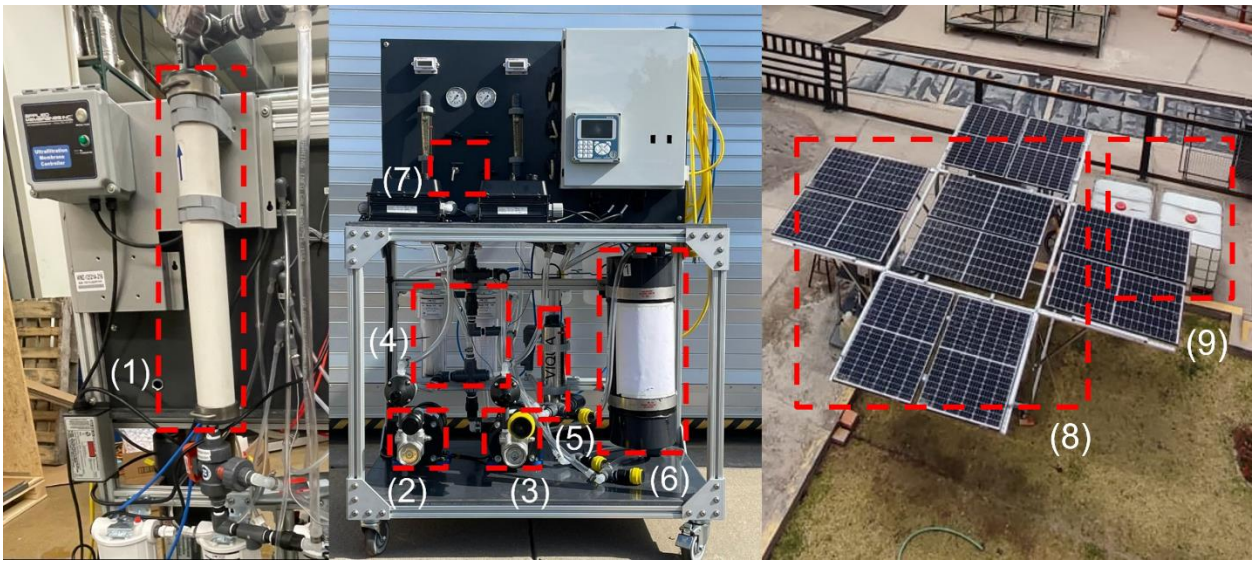


Figure 4.1 Pilot-scale membrane contactor: (1) Ultrafiltration membrane, (2) Feed solution pump, (3) Distillate solution pump, (4) 20 µm and 0.45 µm cartridge filter, (5) UV-lamp, (6) PP membrane module, (7) sampling port, (8) solar array, (9) mining effluent storage. Image of (8) and (9) was taken on location in Arequipa.

The system employed a commercially available 3M™ Liqui-Cel™ EXF-8x20” Industrial Series Membrane Contactor, with a polypropylene hollow fiber membrane. Membrane specific parameters such as number of fibers, thickness of membrane, and membrane surface area are considered proprietary information by the manufacturer and not disclosed. However, for the purposes of calculating the overall

mass transfer coefficient (K), a similar fiber packing density was assumed as the smaller 2.5x8" 1.5 $m^2$ module from the same manufacturer, which yields an estimated membrane surface area of 40 $m^2$.

### 4.3.4 Data Analysis and Modelling

The overall mass transfer coefficient (K) was used as the performance metric to compare the cyanide transfer of the membrane contactor at different operational parameters and effluent compositions in this study. *K* is required for the calculation of cyanide flux and required membrane size for the economic analysis (equations 4.2, C.2, and C.3). K, expressed in m/h was calculated from the linear regression of the natural logarithm of normalized feed concentration plotted against membrane area- and feed volume-normalized time axis using Eqn 4.1:

$$\mathrm{K} = \frac{\mathrm{V}}{\mathrm{At}} \ln\left(\frac{[\mathrm{HCN}]_{\mathrm{f},0}}{[\mathrm{HCN}]_{\mathrm{f}}}\right) \tag{4.1}$$

where V is the volume of the feed ($m^3$), A is the membrane area ($m^2$), t is the time (h), $[HCN]_{f,0}$ is the initial feed hydrogen cyanide concentration, and $[HCN]_f$ is the feed hydrogen cyanide concentration at time t (Huo et al., 2020). Given variable cyanide concentrations across the analyzed effluents, cyanide flux was used as a measurement of mass transfer. Cyanide flux ($g/m^2h$) was calculated as:

$$J_{CN^-} = K([HCN]_f - [HCN]_d) \tag{4.2}$$

where [HCN]f and [HCN]d are the concentrations of volatile hydrogen cyanide ($g/m^3$) in the feed and distillate, respectively (Huo et al., 2020). As HACH TNT 862 vials only measure dissolved cyanide [$CN^-$], the total free cyanide concentration ($CN_{free}$) was calculated from the measured cyanide ion ($CN^-$) concentration and measured pH using the Henderson–Hasselbach equation:

$$[HCN] = \frac{[CN^-]}{10^{pH-pK_a}} \tag{4.3}$$

For calculations using Eqn 3, the pKa of hydrogen cyanide assumed to be 9.21 at 20 °C (Dzombak et al., 2006).

A sequential mass balance model was performed using the calculated *K* and measured pH values to model cyanide concentrations in the system. Initial cyanide flux was calculated using equations 4.1–4.3 based on starting feed cyanide concentration and pH. In subsequent time steps, cyanide concentrations were calculated based on measured cyanide removal and the assumption that removed cyanide was completely transferred to the distillate. From these concentrations, a new flux was calculated and further iterated for each time step. The resulting data were used for the development of the cost model which is dependent on calculated flux and *K* values.

### 4.3.5 Economic Analysis

The economic model developed in this study was used to evaluate the economic viability of cyanide recovery using effluents from 3 mining and gold cyanidation facilities (see Table 4.1). Two cases of low (100 mg/L – $CN^-$) and high (1000 mg/L – $CN^-$) cyanide concentrations were considered for the US effluent whereas one case was considered for Aq1 and two cases for Aq2. The US effluent scenarios assumed a large-scale processing facility with a representative effluent flow rate of 200 $m^3$/h. Considering the Aq1 effluent originated from a medium-scale gold cyanidation facility in the Arequipa region, a representative effluent flow rate of 17.5 $m^3$/h was assumed based on the ore processing capacity and previous research (Hammer et al., 2024). Lastly, an effluent flow rate of 86.5 $m^3$/h was assumed for Aq2 based on the ore processing capacity of the facility. The modelled treatment system for all cases is a batch-style treatment system designed to sufficiently treat the effluent flows. If residual cyanide concentrations in the feed exceeded 50 mg/L following the cyanide removal process, a secondary treatment step in the form of chemical oxidation ($SO_2$ + air) was assumed. This treatment was to reduce the remaining feed cyanide concentration to 50 mg/L in accordance to the international cyanide management code (Akcil, 2010). Given that most gold cyanidation facilities already possess infrastructure for traditional cyanide treatment, only operational costs for $SO_2$ + air were considered.

Formulas and relevant parameters used in the economic analysis are summarized in Table C.2 of the Supporting Information.

### 4.3.6 Synthetic Effluent Integrity Test

Experiments to confirm the functionality and condition of the membrane contactor were carried out using tap water spiked with sodium cyanide. Owing to the limited availability of DI water at the Arequipa field location, tap water was chosen as the primary solvent for baseline experiments. All baseline experiments were carried out under the same parameters with a nominal feed cyanide concentration of 100 mg/L $CN^-$, a membrane flow rate of 10 L/min, a pH of 6 in the feed solution and 11.5 in the distillate solution and using 30 L feed and distillate tanks. These differences in membrane performance can likely be explained by differences between baseline experiments carried out in Colorado and Arequipa and differences in tap-water composition, NaCN purity, $H_2SO_4^{2-}$ purity, and NaOH purity. Furthermore, it is known that temperature influences the mass transfer resistances of cyanide recovery (Estay et al., 2013; Hammer et al., 2023). While experiments in Colorado took place in a temperature-controlled setting, those in Arequipa were performed outdoors without direct temperature control (see Figure 4.1). Even small differences in temperature, water quality (e.g. turbidity), and chemical purity could have a cumulative effect to explain the observed differences in *K* values between the two locations (Hammer et al., 2024; Quilaqueo et al., 2020; Shen et al., 1997). While the system's functionality was demonstrated in

both the Colorado and the Arequipa synthetic water trials, observed performance variations necessitated the inclusion of baseline experiments between real mining effluent experiments. This approach served as a consistency check, ensuring no membrane performance decline or damage had occurred during the experiments with real mining effluents or transportation.

## 4.4 Results and Discussion

### 4.4.1 Cyanide Recovery from US Mining Effluents

To evaluate the effect of system flow rates on treatment efficacy, US process effluents were utilized for a series of experiments with varying flow rates using a feed volume of 30 L. Previous studies have shown increases in *K* values with increasing flow rates (Estay et al., 2014, 2013; Hammer et al., 2023). These results were replicated using the pilot-scale system: higher flow rates and the resulting liquid turbulence improve mass transfer and *K* (Figure 4.2), and subsequently result in shorter treatment times. Our results further indicate that the flow rate had a stronger impact on the membrane performance of low cyanide concentration waters than that of high cyanide concentration waters. The impact of higher cyanide concentrations on mass transfer coefficient (*K*) values appeared less pronounced at flow rates of 5 L/min and 10 L/min. However, a more substantial difference in *K* values was observed at a flow rate of 15 LPM.

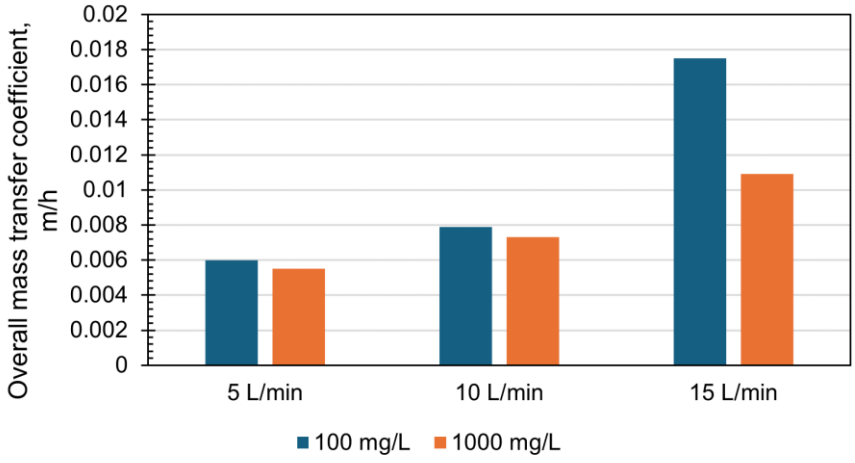


Figure 4.2 Influence of flow rate on membrane coefficients using US effluents at a $CN^-$ concentration of 100 and 1000 mg/L. Feed and distillate pH were 6 and 11.5 respectively.

A previous study using a lab-scale membrane contactor has shown a decrease in *K* with increasing cyanide concentrations. Experiments using the US effluents at cyanide concentrations of 100 mg/L and 1000 mg/L showed a slight decrease in *K* with the higher concentration (Hammer et al., 2023). Cyanide

flux increased proportionally, demonstrating that the membrane contactor maintained consistent recovery across a range of cyanide concentrations (Figure 4.3). The calculated initial cyanide flux increased from 0.79 g/m²h at 100 mg/L to 7.3 g/m²h at 1000 mg/L. The near constant *K* across the two cyanide concentrations indicates that the membrane was not saturated with cyanide during the experiments and no increase in mass transfer resistance was noted. This suggests potential for further optimization as the membrane contactors maximum capacity for cyanide transfer (i.e. the maximum flux) was not saturated under the tested concentrations and operating conditions. A much stronger drop in *K* value was observed with ammonia recovery with membrane contactors (33%) where the ammonia flux maxed out at 25 $g/m^2.h$ at a feed concentration of 2 g/L $NH_4^+$ (Schwiebert et al., 2024).

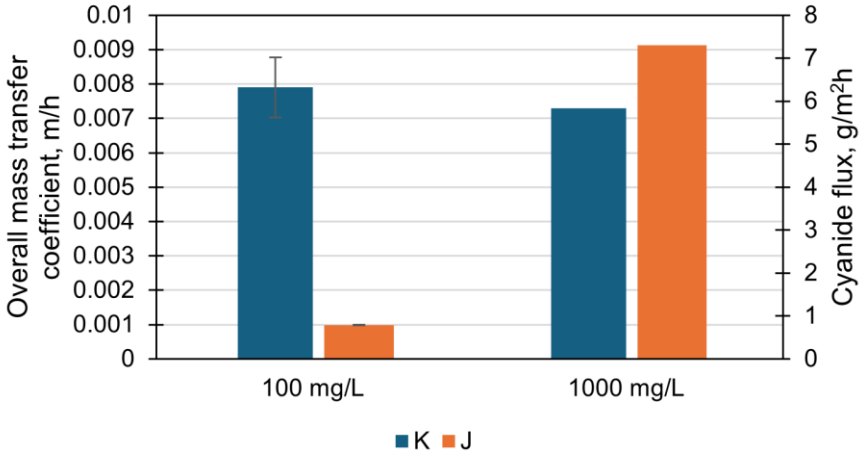


Figure 4.3 Effect of initial cyanide concentration on overall mass transfer coefficient and initial cyanide flux using US effluent at a flow rate of 10 L/min.

Two additional experiments were conducted utilizing larger 220 L tanks and 10 L/min flow rate. These experiments were carried out at two feed cyanide concentrations of 143 mg/L and 580 mg/L to investigate the system's response across an industrially relevant concentration range. Results show near complete recovery of free cyanide after both experiments, with 98% for 143 mg/L and 99% for 580 mg/L (Figure 4.4B). In contrast to the trends observed in previous studies (Hammer et al., 2023), where a decrease in *K* values with increasing free cyanide concentration was identified, the experiment using water with an initial free cyanide concentration of 580 mg/L exhibited a similar *K* (0.0088 m/h) compared to the 143 mg/L solution (0.0077 m/h) (Figure 4.4A). The comparable mass transfer coefficients obtained from both large-volume and smaller-volume (Figure 4.3) experiments suggest that the membrane performance remains consistent across different scales of treatment volume and cyanide concentrations (average K of 0.0079 m/h ± 0.00032). This finding further supports the scalability of membrane contactors for cyanide treatment and allows for the effective treatment of effluents from gold cyanidation

facilities of varying capacities using this pilot-scale system. However, even more important is the fact that treatment times to achieve similar cyanide recoveries are almost independent of feed cyanide concentrations. This is because the cyanide flux scales with the feed concentration, but at higher concentrations also proportionally more cyanide needs to be removed which leads to a similar treatment time at different cyanide concentrations. If a certain final feed concentration needs to be reached instead of a specific recovery, higher feed concentrations will obviously lead to higher treatment times. Baseline experiments using synthetic water resulted in an overall mass transfer coefficient of 0.0109±0.0005 m/h throughout experimentation with the US effluent.

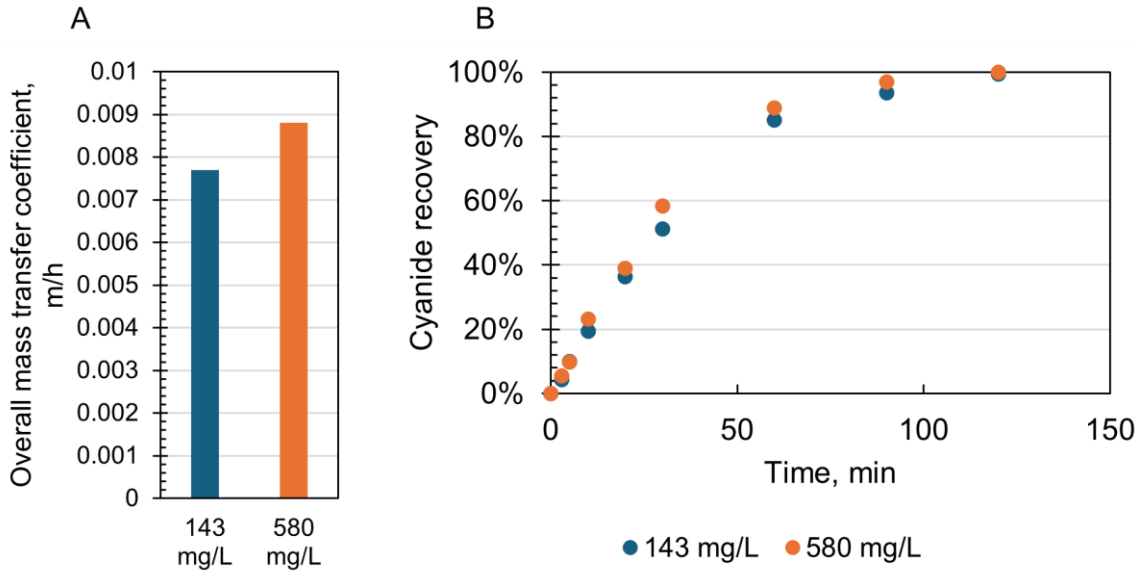


Figure 4.4 Cyanide recovery using high volume feed solutions (220 L) at 10 L/min showing *K* (A) and overall cyanide recovery (B). Feed and distillate pH were 6 and 11.5 respectively.

### 4.4.2 Cyanide Recovery from Arequipa Mining Effluent

Prior to cyanide treatment using a membrane contactor, gold cyanidation effluents need to undergo pH adjustment to enable cyanide transfer. This necessary step resulted in the formation of precipitates when applied to the effluents of Aq1 and Aq2. Both effluents are rich in copper and zinc concentrations (Table 4.1), which suggests that the resulting precipitation primarily consists of metal-cyanide complexes. Precipitation of metal-cyanide complexes at low pH values is well known and can even be an effective method of copper removal from gold cyanidation plants (Alonso-González et al., 2009; Leaver and Woolf, 1931). While precipitation of metal-cyanide complexes can be beneficial in some applications, it poses challenges for membrane-based cyanide recovery processes. The effects of precipitation from the effluents of Aq1 and Aq2 on membrane performance are discussed in the following section.

Effluent received from Aq1 exhibited high turbidity upon arrival, necessitating pretreatment via ultrafiltration to avoid damage to the membrane contactor. To determine the effects of feed water quality on membrane contactor performance, experiments with effluents from Arequipan gold processing plants were evaluated under baseline conditions (pH 6 feed, pH 11.5 distillate, and 10 L/min flow). These operating parameters resulted in a limited free cyanide recovery of 45% (Figure 4.5) and a correspondingly low *K* value of only 0.0016 m/h. This is almost 5 times lower than with the US mining effluent that only had a slightly higher feed concentration of 1000 mg/L compared to 863 mg/L (Figure 4.3). This suggests effluents from Aq1 may not be suitable for treatment using membrane contactors at pH 6. An important reason for the lower performance is that, as the feed pH was lowered to 6, red precipitation was observed. Accumulation of these precipitants within the cartridge filters increased the feed-side pressure and differential pressure across the membrane contactor. Pressure relief valves were installed beforehand to protect the membrane against pressure spikes, however, this increase remained within acceptable levels during experimentation. The amount of energy required to maintain the desired flow rate of 10 L/min also increased. These operational challenges potentially increase strain on pumps and necessitate more frequent cartridge filter replacements. Moreover, the cartridge filters probably were not able to remove all the precipitates, hence the significantly lower mass transfer coefficient (Kenfield et al., 1988; Shen et al., 1997).

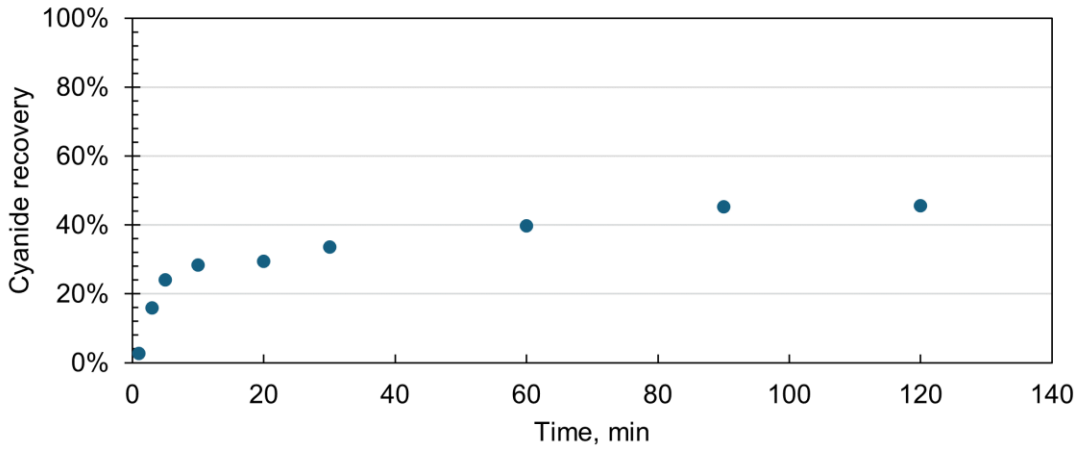


Figure 4.5 Cyanide recovery using real mining effluents from Aq1. (pH 6 feed, pH 11.5 distillate, and 10 L/min flow)

Mineral precipitation is expected to significantly impact membrane contactor performance and cyanide recovery (Kenfield et al., 1988; Shen et al., 1997). Insoluble cyanide metal complexes formed within the feed solution remove cyanide species from the liquid phase, potentially reducing the driving force for mass transfer across the membrane and affecting overall cyanide recovery. Precipitate deposition at the

entrance to the hollow fiber membranes obstructs fluid flow, increasing cross membrane pressure and risk of causing membrane rupture (Prasad and Sirkar, 1989). Within the membrane module, precipitation can further lead to membrane fouling (Han et al., 2005), reducing its permeability and decreasing cyanide transfer. The resulting decline in cyanide recovery would necessitate more frequent cleaning or replacement of the membrane (Han et al., 2005). Furthermore, the formation of precipitates could have implications for downstream processing of these effluents and the disposal of precipitate-laden wastewater potentially requires additional treatment to avoid environmental contamination. As a result, for this specific wastewater, operating at higher pH values of 7 or more to avoid precipitation is recommended. This will also decrease mass transfer rates and maximum recovery, but the impact could be less severe than that of precipitation as is demonstrated below with the wastewater from Aq2. In general, a simple jar test can inform at what pH precipitates start to form and the membrane contactor should be operated at a slightly higher pH.

The effluent used from Aq2 originated from a gold processing facility employing the Merrill-Crowe process. To achieve effective gold recovery through zinc dust cementation, the process fluid needs to be prefiltered extensively. As a result, unlike the effluent from site 1, this effluent allowed for direct processing in the membrane contactor without the need for additional ultrafiltration. However, the Merrill-Crowe process does add substantial amounts of zinc ions that can form insoluble cyanide complexes in the pH 5-7 range (Hampton, n.d.). Indeed, precipitation was encountered during the experiment upon lowering the feed solution pH to 5. The extent of red precipitation observed with the Arequipa site 2 effluent was much lower compared to that from Aq1, with a resulting diminished degree of clogging within the cartridge filters observed. Consequently, the treatment process achieved a higher cyanide recovery of 81% with a $K$ value of 0.0026, suggesting improved overall treatment performance compared to Aq1 (Figure 4.6). Despite a minor reduction in $K$ during membrane integrity tests, experiments with the effluent of Aq2 did not show a clear declining trend in $K$ value.

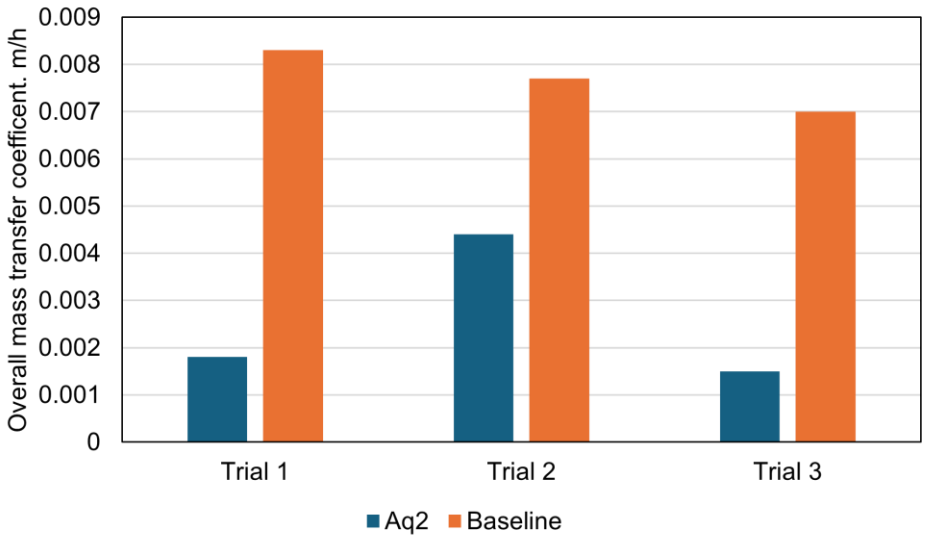


Figure 4.6 Cyanide recovery using real mining effluents from the Merrill-Crowe process of Aq2. Three trials were performed for this effluent (pH 6 feed, pH 11.5 distillate, and 10 L/min flow) and membrane integrity was confirmed after each trial with a baseline experiment (pH 6 feed, pH 11.5 distillate, and 10 L/min flow).

To circumvent precipitation issues observed at a feed pH of 5, an additional experiment was conducted at a feed pH of 7 which resulted in a lower *K* value of 0.0018 m/h compared to 0.0024 m/h at pH 5. Consequently, cyanide removal took longer at the higher pH due to the decreased mass transfer rate, reaching 81% recovery at 120 min instead of 90 min (Figure 4.7). However, this compromise minimized problems associated with precipitate formation and potential filter and membrane clogging. To maximize free cyanide removal, a 2-stage approach was implemented: following the initial recovery stage (pH 7), the feed pH was further reduced to 5 to recover any remaining free cyanide. By first removing free cyanide at a pH above which zinc cyanide precipitates don't form, the amount of precipitates that can form when dropping the pH below 7 afterwards is minimized. The 2-stage pH adjustment process yielded indeed an improved recovery of 95%, achieving almost complete recovery of the measured free cyanide. Lowering the pH to 5, although beneficial for capturing additional free cyanide, resulted in the formation of white precipitates which could also negatively impact system performance (Figure C.2).

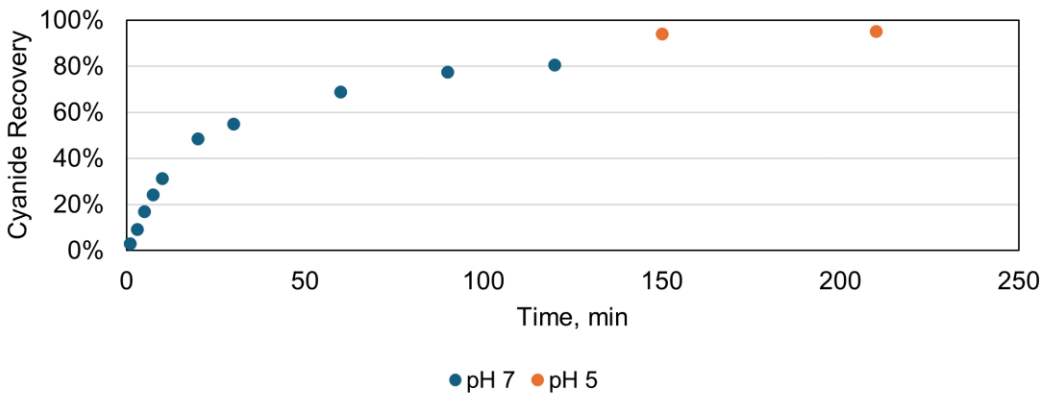


Figure 4.7 Cyanide recovery using real mining effluents from the Merril-Crow process of Aq2 (feed pH 7, dist. pH 11.5, 10 L/min flow). Additional pH drop was performed after initial cyanide recovery had slowed. Subsequently, feed pH was lowered to pH 5 to achieve additional cyanide recovery.

Samples of red and white precipitates, obtained from Aq2 effluent experiments at initial feed pH 5 and pH 7 with 2nd pH drop to 5 (henceforth called "2-stage pH drop") respectively, were dried and subsequently analyzed through EDS. Unfortunately, standard EDS detectors have a poor detectability of nitrogen species, so cyanide complex precipitates cannot be identified (Buck, 2017). The primary elements in the initial Aq2 precipitant (feed pH 5) are Zn, C and Na (Figure 4.8). The composition of precipitants from Aq2 (2-stage pH drop) are notably different. Zn has increased while O, Cu, and Ca emerged as new components. The observed increase in zinc and copper content in the Aq2 (2-stage pH drop) precipitate suggests that the additional pH reduction increased the precipitation of metal species relative to other species. EDS is, however, not a quantitative technique, so it is possible that with Aq2 (2-stage pH drop) there may still have been less metal cyanide precipitates by mass compared to Aq2 allowing a higher overall cyanide recovery. Jar tests using the Aq1 and Aq2 effluents at different pH reveal similar amounts of precipitation between pH6, pH 7 and the 2-stage pH drop for Aq2 and higher amounts of precipitation for Aq1 at pH 6 (Figure 4.8 (C). The 2-stage pH drop for Aq2 resulted in slightly lower precipitation mass compared to the single stage pH adjustments to pH 6 and 7. This suggests further potential benefits in terms of reduced filter clogging in addition to higher cyanide recovery. Furthermore, it appears that the process of cyanide recovery itself may influence the composition of precipitants as seen for Aq2 (2-stage pH drop). Overall, the sites from which Aq1 and Aq2 originated would have to expect an estimated 477 kg and 1470 kg of precipitants per day. Given the predominance of zinc in the precipitates, further investigation into the recovery of zinc as a byproduct of cyanide recovery could be considered. Further analysis is necessary to reveal the exact mechanisms behind the observed precipitations and to assess their influence on the gold cyanidation process.

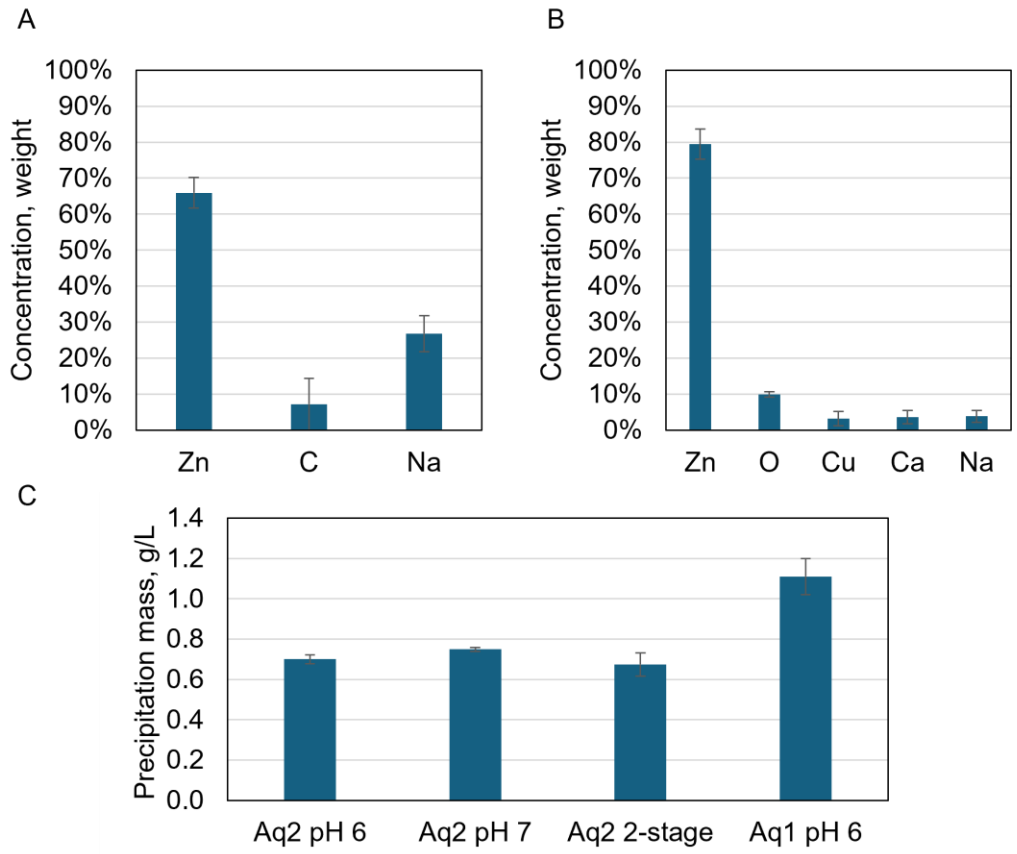


Figure 4.8 Elemental composition of precipitates formed in the effluent of Aq2 at (A) pH 5 and (B) 2-stage pH drop first to pH 7 and then to 5. Data was normalized for elements ≥ Na. (C) shows the precipitation mass of Aq1 and Aq2 effluents at relevant pH values.

### 4.4.3 Economic Analysis

An economic analysis was performed to evaluate the cost effectiveness of cyanide recovery for each of the analyzed gold cyanidation effluents. Additionally, free cyanide concentrations of 100 mg/L and 1000 mg/L were considered for the US effluent (US1 and US2), while the 2-stage approach was considered for the Aq2 effluent (2-stage pH drop). Case-specific parameters, including processing capacity and treatment volume, were determined through direct communication with the facilities that provided effluents for this study and are listed in Tables C.2 and C.3 (Hammer et al., 2024, 2023). Figure 4.9 presents the costs for the recovery of cyanide for each case. Recovery costs are expressed in US dollars per kilogram ($/kg) of recovered cyanide ($CN^-$) to facilitate comparison across each case and to the cost of new cyanide. For the cost of new cyanide, a value of $5/kg $CN^-$ was assumed consistent with past studies on cyanide recovery technologies (Hammer et al., 2023). However, cyanide costs can be highly volatile. Cyanide is synthesized through the Andrussow process from methane, oxygen and ammonia, the latter in turn is derived from methane. As a result, increasing global natural gas prices will lead to an increase in the price

of cyanide. Other chemical costs were obtained through vendor quotes, considering NaOH and $H_2SO_4$ as the primary choice for base and acid control according to present industry practices. Prefiltration, although required for Aq1, was not considered for this economic analysis to allow for a more consistent comparison between the recovery process costs of each case. Moreover, as demonstrated with Aq2, the pH adjustment strategy can greatly reduce precipitate formation and overall cyanide recovery. Additional cyanide treatment costs were considered whenever residual cyanide remained in the feed solution after experimentation. Cyanide oxidation with $SO_2$ and air was chosen as a representative traditional treatment method as it is commonly implemented technology. Employing cyanide recovery also greatly reduces or eliminates the need for traditional cyanide treatment through oxidation resulting in an additional estimated cost savings of \$4/kg $CN^-$. The value of recovered cyanide was estimated to be equivalent to new cyanide. The high pH of the distillate solution minimizes further cyanide losses during storage and facilitates the direct reuse of recovered cyanide in the gold cyanidation process.

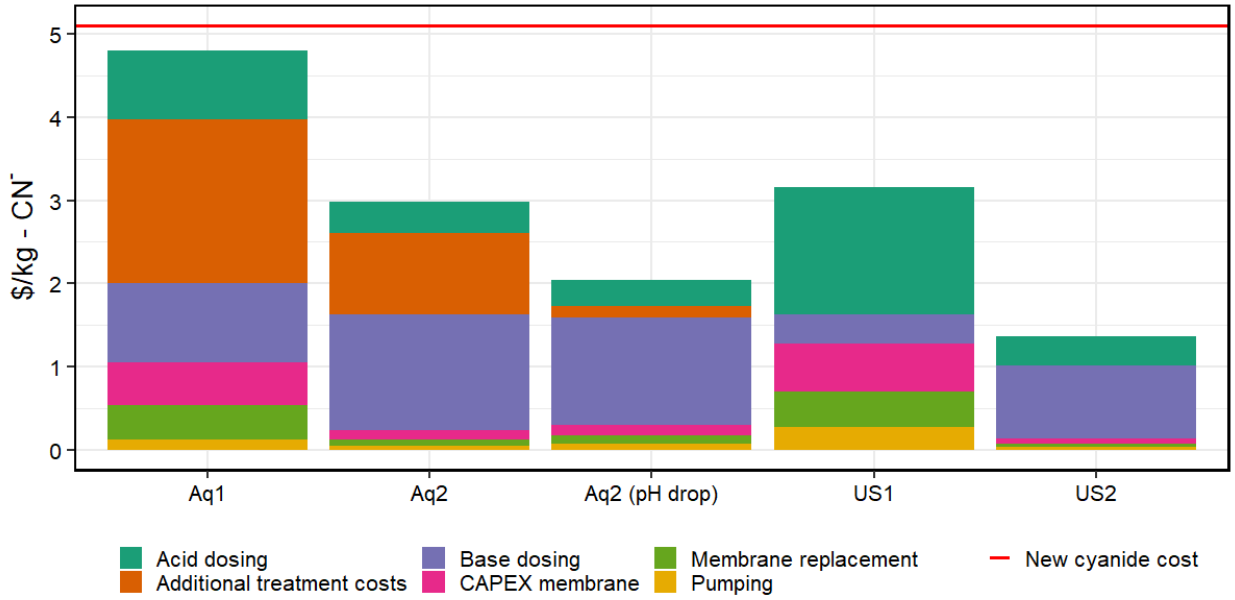


Figure 4.9 Cost distribution of recovered cyanide for medium- and large-scale gold cyanidation facilities explored in section 3.2. The cost of new cyanide was estimated to be \$5.0/kg CN in all cases based on industry quotes for gold processing plants of similar sizes. Additional treatment costs of a $SO_2$/air cyanide oxidation system were applied whenever residual cyanide remained in the feed solution.

Economic analysis revealed that of all investigated cases, Aq1 exhibited nearly identical cost for recycled cyanide compared to the purchase of new cyanide. The highest cost for this scenario were identified as chemical dosing and additional treatment costs. Low cyanide flux with only 45% cyanide recovery rate results in process inefficiencies that decrease the economic viability of cyanide contactors

with waters from Aq1. Low flux and low recovery further increase the per-unit costs of acid dosing and membrane costs.

Results from all other cases indicate cyanide recovery using membrane contactors to be cost-effective compared to new cyanide. The Aq2 effluent incurred base dosing and additional treatment costs as the highest per-unit costs. Other costs such as acid dosing and membrane CAPEX and replacement are lower due to the amount of cyanide recovered. Additional treatment costs can be further reduced by implementing a 2-stage pH adjustment (Aq2 (2-stage-pH drop)), to increase cyanide recovery. Acid dosing constituted the primary cost for US1, driven by the substantial acid requirement to decrease feed solution pH relative to the low potential cyanide recovery, even if 99% was recovered, due to the low feed concentrations of 100 mg/L. Membrane and pumping energy expenditures were likewise elevated compared to other scenarios. Despite incurring high per-unit costs, cyanide recovery in case US1 remains economically viable compared to purchasing new cyanide. Lastly, US2 is the case with the lowest costs at only 27% the cost of new cyanide. High cyanide flux with high free cyanide concentrations in the feed allow for a very efficient transfer of cyanide and low per-unit costs. A sensitivity analysis was performed to evaluate the influence of pump flow rate and feed cyanide concentration on the costs of cyanide recovery for the US effluent. Similarly to results observed in the lab-scale study (Hammer et al., 2023), an increase in flow rate increased membrane performance (K) and cyanide flux (J). Improved cyanide flux allows for the use of smaller membrane areas, reducing CAPEX and membrane replacement costs. Costs through increased energy consumption through pumping are offset by these savings, indicating that operating the membrane contactor at higher flow rates is beneficial for the US1 effluent. Per-unit costs of cyanide recovery were reduced by 4.6% at 15 L/min compared to 10 L/min, whereas costs increased by 5.3% at 5 L/min (Figure C.4). Furthermore, the sensitivity analysis demonstrated that treatment of effluents with high cyanide concentrations and the resulting increase in cyanide flux generally benefits economic viability. While base dosing costs increased due to the rapid cyanide transfer, reduced per-unit acid dosing, CAPEX, membrane replacement, and pumping costs offset this rise. A feed cyanide concentration of 600 mg/L was found to be the optimal concentration, reducing per-unit costs by 60.1% compared to 100 mg/L but only 7.4% compared to 1000 mg/L (Figure C.6).

Additional costs not directly considered in this economic analysis could significantly impact the overall economic viability of cyanide recovery, particularly for the effluent stream of Aq1. As the only effluent that requires pretreatment through ultrafiltration, overall operational expenses are expected to increase beyond the cost of cyanide recovery. However, much of past research has primarily focused on the intrinsic cost of cyanide recovery process, allowing comparison between different cyanide recovery technologies and membrane contactors of previous studies (Table 4.2). While cyanide recovery using the pilot-scale membrane contactor is generally competitive with other cyanide recovery technologies, the

system exhibited limitations when treating complex effluents like Aq1. Specifically, cyanide recovery using the US2, employing identical effluent and parameters to Hammer et al.'s case1, achieved similar recovery costs (Hammer et al., 2023). This indicates that membrane contactors are a comparable alternative to AVR, SART, ion exchange and the ReCyn process. Results of the 2-stage process for Aq2 further indicate that the treatment of complex effluents is economically viable through the implementation of staged feed pH reduction. This approach yielded comparable treatment costs to AVR and ReCyn and demonstrated better economic performance than ion-exchange. AVR, SART, and the ReCyn process show lower recovery costs compared to Aq1, Aq2, and US1, suggesting that these methods might be more cost effective compared to the membrane contactor used in this study. However, a more direct comparison between these technologies would necessitate using the same gold cyanidation effluent.

Table 4.2 Comparison of lab- and pilot-scale cyanide recovery technology costs with other technologies

| | Method | Cost of recycled cyanide ($/kg) | Cost of new cyanide ($/kg) | Recovery cost as % of new cyanide cost |
|---|---|---|---|---|
| This study (Aq1) | Membrane contactor (pilot) | 4.80 | 5 | 96 |
| This study (Aq2) | Membrane contactor (pilot) | 2.98 | 5 | 60 |
| This study (Aq2 (2-stage pH drop) | Membrane contactor (pilot) | 2.05 | 5 | 41 |
| This study (US1) | Membrane contactor (pilot) | 3.16 | 5 | 63 |
| This study (US2) | Membrane contactor (pilot) | 1.36 | 5 | 27 |
| Hammer et al., 2023 | Membrane contactor (lab) (case1) | 1.31-1.80 | 5 | 26-36 |
| Hammer et al., 2023 | Membrane contactor (lab) (case2) | 3.60-4.31 | 7.34 | 49-59 |
| Adams and Lloyd, 2008) | AVR | 1.02-1.39 | 2.64 | 39-53 |
| Adams and Lloyd, 2008 | SART | 0.60-0.73 | 2.64 | 23-28 |
| Fleming, 2016 | Ion exchange | 1.60-2.17 | 1.88-2.82 | 57-115 |
| Whittle and Pan, 2018 | ReCyn | 2.50 | 5 | 50 |

## 4.5 Conclusions

Membrane contactors are a promising technology for the recovery of cyanide from diverse gold cyanidation effluents. This study successfully demonstrated cyanide recovery from the complex effluents prevalent in the Arequipan gold processing industry using a pilot-scale membrane contactor. However, the treatment of such effluents presented significant challenges. Turbidity of carbon in pulp effluents and precipitation of metal-cyanide complexes in the low pH feed solution reduce cyanide recovery and negatively affect membrane performance. These findings raise concerns about the economic viability of membrane contactors to recover cyanide from complex effluents. However, this study shows that a stepwise reduction in feed pH can reduce precipitate formation and increase cyanide recovery, allowing for more cost-effective cyanide removal from complex effluents. Moreover, membrane contactors are a promising technology for cyanide recovery from cleaner effluents such as those originating from the US site or effluents from the Merril-Crowe process. These effluents exhibit higher cyanide recovery at higher membrane performance, leading to reduced operational costs. It was further discovered that similar treatment times can be expected independently of feed cyanide concentration. As such, membrane contactors, when optimized for effluent characteristics, are a suitable candidate for cyanide treatment and are cost-competitive with other cyanide recovery technologies. Further research should confirm the long-term integrity of the membrane and investigate the treatment of complex gold cyanidation effluents and their precipitants.

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# CHAPTER 5 CONCLUSIONS AND FUTURE WORK

## 5.1 Summary of Findings

Gold extraction practices in the Arequipa region of Peru do not currently prioritize active cyanide treatment, and because of their unique operations (i.e., complete reuse of barren water), accumulate significant amounts of cyanide and metal-cyanide complexes within gold extraction systems. This not only increases risks to the environment and human health, but also results in inefficient cyanide usage that impacts operations and economics of gold extraction. This dissertation evaluates the potential of membrane contactors to improve cyanide management in the region. The prospects of active cyanide treatment using membrane contactors could be improved through the benefit of direct cyanide recovery, which in turn would decrease overall cyanide usage and chemical costs for the operators. Findings from this thesis advance the understanding of cyanide treatment using membrane contactors applied to real-world gold processing effluents.

### 5.1.1 Objective 1: Characterization of Medium and Small-Scale Gold Processing Operations, Wastewaters, and Tailings in the Arequipa Region of Peru

The main objective of chapter 2 was to characterize process waters and tailings of gold processing facilities in the Arequipa region of Peru. These facilities stand out in their practices of extensive water reuse and zero effluent discharge policies, resulting in complex process water composition. Secondary objectives were to determine the fate of cyanide in these closed water recycling systems and identify potential opportunities for cyanide reuse technologies. High concentrations of cyanide and metal-cyanide complexes in both processing waters and tailings were a strong indicator that the practice of water recycling leads to the accumulation of these constituents. This assumption was further supported by the high conductivities and high concentrations of cyanide and metals found in the processing water. Similarly, tailings at these facilities were found to contain high concentrations of cyanide, cyanide complexes, and metals, even after remaining inactive for several months. The propensity of tailings storage facilities (TSFs) to retain cyanide after inactivation is especially concerning as cyanide appeared to concentrate on the surface layers, increasing the risk for cyanide exposure.

Free cyanide speciation based on a pKa of 9.48 at 15°C (Visual MINTEQ 3.1) and measured pH, suggests that a high fraction of volatile cyanide, HCN, was present in the process waters. A model developed to study the fate of cyanide in these facilities confirmed high amounts of “unaccounted free cyanide” throughout the gold cyanidation process. While biological processes and UV-light exposure contribute to cyanide exiting the process water, the dominant mechanism for unaccounted cyanide is likely volatilization considering the fraction of volatile cyanide in the process waters.

Cyanide recovery technologies, including membrane contactors, could serve as a more direct pathway for cyanide reuse than the currently implemented extensive decant water reuse. Treatment of barren waters containing high amounts free cyanide would greatly limiting cyanide discharge to the TSF and prevent cyanide losses occurring within the TSFs.

### 5.1.2 Objective 2: Membrane Contactors as a Cost-Effective Cyanide Recovery Technology for Sustainable Gold Mining

Chapter 3 aimed to evaluate membrane contactors as a suitable treatment method for cyanide impacted waters at the laboratory-scale. Two membrane materials, hollow fiber polypropylene (PP) and flat sheet polytetrafluoroethylene (PTFE), were evaluated under a variety of different conditions using a gold cyanidation effluent from a US based processing facility. This work demonstrated the effective recovery and concentration of cyanide in the distillate from actual mining effluents. Parameter variations for both membrane types showed the influence of flow rate, cyanide concentration, feed and distillate pH, and temperature on cyanide recovery using membrane contactor systems. Moreover, the new PTFE membrane achieved more than double the mass transfer of previously proposed PP membrane contactors, highlighting its potential for use for efficient cyanide recovery. A techno-economic analysis of the lab-scale membrane contactor was performed for a typical large- and small-scale gold processing facility. Results of this indicate that cyanide recovery using membrane contactors at both scales is more economical than buying new cyanide. Large-scale processing facilities offer economic promise for cyanide recovery as the economy of scale lowers operational costs per unit of recovered cyanide. The PTFE membrane system exhibited slightly lower costs at smaller scales compared to the PP membrane system, indicating that appropriate membrane selection may improve the potential cost savings for cyanide recovery.

Overall, membrane contactors offer a suitable alternative to traditional cyanide destruction and detoxification processes due to the ease of cyanide ruse and lack of byproducts that could lead to eutrophication of receiving surface waters. This work showed that membrane contactors could compete with other cyanide recovery technologies due to their low capital costs, easy scalability, and more safe operability.

### 5.1.3 Objective 3: Pilot-Scale Assessment of a Mobile Off-Grid Membrane Contactor System for the Treatment of Cyanide in Gold Processing Wastewater in Arequipa

Chapter 4 summarizes the research that was developed based on findings from Chapter 2 and Chapter 3 to perform a pilot-scale evaluation of a membrane contactor system for cyanide recovery. A pilot-scale system using PP membrane contactor was developed and deployed to the Arequipa region of Peru with the goal of demonstrating the recovery of cyanide from the region’s complex gold cyanidation effluents.

Experiments were conducted with the same US-based effluent used in Chapter 3, along with two actual gold processing effluents from Arequipan gold processing facilities. Treatment of the US-based effluent yielded expected results based off the lab-scale treatment detailed in Chapter 3. Experimentation at cyanide concentrations of 100 mg/L and 1000 mg/L and at large volumes (220 L tanks) revealed the scale-up potential of the membrane contactor as membrane performance remained consistent across different cyanide concentrations and treatment volumes. This study further demonstrated cyanide recovery from the Arequipan effluents, however presented significant challenges. Carbon in pulp extraction and extensive water reuse resulted in high turbidity which necessitated pretreatment (such as ultrafiltration) of one of the Arequipan effluents. Additionally, precipitation of metal-cyanide complexes (zink and copper) in the low pH feed solution reduced cyanide recovery and negatively impacted membrane performance. A stepwise reduction in feed pH was shown to reduce precipitation formation and increase cyanide recovery. A techno-economic analysis was performed on data generated from cyanide recovery experiments with effluents evaluated in this chapter, mirroring results from Chapter 3 for the cyanide recovery from cleaner effluents such as those originating from the US site. While cyanide recovery from more complex effluents was demonstrated to be more economical than the purchase of new cyanide, the economic viability of this process may depend on the formation of cyanide complexes and the need for potential pre-treatment steps. Further research is required to enhance the applicability for treating complex gold cyanidation effluents, particularly those with high salinity, and high concentrations of metals-cyanide complexes.

## 5.2 Recommendations for Future Work and Directions of Research

### 5.2.1 Validation of Pilot-Scale Results and Experimentation with Different Effluents.

Chapters 3 and 4 demonstrate membrane contactors as a viable technology for the recovery of cyanide from real gold processing effluents. However, further research and development are necessary to determine the applicability to a range of cyanide recovery scenarios to further investigate life cycle costs. Although the pilot study of Chapter 4 provided valuable insight into the performance of membrane contactors in treating the Arequipas gold processing effluents evaluated, it is also important to acknowledge the limitations of this dataset. Effluent characteristics vary largely throughout the Arequipa region (see Chapter 2) and may present additional challenges compared to the two analyzed effluents in this study. Confirmation of the results described in Chapter 4 with a wider range of effluents would further improve the understanding of the treatment of complex effluents using membrane contactors and demonstrate their applicability in locations with different operating characteristics and water management policies. Long-term studies (e.g., months of operation) should also be conducted to assess the longevity of

the membranes and contactor system during the treatment of complex gold cyanidation effluents and their precipitants.

Parameter variation could be further explored to improve membrane performance. Chapter 3 demonstrated an increase in cyanide flux because of higher temperatures. The pKa of free cyanide is temperature dependent, decreasing with higher temperatures (Dzombak et al., 2006). Consequently, operating a membrane contactor at higher temperatures (e.g. through solar collectors) could thus reduce acid and base consumption, making the process more economical.

Lastly, conducting a life cycle assessment (LCA) on cyanide recovery using membrane contactors would provide a more comprehensive evaluation of their environmental sustainability. Cyanide is produced through the Andrussow process using a chemical reaction of methane, ammonia, and oxygen over a platinum catalyst. Given that methane is derived from natural gas, the Andrussow process carries an associated and significant environmental footprint (Dzombak et al., 2006). Reports have estimated that the production of hydrogen cyanide has a $CO_2$ equivalent emission factor of 7.06 per unit of cyanide (City of Winnipeg). Analysis of data from Chapter 3 suggests that the greenhouse gas emissions associated with cyanide usage in the gold cyanidation process ranges from 800 to 1800 tonnes of $CO_2e$ per tonne of gold produced, depending on gold yield and NaCN consumption. Recycled cyanide from membrane contactors could prove a more sustainable alternative to commonly used cyanide production methods and could be an additional incentive for sustainability focused facilities to reduce their carbon footprint.

### 5.2.2 Evaluation of Membrane Materials

PTFE membranes were considered in early cyanide recovery studies using membrane contactors and are currently used in cyanide detection and monitoring devices (Han et al., 2005; Marion et al., 1990; Rosentreter et al., 2015). Despite potential advantages of PTFE membranes, their application in cyanide recovery has been less explored compared to PP membranes. PTFE membranes generally offer higher gas permeability due to higher porosity and pore size and can be densely packed in spiral wound membranes, resulting in similar footprints compared to hollow fiber PP membranes. Furthermore, PTFE membranes offer high mechanical strength, making them less susceptible to damage and ensuring longer lifetime. Studies applying PTFE membranes to CO2 absorption also suggest that PTFE membranes can maintain their initial performance better than PP membranes (Demontigny et al., 2006; Khaisri et al., 2009). Polyvinylidene fluoride (PVDF) represent another potential membrane material for cyanide recovery with promising flux for CO2 absorption (Khaisri et al., 2009). However, the application of this membrane materials for cyanide recovery might require more frequent cleaning as it does not maintain absorption performance (Khaisri et al., 2009). Given the promising performances of different membrane materials, further investigation into their suitability for membrane contactors is warranted.

### 5.2.3 Recovery of Metal Precipitants

Zinc, iron, and copper are commonly found in the ores of the Arequipa region of Peru and readily bind with cyanide to form complexes (De Haller and Fontbote, 2009). The presence of unbound metals in the recirculated decant water could increase cyanide consumption as the cyanide binds with these metals instead of gold. Extraction of metals combined with the recovery of cyanide could alternative treatment method to remove elements competing with the complexation of gold while also reducing cyanide costs (Alonso-González et al., 2009; Dai et al., 2012). Recovery of metals would also be an incentive to processing plant operators to treat barren solutions and further improve the environmental risk assessment of their TSFs through the removal of metals. The development of a combined cyanide and metal precipitant recovery system could improve the economic viability of cyanide recovery from gold processing effluents with high precipitation potential.

The findings of Chapter 2 highlight the potential of TSFs to retain both cyanide and metals. Cyanide recovery and metal precipitation could be pursued as post-closure opportunities for resource recovery and tailings processing. Extraction of cyanide and metals from the TSFs would be environmentally beneficial by addressing the issue of cyanide contamination outlined in Chapter 2. Although this approach could contribute to a more sustainable and environmentally responsible management of gold mining waste, significant research into its feasibility would be necessary.

### 5.2.4 Barriers to Full-Scale Implementation

The adoption of novel technologies into well-established industries presents a complex challenge. While membrane contactors offer promising advancements to cyanide management, their full-scale implantation necessitates extensive research and the cooperation of gold processing facilities. While large facilities possess the resources to test and implement novel technologies, small- and medium-scale facilities often face budget constraints and may lack the infrastructure to adopt such innovations. Additionally, successful adoption may be hindered by resistance to change, as existing operational practices and management habits would need to undergo substantial changes for the adoption of membrane contactors. The successful implementation of novel technologies often requires additional knowledge and skills. Hiring and training new or existing personnel can be costly and time-consuming, posing additional barriers to adoption. Lastly, facilities currently using cyanide treatment are likely to already have substantial investments in existing treatment methods and infrastructure. Switching to the adoption of membrane contactors could render these investments obsolete, and introduce additional, unforeseen costs, making the transition less attractive.

Solutions to these challenges lie in further research and development of membrane contactors for cyanide recovery. More detailed economic analysis, including factors such as workforce expenses and

infrastructure changes, could reduce the risks of unforeseen costs though the adoption of membrane contactors. Pilot-scale demonstrations can introduce operators to the concept of membrane contactors, highlighting the system's performance and viability. Finally, government policies, such as tax incentives, subsidies, and supportive regulations, can incentivize the adoption of innovative technologies like membrane contactors.

### 5.3 References


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APPENDIX A APPENDIX CHAPTER 2

## A.1 Water Samples and Tailings

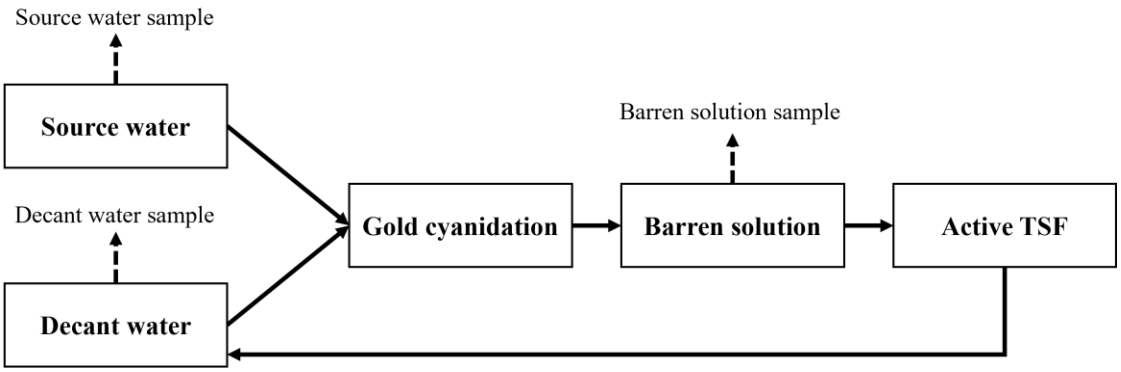


Figure A.1 Simplified water flow diagram with sampling locations

Table A.1 Samples taken

| Site # | Barren water | Decant water | Source water | TSF surface (0-1 cm) | TSF subsurface (15-20 cm) |
|---|---|---|---|---|---|
| 1 | ✓ | ✓ | × | ✓ | ✓ |
| 2 | ✓ | ✓ | × | ✓ | × |
| 3 | ✓ | ✓ | ✓ | ✓ | ✓ |
| 4 | ✓ | ✓ | × | ✓ | ✓ |
| 5 | ✓ | ✓ | ✓ | × | × |
| 6 | ✓ | ✓ | ✓ | ✓ | ✓ |

## A.2 Summary of the Gold Cyanidation Process in the Arequipa Region

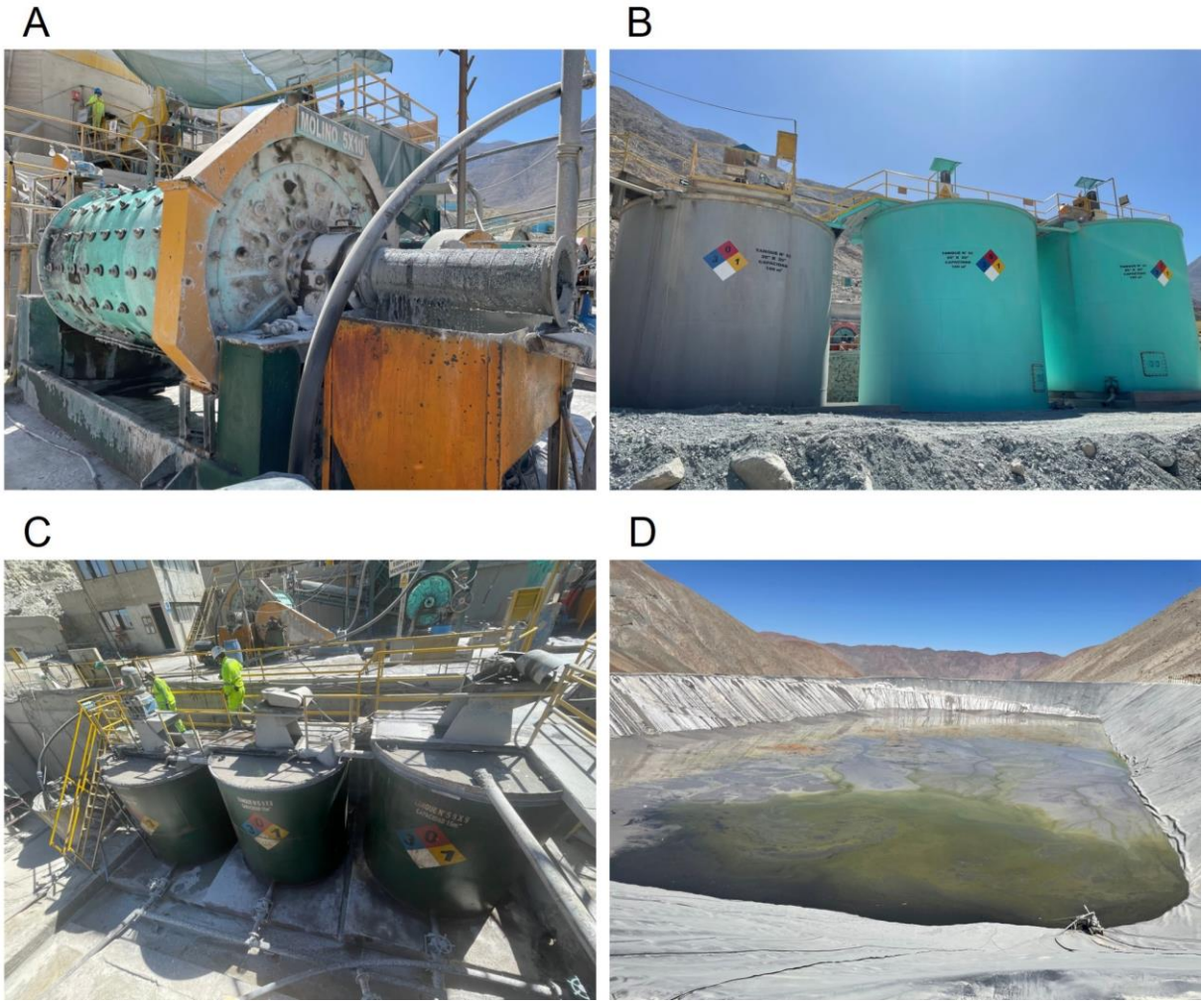


Figure A.2 A – Ball mill for ore crushing; B – Lixiviation tanks; C – Adsorption tanks; D – Tailings storage facility.

## A.3 Barren and Decant Water Characterization

Table A.2 pH values of barren water and decant water

| Site # | Barren water pH | Decant water pH |
|---|---|---|
| 1 | 10.84 | 10.03 |
| 2 | 10.89 | 10.15 |
| 3 | 10.1 | 10.39 |
| 4 | 10.1 | 9.5 |
| 5 | 9.97 | 9.78 |
| 6 | 9.72 | 9.29 |

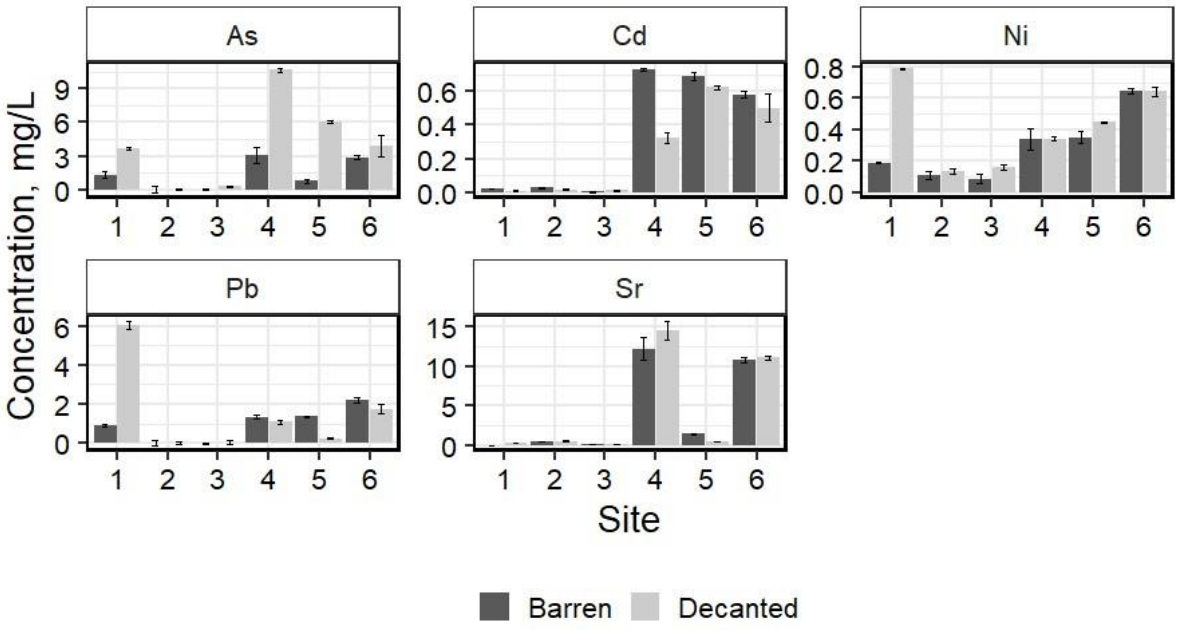


Figure A.3 Concentrations of arsenic, cadmium, nickel, lead, and strontium in the barren and decant waters of the visited sites.

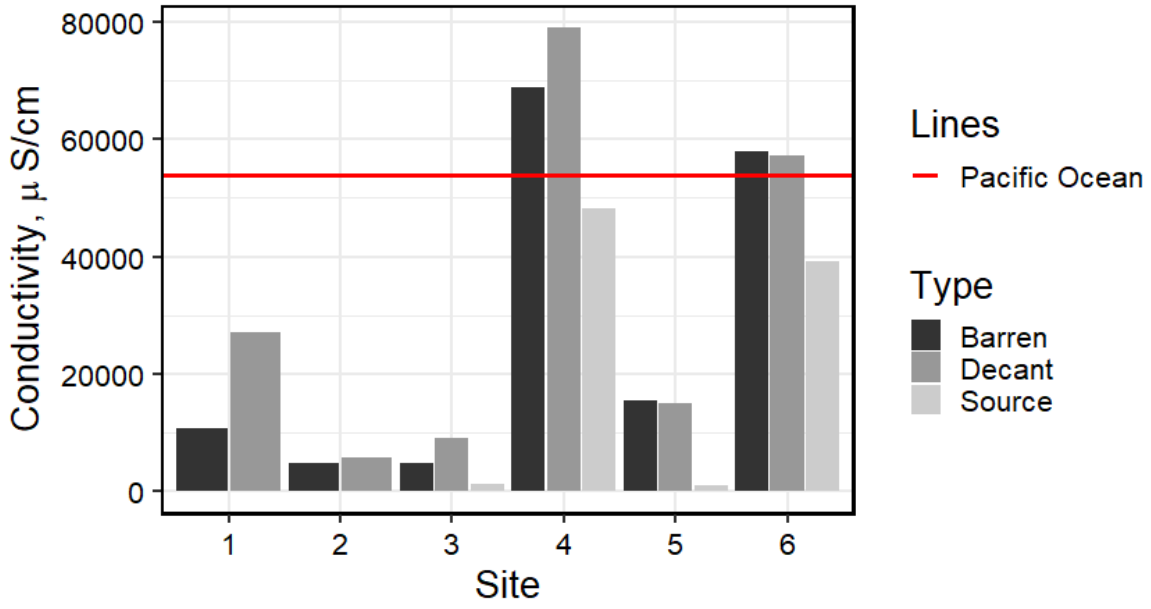


Figure A.4 Conductivity of barren, decent, and source water compared to the conductivity of the Pacific Ocean.

## A.4 Tailings Solids Characterization

Figure A.5 Surface crust of the inactive TSFs at site 3 (left) and site 4 (right)

Table A.3 Gravimetric water content, and cyanide concentrations of analyzed tailings including standard errors. Site 1 contained only one sample

| | 1S | 1U | 2S | 3S | 3U | 4S | 4U | 6S | 6U |
|---|---|---|---|---|---|---|---|---|---|
| Gravimetric water content (%) | 19% | 35% | 29%±2% | 12%±3% | 35%±16% | 9%±0.4% | 20%±1% | 24%±2% | 24%±4 |
| $CN^-$ (mg/kg – tailings) | 19.6 | 0.5 | 0 | 38,589±6,559 | 1,130±625 | 0 | 0 | 731±244 | 349±298 |
| WAD – $CN^-$ (mg/kg – tailings) | 357 | 17.5 | 1.9±0.2 | 78,614±17,062 | 4,234±2,238 | 0.28±0.28 | 2.9±2.9 | 1,483±496 | 852±515 |
| SAD – $CN^-$ (mg/kg – tailings) | 6,807 | 910 | 89.3±3 | 14,552±1,685 | 2,485±1,375 | 96.3±20.3 | 283±198 | 637±214 | 383±264 |

Table A.4. Concentration of metals in tailings including standard errors. Site 1 contained only one sample.

| Metal, mg/kg | 1S | 1U | 2S | 3S | 3U | 4S | 4U | 6S | 6U |
|---|---|---|---|---|---|---|---|---|---|
| Al | 3,647 | 2,771 | 22,389±2,056 | 5,464±1,064 | 15,981±7,356 | 5,152±409.9 | 7,718±1,224 | 5,007±522.0 | 6,452±894.0 |
| As | 239.1 | 155.6 | 109.5±14.5 | 240.1±49.0 | 131.1±12.9 | 4,611±1,179 | 3,506±1,439 | 6,653±1,792 | 5,547±1,047 |
| Cd | 22.3 | 5.2 | 4.2±0.4 | 19.1±0.3 | 45.2±1.1 | 346.0±9.2 | 708.6±12.7 | 558.5±13.7 | 930.0±12.5 |
| Cu | 3,272 | 7,054 | 139.0±9.2 | 107,243±21,328 | 3,469±467.8 | 3,169±1,109 | 1,987±2.5 | 4,205±625.8 | 3,861±1,430 |
| Fe | 210,058 | 14,078 | 49,136±192.0 | 19,808±5,324 | 30,476±4,174 | 75,798±24,050 | 69,704±15,836 | 147,015±23,568 | 122,698±20,283 |
| Ni | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Pb | 1,403 | 294.2 | 68.3±12.0 | 441.8±84.3 | 51.1±10.0 | 3,777±911.5 | 3,129±1,507 | 11,250±3,655 | 8,424±1,562 |
| Zn | 568.1 | 313.0 | 41.2±1.4 | 156.7±26.5 | 34.8±10.3 | 3,966±1,458 | 4,347±2,219 | 6,739±998.4 | 6,904±1,442 |
| Co | 53.7 | 14.0 | 29.9±1.3 | 84.5±34.0 | 25.2±4.2 | 62.9±14.2 | 58.4±9.9 | 63.5±12.1 | 49.8±10.2 |

APPENDIX B APPENDIX CHAPTER 3

## B.1 Economic Analysis, Materials and Methods

The overall mass transfer coefficient K as a function of cyanide concentration were determined through a linear extrapolation between the two measured values at 0.1 g/L and 1 g/L. The equation for PTFE and PP membranes are given in equations B.1 and B.2:

$$Kc_{PTFE} = -0.0758*[CN_{tot}]+0.1356 \quad \text{(B.1)}$$

$$Kc_{PP} = -0.0338 * [CN_{tot}] + 0.0511 \quad \text{(B.2)}$$

With $Kc_{PTFE}$ and $Kc_{PP}$ being the overall mass transfer coefficient at a specific cyanide concentration for PTFE and PP membranes respectively in m/h and $[CN_{tot}]$ being the total cyanide concentration in the feed prior to treatment in g/L.

Overall mass transfer coefficients for specific feed pH values were determined using Kc values as described in equations B.1 and B.2 for the assumed process water cyanide concentrations and by linear extrapolation of known K values at feed pH values of 10.5 and 11.5. Equation B.3 and B.4 show this linear extrapolation for case 1 using both PTFE and PP membranes:

$$Kf1_{PTFE} = 0.0237 * D1_{b,PTFE} - 0.0609 \quad \text{(B.3)}$$

$$Kf1_{PP} = 0.0079 * D1_{b,PP} - 0.0134 \quad \text{(B.4)}$$

Where $Kf1_{PTFE}$ and $Kf1_{PP}$ are the pH specific overall mass transfer coefficients for case 1 in m/h and $D1_{b,PTFE}$ and $D1_{b,PP}$ respectively are the NaOH dosing for case 1 in ml/L as described in equation B.18 and B.19.

The linear extrapolations for pH specific overall mass transfer coefficients of case 2 are provided in equation B.5 and B.6.

$$Kf2_{PTFE} = 0.0056 * D2_{b,PTFE} - 0.03746 \quad \text{(B.5)}$$

$$Kf2_{PP} = 0.0016 * D2_{b,PP} = 0.0071 \quad \text{(B.6)}$$

Where $Kf2_{PTFE}$ and $Kf2_{PP}$ are the pH specific overall mass transfer coefficients for case 2 using PTFE membranes in m/h and PP membranes and $D2_{b,PTFE}$ and $D2_{b,PP}$ are the dosing volumes for case 2 in ml/L as described in equations B.20 and B.21.

To account for flux decline over the treatment time, the average was taken of the flux at the starting concentration and end concentration of the process water. The average flux is calculated as:

$$J_{aCN^-} = K((\frac{[HCN]_0 - [HCN]_{end}}{2} - [HCN]_{dist}) \tag{B.7}$$

Where $J_{aCN-}$ is the average cyanide flux in $g/m^2h$, K is the overall mass transfer coefficient in m/h, $[HCN]_0$ is the process water hydrogen cyanide concentration prior to treatment in g/L, $[HCN]_{end}$ is the process water hydrogen cyanide concentration at the end of treatment in g/L, and $[HCN]_{dist}$ is the hydrogen cyanide concentration in the distillate.

The size of the membrane required for a model treatment plant was calculated based off cyanide flux values measured in experiments. The required membrane size was used to estimate the cost of the membrane system. The equation used to calculate the membrane area $A_{mem}$ in $m^2$ is:

$$A_{mem} = \frac{[CN_{tot}]_p * Q_{mod} * PC}{J_{aCN^-}} \tag{B.8}$$

Where $[CN_{tot}]_p$ is the cyanide concentration of the process water prior to treatment in $kg/m^3$, $Q_{mod}$ is the flow of the effluent (process water) in $m^3/h$, PC is the plant capacity factor, and $J_{aCN-}$ is the average cyanide flux in $g/m^2h$. The cost of the membrane was estimated to be 50% of the membrane system for large-scale systems and 25% for small scale systems as system costs are expected to be higher for small scale applications (Woods, 2007). Membrane replacements were estimated to occur after 5 years of usage and were thus set at 20% per year.

Costs of membranes were derived from an exponential trendline using known prices obtained by quotes from the manufacturer for typical membrane modules. The same equation was used for both membranes since costs for both PTFE and PP membranes are nearly identical. Figure B.1 shows the known membrane costs and exponential trendline used. The specific membrane costs $C_{mem}$ in $\$/m^2$ is given in equation B.9:

$$C_{mem} = 889.64 * A_{mem}{}^{-0.445} \tag{B.9}$$

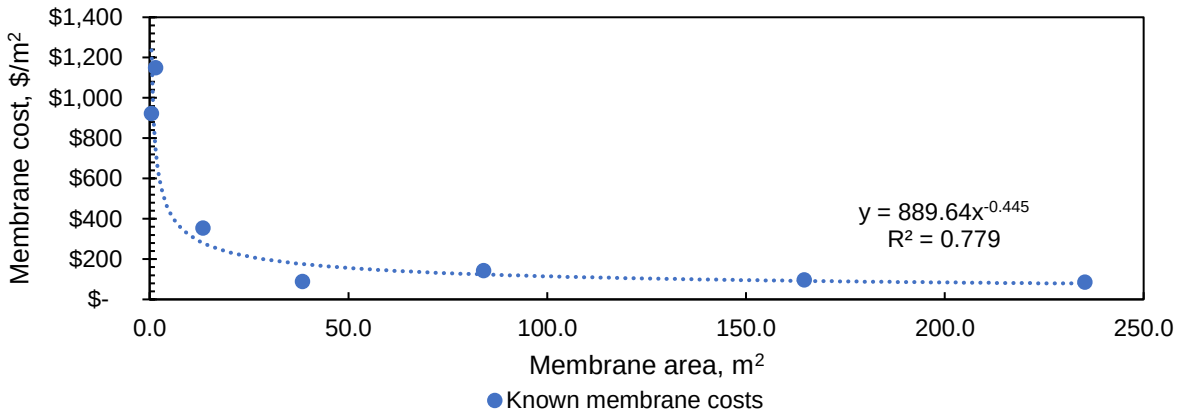


Figure B.1 Estimation of specific membrane prices using an exponential trendline.

The treatment costs of traditional cyanide treatment using $SO_2$ + air was determined by linear extrapolation of data given by industry collaborators. The equation to calculate specific traditional treatment costs $C_{tt}$ is given in equation B.10:

$$C_{tt} = 3.9221 * [CN_{tot}] + 0.0289 \quad \text{(B.10)}$$

Where $C_{tt}$ is the cost of $SO_2$ + air treatment in \$/m$^3$ and $[CN_{tot}]$ is the total cyanide concentration in the process water.

The pumping energy required was calculated for both the determination of OPEX energy costs, as well as the CAPEX costs of the pumps themselves. The pumping energy is calculated using equation B.11

$$E_{pump} = Q_{eq} * \frac{\Delta P_{flow}}{\eta_{pump}} \quad \text{(B.11)}$$

where $E_{pump}$ is the pumping energy in kW, $Q_{eq}$ is the equivalent flow rate of the system in m$^3$/h, $\Delta P_{flow}$ is the pressure drop of the membrane at the crossflow rate of the experiment in kPa, and η is the efficiency of the pump. $\Delta P_{flow}$ was estimated to be 39 kPa for PTFE membranes and 33 kPa for PP membranes and was assumed to remain constant as membrane modules can be put in parallel to accommodate higher flow rates. The cost for the pumps was calculated through a standard centrifugal pump price, pumping energy, and a variety of factors using Equation B.12 (Woods, 2007):

$$C_{liquid\ pump} = N \left( \frac{E_{pump} * X_{size}}{E_{referene}} \right)^{X_{scale}} * X_{L+M^*} * X_{corr} * X_{304} * X_{CEPCI} \quad \text{(B.12)}$$

Where $C_{liquid\ pump}$ is the total cost of the liquid pumps in $, N is the number of pumps required, $E_{pump}$ is the pumping power in kW, $E_{reference}$ is the reference centrifugal pump power, $X_{size}$ is the oversizing factor, $X_{scale}$ is the motor scale factor, $X_{L+M*}$ is labor and material costs factor, $X_{corr}$ is the labor and material costs corrected for stainless steel, $X_{304}$ is the alloy: SS 304 factor, and $X_{CEPCI}$ is the CEPCI ratio (Scott, 2020). The specific values for these parameters are given in Table B.1.:

Table B.1 Factor values (Woods, 2007)

| Parameter | Value | |
|---|---|---|
| $E_{reference}$, Reference centrifugal pump power | 23 | kW |
| $X_{size}$, Oversizing factor | 2.00 | |
| $X_{scale}$, Motor scale factor | 0.79 | |
| $X_{L+M*}$, Labor and material costs factor | 1.47 | |
| $X_{corr}$, Labor and material costs corrected for stainless steel | 0.6 | |
| $X_{304}$, Alloy: SS 304 factor | 1.9 | |
| $X_{CEPCI}$, CEPCI ratio | 0.61 | |

The amount of acid and base dosing required during the treatment process was calculated from required dosing determined during experiments. The calculation of both acid and base amounts needed are shown in equation B.13:

$$Acid, base\ consumption\ = \frac{D_{a,b}}{1000} * [acid, base]_{dose} * Q \tag{B.13}$$

where acid, base consumption is described in kg/day, $D_{a,b}$ is the dosing of acid/base during the experiment in ml/L, $[acid, base]_{dose}$ is the concentration of the acid/base used in the experiment, and Q is the flow of process water in $m^3$/day. Experiments and the model used sulfuric acid for pH control. However, the model also considers the use of bases other than sodium hydroxide. The amount of other bases needed is calculated stoichiometrically based on the experimental dosing of sodium hydroxide.

The amount of acid or base needed for specific parameters was linearly extrapolated from dosing volumes during experiments. The amount of acid (0.2 M sulfuric acid and 2 M sodium hydroxide) and base dosed using PTFE and PP membranes for specific cyanide concentrations is given in equations B.14, B.15, B.16, and B.17 respectively:

$$Dc_{a,PTFE} = \frac{7.778 * [CN_{tot}] + 1.222}{V_{feed}} \tag{B.14}$$

$$Dc_{b,PTFE} = \frac{88.978 * [CN_{tot}] + 10.702}{V_{feed}} \tag{B.15}$$

$$Dc_{a,PP} = \frac{6.09 * [CN_{tot}] + 0.7211}{V_{feed}} \quad \text{(B.16)}$$

$$Dc_{b,PP} = \frac{83.111 * [CN_{tot}] + 10.389}{V_{feed}} \quad \text{(B.17)}$$

Where $Dc_{a,PTFE}$ is the concentration specific dosing of acid using a PTFE membrane in ml/L, $Dc_{b,PTFE}$ is the concentration specific dosing of base using a PTFE membrane in ml/L, $Dc_{a,PP}$ is the concentration specific dosing of acid using a PP membrane in ml/L, $Dc_{b,PP}$ is the concentration specific dosing of base using a PP membrane in ml/L, $[CN_{tot}]$ is the total concentration of cyanide the process water in g/L, and $V_{feed}$ is the volume of the feed tank.

The Equations for the extrapolation of pH specific base dosing are:

$$D1_{b,PTFE} = 2.9807 * pH - 26.788 \quad \text{(B.18)}$$

$$D1_{b,PP} = 1.628 * pH - 11.642 \quad \text{(B.19)}$$

$$D2_{b,PTFE} = 7.8 * pH - 70.1 \quad \text{(B.20)}$$

$$D2_{b,PP} = 4.3 * pH - 30.75 \quad \text{(B.21)}$$

Where $D1_{b,PTFE}$ and $D1_{b,PP}$ are the base dosing for case 1 in m/h using PTFE and PP membranes respectively, $D2_{b,PTFE}$ and $D2_{b,pp}$ are the base dosing for case 2 in m/h for PTFE and PP membranes respectively, and pH is the specific pH.

The net present value (NPV) of the modelled system is calculated as detailed in equation B.22:

$$NPV = -C_{system} - CF(C_{mem,r} + C_{E,pump} + C_{Base} + C_{Acid} - C_{NaCN}) \quad \text{(B.22)}$$

where $C_{system}$ is the total cost of the system in $, CF is the constant cash flow NPV factor, $C_{mem,r}$ is the cost of membrane replacements in $/year, $C_{E,pump}$ is the pumping energy cost in $/year, $C_{base}$ and $C_{acid}$ are the cost of base and acid dosing in $/year respectively, and $C_{NaCN}$ is the cost of cyanide that is recovered during treatment in $/year. $C_{system}$ consists of the CAPEX membrane costs and cost of liquid pumps for the circulation of process water and distillate solution. The constant cash flow NPV factor is determined by equation B.23:

$$CF = \frac{1}{I} * \left(1 - \frac{1}{(1+I)^{t_{system}}}\right) \quad \text{(B.23)}$$

where I is the interest rate and $t_{system}$ is the expected lifespan of the system.

Table B.2 Economic analysis assumptions

| | **Case 1 (large scale)** | **Case 2 (small scale)** |
|---|---|---|
| Processed ore ($m^3$/day) | 90,000 | 10 |
| Flow rate of process water ($m^3$/h) | 200 | 0.139 |
| Effluent $CN^-$ concentration (g/L) | 0.25 | 0.843 |
| **System Costs** | | |
| Membrane replacement (%/year)[1] | 20 | 20 |
| Membrane cost to total system (%) | 50 | 25 |
| Plant lifetime (years) | 20 | 20 |
| Plant capacity factor (%) | 90 | 90 |
| Pump efficiency (%) | 70 | 70 |
| Contingency (%) | 30 | 30 |
| Interest rate (%) | 7 | 7 |
| **Chemical and electricity costs** | | |
| Sodium cyanide ($/kg) | 2.66 | 3.9 |
| Free cyanide, $CN^-$ ($/kg) | 5.01 | 7.34 |
| Calcium oxide ($/kg) | 0.11 | 0.3 |
| Sulfuric acid ($/kg) | 0.72 | 0.59 |
| Electricity ($/kWh) | 0.058 | 0.065 |

[1] No decrease in membrane performance, fouling, or damage to the membrane was observed over the experimental period. As such, normal membrane life was expected.

Table B.3 Calculated values for economic model

| Parameter | Case 1 | Case 2 |
|---|---|---|
| Recovered free cyanide (kg/year) | 394,200 | 923 |
| Overall mass transfer coefficient PTFE | 0.1167 | 0.717 |
| Overall mass transfer coefficient PP | 0.0427 | 0.0226 |
| Avoidable sodium cyanide consumption (kg/year) | 742,344 | 1,738 |
| PTFE membrane area ($m^2$) | 3,086 | 3.5 |
| PTFE module cost ($/$m^2$) | 25 | 511 |
| PTFE cyanide flux (g/$m^2$h) | 14.6 | 30.2 |
| PTFE base dosing amount (kg/year) | 1,113,050 | 5,232 |
| PTFE acid dosing amount (kg/year) | 274,125 | 467 |
| PP membrane area ($m^2$) | 8,440 | 11.1 |
| PP module cost ($/$m^2$) | 16 | 305 |
| PP cyanide flux (g/$m^2$h) | 5.3 | 9.5 |
| PP base dosing amount (kg/year) | 1,052,924 | 4,911 |
| PP acid dosing amount (kg/year) | 194,220 | 352 |
| Avoided traditional treatment costs ($/year) | 737,785 | 4,058 |

## B.2 Results and Discussion

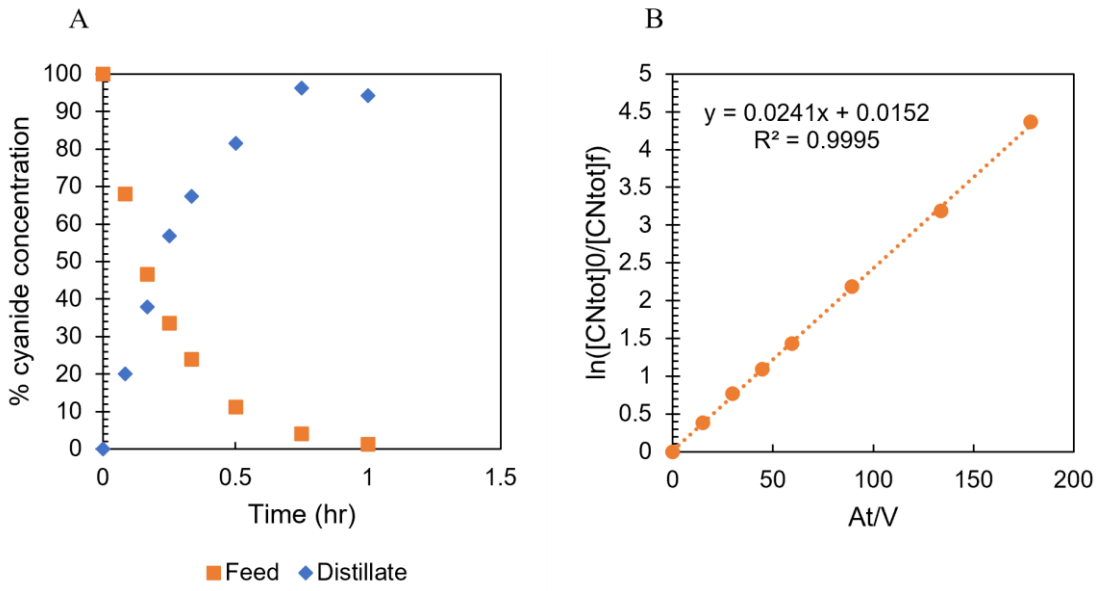


Figure B.2 Recovery of cyanide using the same membrane and parameters as described by Estay et al. (2013) (A). Successful recovery was achieved after a 1-hour runtime with 96% of cyanide recovered. The K is here depicted as the gradient $At/V$ and ln ($\frac{[CN_{tot}]_0}{[CN_{tot}]_f}$) as described by equation (3.1).

## B.3 Controlling Parameter Evaluation

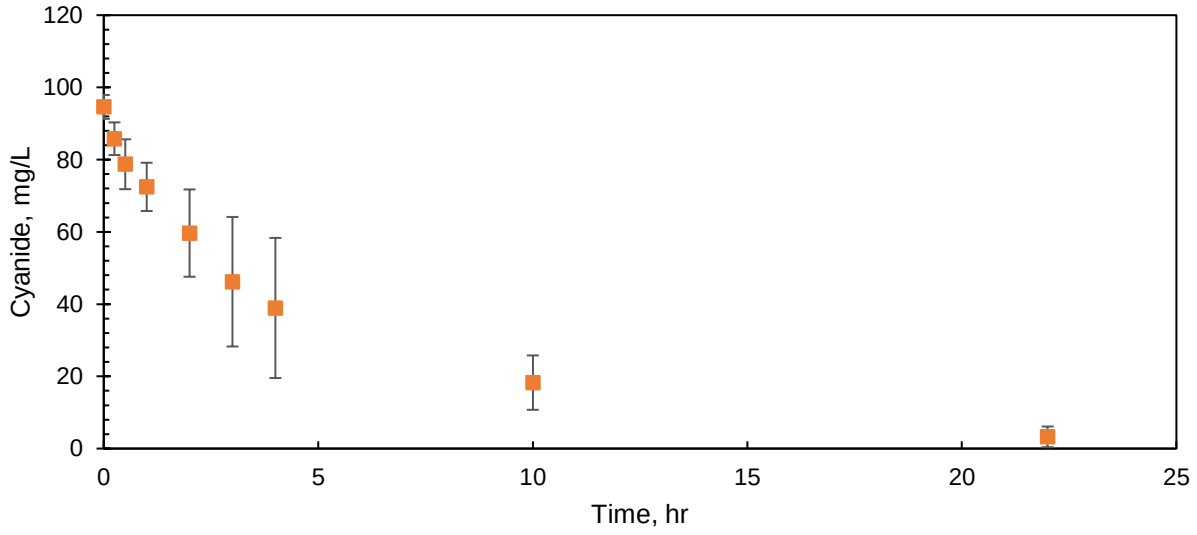


Figure B.3 Initial cyanide recovery tests done with PTFE membranes using process water spiked with 100 mg/L of free cyanide at 1 L/min flow, feed pH of 6, distillate pH of 11.5, and temperature of 20 °C.

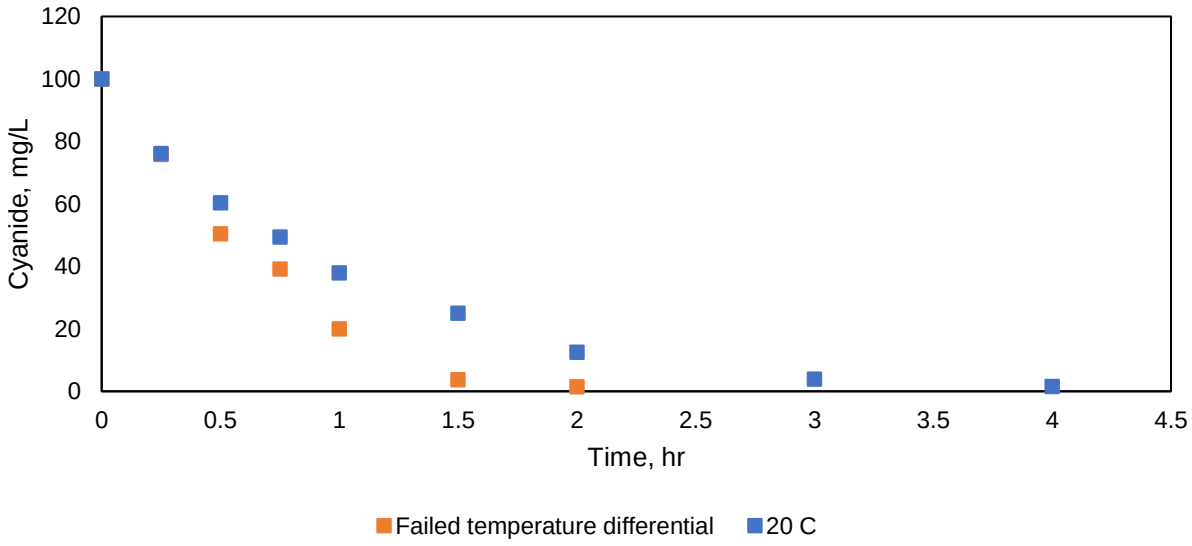


Figure B.4 Increase in K and decrease in runtime observed after a temperature differential could not be maintained. K values increased by 47% and the runtime was reduced from 4 hours to 2 hours.

## B.4 Economic Analysis

Case1:

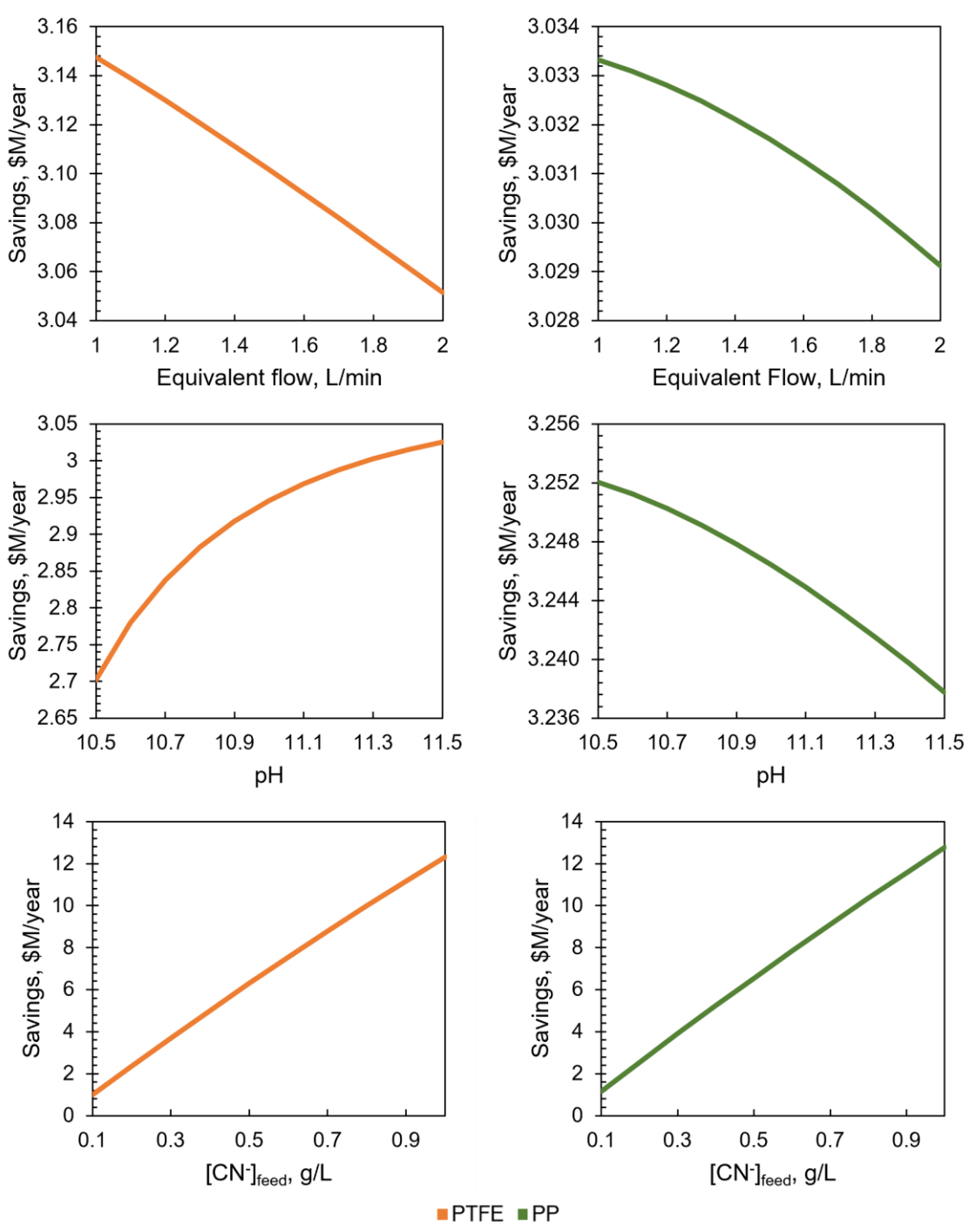


Figure B.5 Sensitivity analysis for both PTFE and PP membranes at a large-scale operation.

Case2

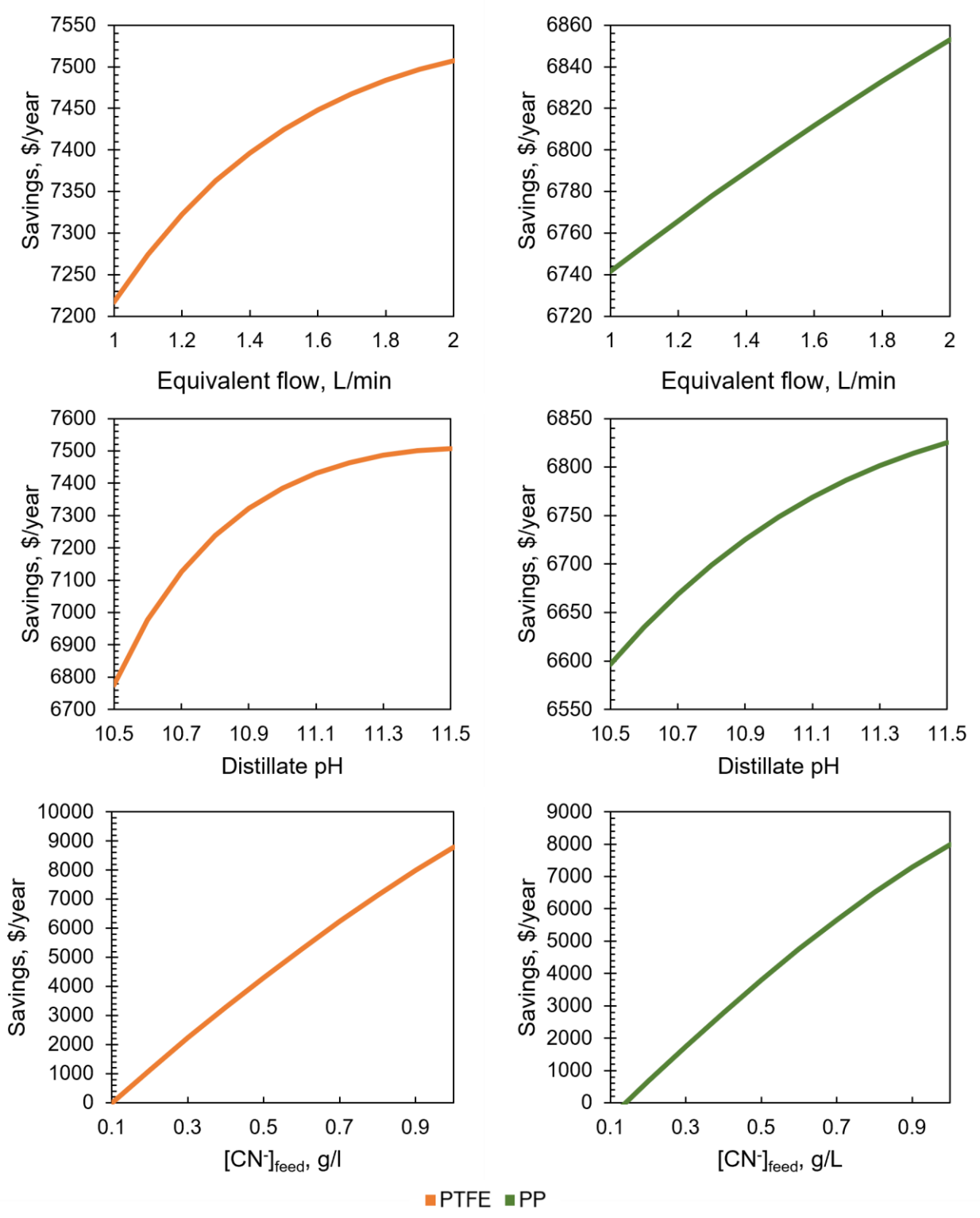


Figure B.6 Sensitivity analysis for both PTFE and PP membranes at a small-scale operation.

## B.5 References

Estay, H., Ortiz, M., Romero, J., 2013. A novel process based on gas filled membrane absorption to recover cyanide in gold mining. Hydrometallurgy 134–135, 166–176. https://doi.org/10.1016/j.hydromet.2013.02.012

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Woods, D.R., 2007. Rules of thumb in engineering practice. Wiley-VCH, Weinheim

APPENDIX C APPENDIX CHAPTER 4

## C.1 Economic Analysis, Materials and Methods

The overall mass transfer coefficient K as a function of cyanide concentration in the case of US effluents were determined through a linear extrapolation between the two measured values at 0.1 g/L and 1 g/L:

$$Kc = -0.00067*[CN_{tot}]+0.008 \quad (C.2)$$

With Kc being the overall mass transfer coefficient at a specific cyanide concentration in m/h and $[CN_{tot}]$ being the total cyanide concentration in the feed prior to treatment in g/L.

To account for flux decline over the treatment time, the average was taken of the flux at the starting concentration and end concentration of the process water. The average flux is calculated as:

$$J_{aCN^-} = K((\frac{[HCN]_0 - [HCN]_{end}}{2} - [HCN]_{dist}) \quad (C.2)$$

Where $J_{aCN^-}$ is the average cyanide flux in $g/m^2h$, K is the overall mass transfer coefficient in m/h, $[HCN]_0$ is the process water hydrogen cyanide concentration prior to treatment in g/L, $[HCN]_{end}$ is the process water hydrogen cyanide concentration at the end of treatment in g/L, and $[HCN]_{dist}$ is the hydrogen cyanide concentration in the distillate.

The size of the membrane required for a model treatment plant was calculated based off cyanide flux values measured in experiments. The required membrane size was used to estimate the cost of the membrane system. The equation used to calculate the membrane area $A_{mem}$ in $m^2$ is:

$$A_{mem} = \frac{[CN_{tot}]_p * Q_{mod} * PC}{J_{aCN^-}} \quad (C.3)$$

Where $[CN_{tot}]_p$ is the cyanide concentration of the process water prior to treatment in $kg/m^3$, $Q_{mod}$ is the flow of the effluent (process water) in $m^3/h$, PC is the plant capacity factor, and $J_{aCN^-}$ is the average cyanide flux in $g/m^2h$. The cost of the membrane was estimated to be 50% of the membrane system for large-scale systems and 25% for small scale systems as system costs are expected to be higher for small scale applications. (Woods, 2007) Membrane replacements were estimated to occur after 5 years of usage and were thus set at 20% per year.

Costs of membranes were derived from an exponential trendline using known prices obtained by quotes from the manufacturer for typical membrane modules. Figure C.1 shows the known membrane costs and exponential trendline used. The specific membrane costs $C_{mem}$ in $\$/m^2$ is given in equation C.4:

$$C_{mem} = 889.64*A_{mem}^{-0.445} \quad (C.4)$$

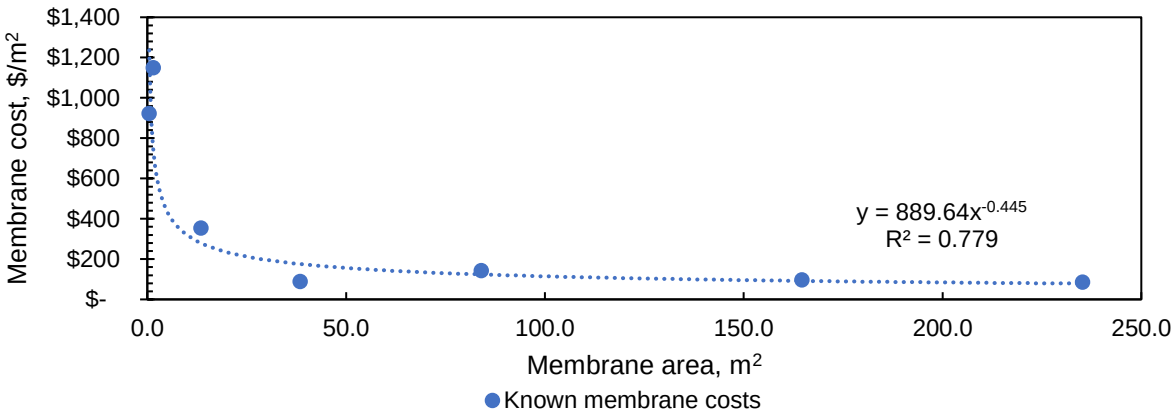



Figure C.1 Estimation of specific membrane prices using an exponential trendline.

The treatment costs of traditional cyanide treatment using $SO_2$ + air was determined by linear extrapolation of data given by industry collaborators. The equation to calculate specific traditional treatment costs $C_{tt}$ is given in equation C.5:

$$C_{tt} = \frac{3.9221 * [CN_{tot}] + 0.0289}{[CN_{end}]} \quad (C.5)$$

Where $C_{tt}$ is the cost of $SO_2$ + air treatment in \$/m$^3$ and $[CN_{tot}]$ is the total cyanide concentration in the process water, and $[CN_{end}]$ is the cyanide concentration in the feed solution at the end of the experiment. Additional traditional treatment costs were only calculated whenever the cyanide concentration of the feed solution remained above 50 mg/L in order to comply with the international cyanide management code (Akcil, 2010).

The pumping energy required was calculated for both the determination of OPEX energy costs, as well as the CAPEX costs of the pumps themselves. The pumping energy is calculated using equation C.6:

$$E_{pump} = Q_{eq} * \frac{\Delta P_{flow}}{\eta_{pump}} \quad (C.6)$$

Where $E_{pump}$ is the pumping energy in kW, $Q_{eq}$ is the equivalent flow rate of the system in m$^3$/h, $\Delta P_{flow}$ is the pressure drop of the membrane at the crossflow rate of the experiment in kPa, and $\eta$ is the efficiency of the pump. $\Delta P_{flow}$ was estimated to be 33 kPa and was assumed to remain constant as membrane modules can be put in parallel to accommodate higher flow rates. The cost for the pumps was calculated through a standard centrifugal pump price, pumping energy, and a variety of factors using Equation C.7 (Woods, 2007):

$$C_{liquid\ pump} = N \left( \frac{E_{pump} * X_{size}}{E_{referene}} \right)^{X_{scale}} * X_{L+M} * X_{corr} * X_{304} * X_{CEPCI} \quad (C.7)$$

Where $C_{liquid\ pump}$ is the total cost of the liquid pumps in $, N is the number of pumps required, $E_{pump}$ is the pumping power in kW, $E_{reference}$ is the reference centrifugal pump power, $X_{size}$ is the oversizing factor, $X_{scale}$ is the motor scale factor, $X_{L+M*}$ is labor and material costs factor, $X_{corr}$ is the labor and material costs corrected for stainless steel, $X_{304}$ is the alloy: SS 304 factor, and $X_{CEPCI}$ is the CEPCI ratio (Scott, 2020). The specific values for these parameters are given in Table C.1:

Table C.1 Factor values (Woods, 2007)

| Parameter | Value | |
|---|---|---|
| $E_{reference}$, Reference centrifugal pump power | 23 | kW |
| $X_{size}$, Oversizing factor | 2.00 | |
| $X_{scale}$, Motor scale factor | 0.79 | |
| $X_{L+M*}$, Labor and material costs factor | 1.47 | |
| $X_{corr}$, Labor and material costs corrected for stainless steel | 0.6 | |
| $X_{304}$, Alloy: SS 304 factor | 1.9 | |
| $X_{CEPCI}$, CEPCI ratio | 0.61 | |

The amount of acid and base dosing required during the treatment process was calculated from required dosing determined during experiments. The calculation of both acid and base amounts needed are shown in equation C.8:

$$\text{Acid, base consumption} = \frac{D_{a,b}}{1000} * [\text{acid,base}]_{dose} * Q \tag{C.8}$$

where acid, base consumption is described in kg/day, $D_{a,b}$ is the dosing of acid/base during the experiment in ml/L, $[\text{acid, base}]_{dose}$ is the concentration of the acid/base used in the experiment, and Q is the flow of process water in $m^3$/day. Experiments and the model used sulfuric acid for pH control. However, the model also considers the use of bases other than sodium hydroxide. The amount of other bases needed is calculated stoichiometrically based on the experimental dosing of sodium hydroxide.

The amount of acid or base needed for specific parameters was linearly extrapolated from dosing volumes during experiments (Hammer et al., 2023). The amount of acid (0.2 M sulfuric acid and 2 M sodium hydroxide) cyanide concentrations is given in equations C.9 and C.10 respectively:

$$Dc_a = \frac{6.09 * [CN_{tot}] + 0.7211}{V_{feed}} \tag{C.9}$$

$$ADc_b = \frac{83.111 * [CN_{tot}] + 10.389}{V_{feed}} \tag{C.10}$$

Where $Dc_a$ is the concentration specific dosing of acid in ml/L, $Dc_b$ is the concentration specific dosing of base in ml/L, $[CN_{tot}]$ is the total concentration of cyanide the process water in g/L, and $V_{feed}$ is the volume of the feed tank.

The net present value (NPV) of the modelled system is calculated as detailed in equation C.11:

$$NPV=-C_{system}-CF(C_{mem,r}+C_{E,pump}+C_{Base}+C_{Acid}-C_{NaCN} \quad (C.11)$$

where $C_{system}$ is the total cost of the system in $, CF is the constant cash flow NPV factor, $C_{mem,r}$ is the cost of membrane replacements in $/year, $C_{E,pump}$ is the pumping energy cost in $/year, $C_{base}$ and $C_{acid}$ are the cost of base and acid dosing in $/year respectively, and $C_{NaCN}$ is the cost of cyanide that is recovered during treatment in $/year. $C_{system}$ consists of the CAPEX membrane costs and cost of liquid pumps for the circulation of process water and distillate solution. The constant cash flow NPV factor is determined by equation C.12:

$$CF=\frac{1}{I}*(1-\frac{1}{(1+I)^{t_{system}}}) \quad (C.12)$$

where I is the interest rate and $t_{system}$ is the expected lifespan of the system.

## C.2 Cyanide Recovery from Arequipa Mining Effluent


Figure C.2 Precipitation of white precipitants at pH 7 with Aq2 effluents and red precipitants at pH 5 with Aq2 effluents.

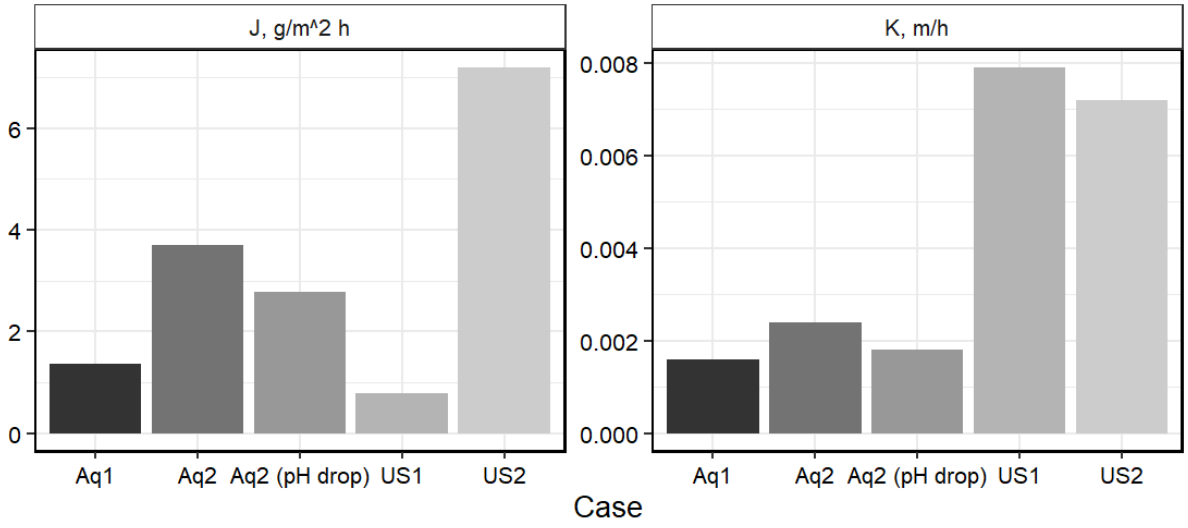



Figure C.3 Flux and overall mass transfer coefficients of real gold processing effluents from Arequipa and the US.

Table C.2 Economic analysis assumptions

| | Aq1 | Aq2 | Aq2 (pH drop) | US1 | US2 |
|---|---|---|---|---|---|
| Processed ore ($m^3$/day) | 350 | 1730 | 1730 | 90,000 | 90,000 |
| Flow rate of process water ($m^3$/h) | 17.5 | 86.5 | 86.5 | 200 | 200 |
| Effluent $CN^-$ concentration (g/L) | 0.86 | 1.53 | 1.53 | 0.1 | 1 |
| Feed pH | 6 | 6 | 7 (5) | 6 | 6 |
| Distillate pH | 11.5 | 11.5 | 11.5 | 11.5 | 11.5 |
| Flow rate (L/min) | 10 | 10 | 10 | 10 | 10 |
| **System Costs** | | | | | |
| Membrane replacement (%/year)[1] | 20 | 20 | 20 | 20 | 20 |
| Membrane cost to total system (%) | 50 | 50 | 50 | 50 | 50 |
| Plant lifetime (years) | 20 | 20 | 20 | 20 | 20 |
| Plant capacity factor (%) | 90 | 90 | 90 | 90 | 90 |
| Pump efficiency (%) | 70 | 70 | 70 | 70 | 70 |
| Contingency (%) | 30 | 30 | 30 | 30 | 30 |
| Interest rate (%) | 7 | 7 | 7 | 7 | 7 |
| **Chemical and electricity costs** | | | | | |
| Sodium cyanide ($/kg) | 2.66 | 2.66 | 2.66 | 2.66 | 2.66 |
| Free cyanide, $CN^-$ ($/kg) | 5.01 | 5.01 | 5.01 | 5.01 | 5.01 |
| Calcium oxide ($/kg) | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 |
| Sulfuric acid ($/kg) | 0.72 | 0.72 | 0.72 | 0.72 | 0.72 |

Table C.2 Continued

| | | | | | |
|---|---|---|---|---|---|
| Electricity ($/kWh) | 0.058 | 0.058 | 0.058 | 0.058 | 0.058 |

[1] No decrease in membrane performance, fouling, or damage to the membrane was observed over the experimental period. As such, normal membrane life was expected.

Table C.3 Calculated values for economic model

| Parameter | Aq1 | Aq2 | Aq2 (pH drop) | US1 | US2 |
|---|---|---|---|---|---|
| Recovered free cyanide (kg/year) | 53,394 | 845,160 | 991,238 | 157,680 | 1,576,800 |
| Overall mass transfer coefficient *K* | 0.0016 | 0.0024 | 0.0018 | 0.0079 | 0.0073 |
| Avoidable sodium cyanide consumption (kg/year) | 100,551 | 1,591,578 | 1,866,666 | 296,938 | 2,969,377 |
| Membrane area ($m^2$) | 5,716 | 4,4159 | 78262 | 45,397 | 49,315 |
| Module cost ($/$m^2$) | 19 | 8 | 6 | 8 | 7 |
| Cyanide flux (g/$m^2$h) | 1.1 | 2.2 | 1.4 | 0.4 | 3.7 |
| Base dosing amount (kg/year) | 352,399 | 8,152,123 | 8,958,377 | 375,792 | 9,557,835 |
| Acid dosing amount (kg/year) | 45,133 | 375,852 | 375,852 | 115,142 | 589,612 |
| Avoided traditional treatment costs ($/year) | 232,687 | 3,683,115 | 4,568,955 | 737,785 | 6,922,152 |

## C.3 Economic Analysis

Sensitivity analysis:

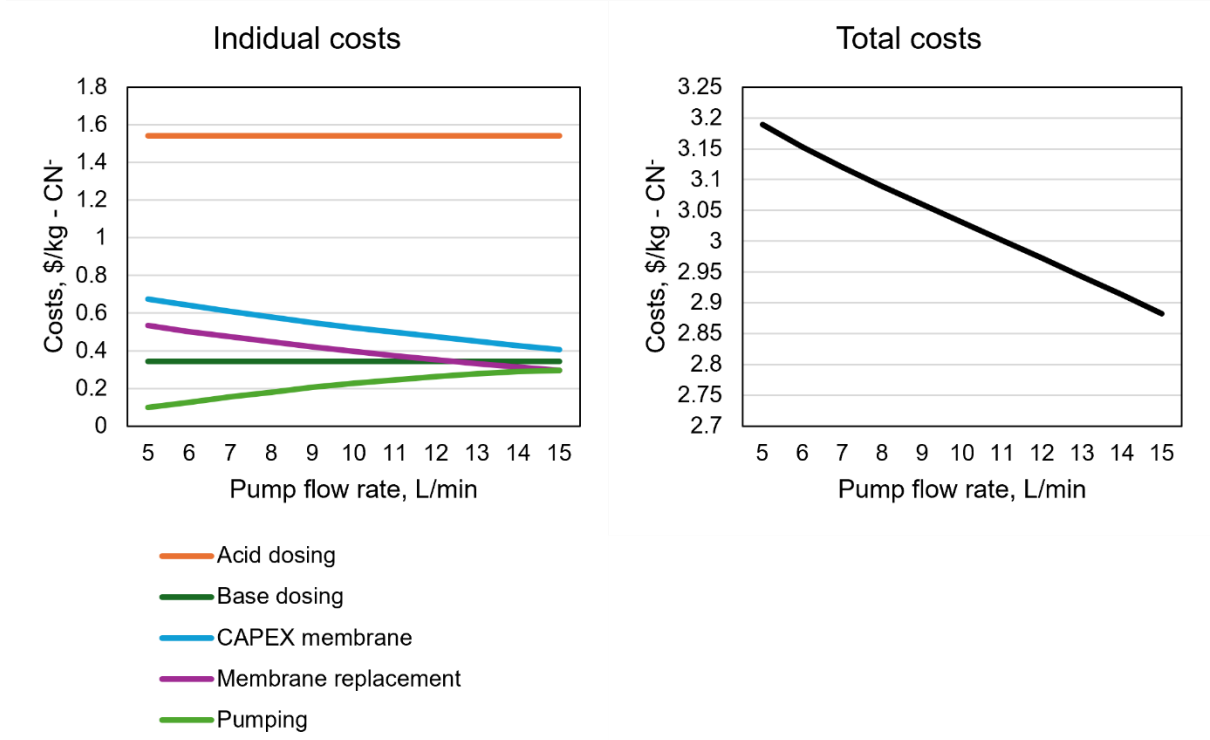



Figure C.4 US1 sensitivity analysis at different pump flow rates.

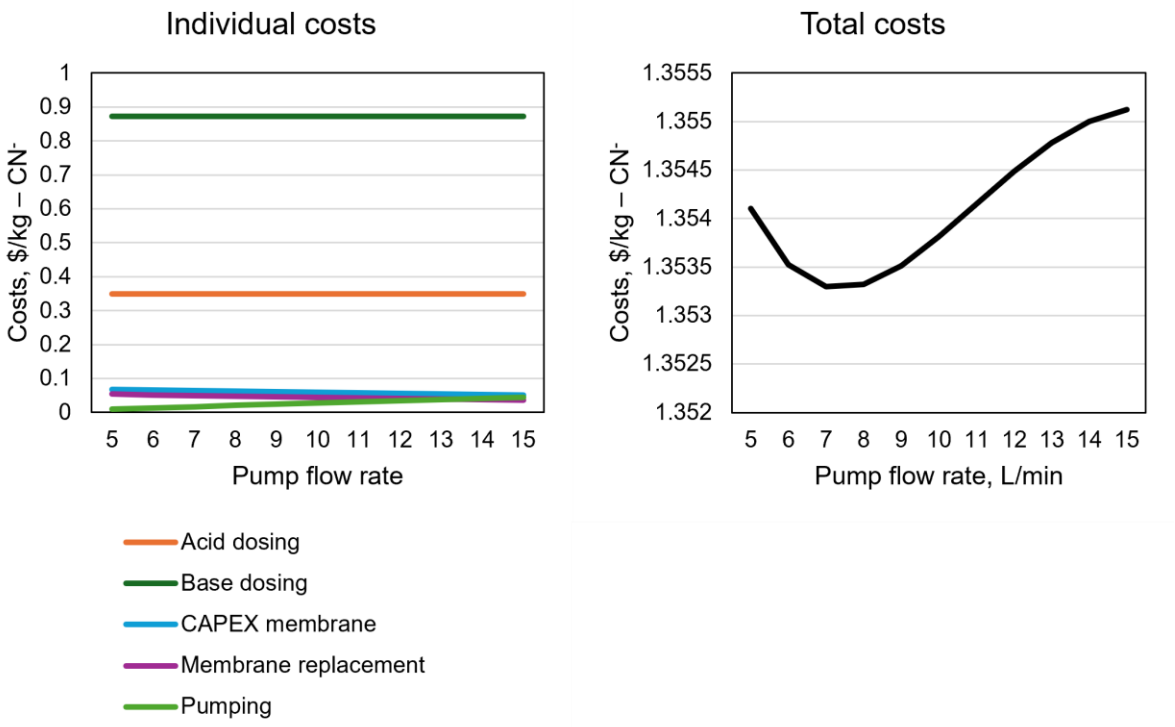



Figure C.5 US2 sensitivity analysis at different pump flow rates.

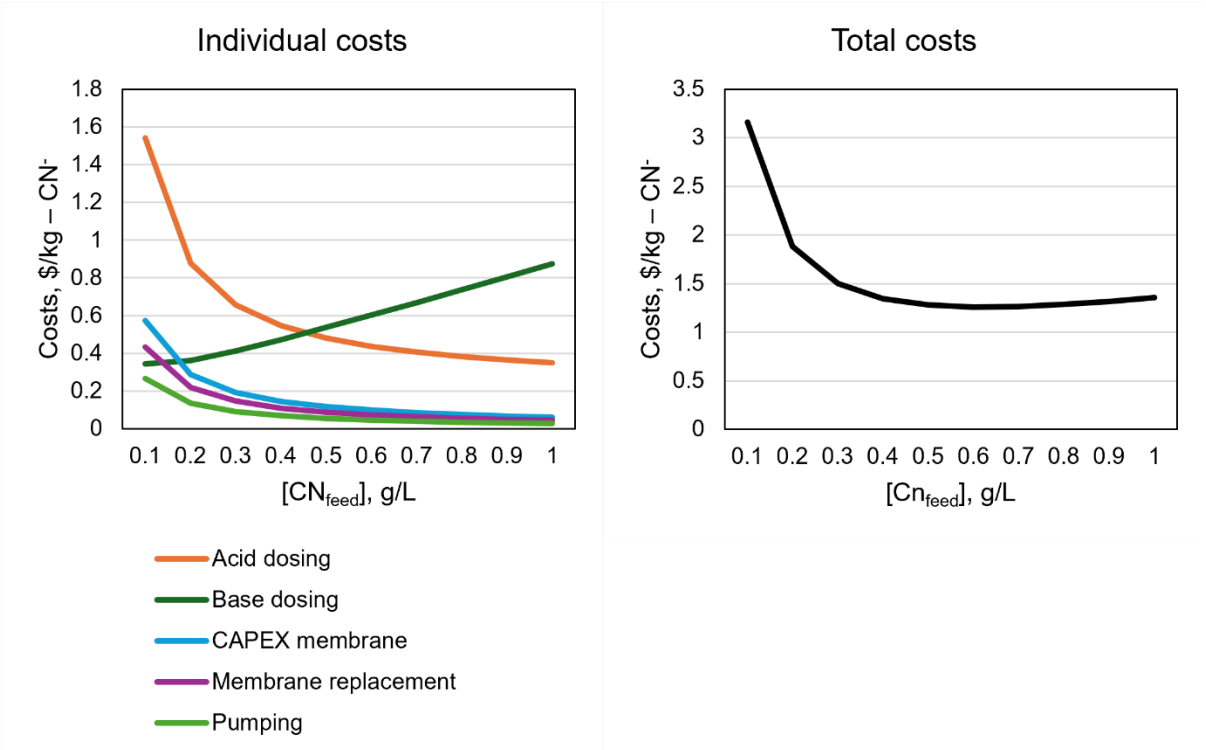



Figure C.6 US effluent sensitivity analysis with different concentrations.

## C.4 References

Akcil, A., 2010. A New Global Approach of Cyanide Management: International Cyanide Management Code for the Manufacture, Transport, and Use of Cyanide in the Production of Gold. Mineral Processing and Extractive Metallurgy Review 31, 135–149. https://doi.org/10.1080/08827501003727022

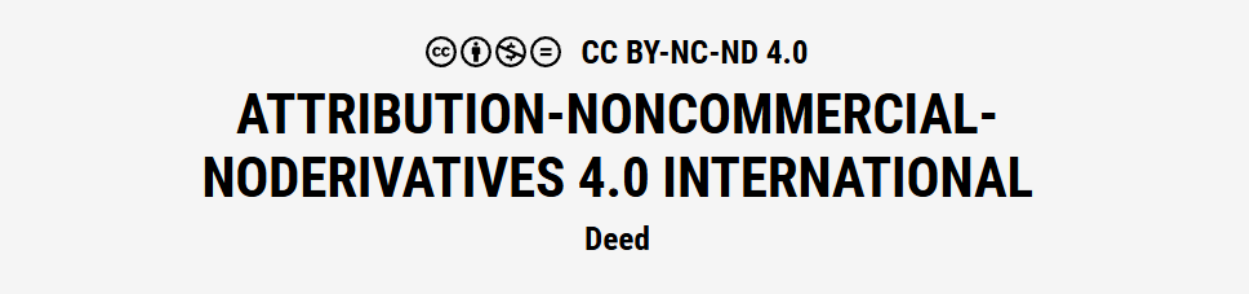
Hammer, V., Vanneste, J., Vuono, D.C., Alejo-Zapata, F.D., Polanco-Cornejo, H.G., Zea, J., Bolaños-Sosa, H.G., Zevallos Rojas, C.A., Figueroa, L.A., Bellona, C., 2023. Membrane Contactors as a Cost-Effective Cyanide Recovery Technology for Sustainable Gold Mining. ACS EST Water. https://doi.org/10.1021/acsestwater.3c00026

Scott, J., 2020. 2019 CHEMICAL ENGINEERING PLANT COST INDEX ANNUAL AVERAGE. Chemical Engineering.

Woods, D.R., 2007. Rules of thumb in engineering practice. Wiley-VCH, Weinheim.

# APPENDIX D PERMISSIONS

## D.1 Chapter 2



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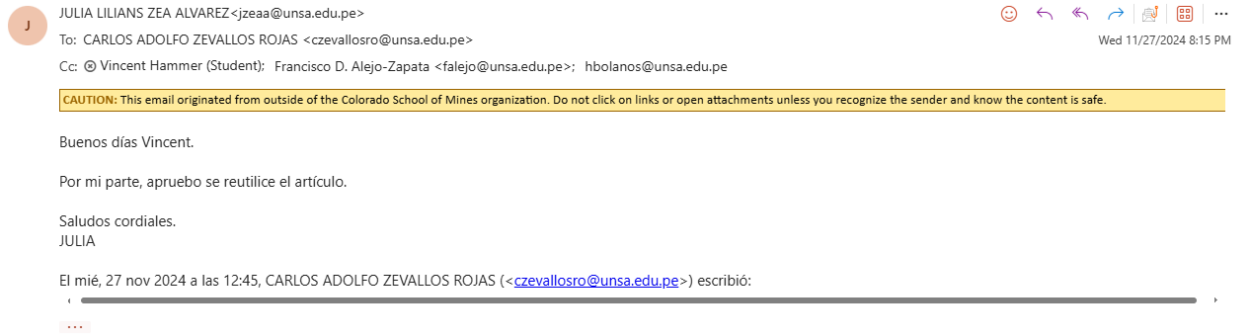

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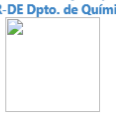

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## D.2 Chapters 3 and 4