Study of Unconventional Techniques to Eliminate Mercury Use from Artisanal Gold Mining Operations

by

Pariya Torkaman
BSc, Shiraz University, 2010
MSc, Shiraz University, 2014

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

Doctor of Philosophy

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(Mining Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

January 2023

The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the dissertation entitled:

Study of unconventional techniques to eliminate mercury use from artisanal gold mining operations

submitted by Pariya Torkaman in partial fulfilment of the requirements for

the degree of Doctor of Philosophy

in Mining Engineering

Examining Committee:

Marcello Veiga, Professor, Mining Engineering, UBC
Co-supervisor

Leslie Lavkulich, Professor, Land and Food Systems, UBC
Co-supervisor

Bern Klein, Professor, Mining Engineering, UBC
Supervisory Committee Member

David B Dreisinger, Professor Materials Engineering, UBC
University Examiner

Maya Kopylova, Professor Earth, Ocean and Atmospheric Science UBC
University Examiner

Pablo Leon Higueras,, Professor, Inst. Applied Geology, Univ. Castilla-La Mancha, Spain
External Examiner

Abstract

Artisanal gold mining significantly contributes to mercury pollution, resulting in severe environmental and health problems, especially for workers and local communities. The annual release of over 2000 tonnes of mercury by artisanal miners is the largest source of artificial mercury pollution. The author offers unconventional and innovative processes for gold leaching to eliminate the use of mercury in artisanal mining activities. A sample from the La Maria deposit, mined by Colombian artisanal miners, was used in all tests to compare the results. Lab tests on the sample with 48.87ppm Au, ground 80% below 0.13mm, showed that amalgamation only extracted less than 20% of the gold, while cyanidation with 1g/L of CN^- for 24h recovered 84% of the gold. One alternative process studied was using a liquid (effluent) from a local cassava plant, common in many artisanal mining areas in Latin America, Africa, and Asia. The liquid contains hydrogen cyanide, generated from the hydrolysis of cyanogenic glycosides in the cassava plant. The study tested two varieties of cassava that produce a liquid with 267 and 600 mg/L of free cyanide. The gold content extracted from ore in 24h was 50.9% and 82.4%, respectively. Another method was using Dimethyl sulfoxide (DMSO), a water-free reagent, as a gold-leaching lixiviant, providing over 95% of gold extraction in 24 hours. Additionally, the author studied a modification of the classical Merrill-Crowe process, zinc cementation, which aimed to simplify the gold extraction process by eliminating filtration and vacuum by using bags filled with zinc (or aluminum) in the pulp agitation process. Over 99% of gold was precipitated on the zinc shavings in two hours when the agitation was reduced to avoid aeration. Chloride application was also studied, with results showing 100% gold extraction in 8h at 50°C. All the alternative strategies herein investigated involve knowledge and investment and must be adapted to site-specific conditions. The ideal conditions to eliminate mercury include transforming the polluting processing centers into small, responsible companies. While technology is essential in this process, a broader approach is required to minimize the negative impact of artisanal mining activities on the environment and local communities.

Lay Summary

This thesis investigates unconventional processes for gold extraction in the artisanal mining sector. The goal is to assist the artisanal mining sector in achieving higher gold extraction rates with more beneficial and cleaner technologies than amalgamation. The purpose is to introduce practical and low-cost alternative reagents and methods to eliminate mercury from artisanal gold mining that contributes to significant impacts in the long term. The processes herein studied are not universal solutions and must be adapted to the site-specific situations of the artisanal mines. They involve specific knowledge and investment to be implemented, but they can replace mercury. Any solution should be brought to the attention of the processing centers that work extracting gold for their clients, the miners. They have the best potential to use the alternative techniques herein studied. However, they need to change their business model from exploiting artisanal miners to offering inefficient amalgamation processes for gold extraction.

Preface

This thesis is an original work by Pariya Torkaman and includes multiple parts.

Dr. Marcello Veiga suggested the core idea. I was the lead investigator, responsible for all major research and concept formation areas, data collection and analysis, and manuscript composition. I performed all the lab experiments at UBC and during the trips to Brazil and Colombia. All the projects and associated methods were approved by Dr. Veiga and done under his supervision.

The DMSO research was conducted in collaboration with Dr. Akihiro Yoshimura, Chiba University, Japan.

Dr. Les Lavkulich was involved in the cyanogenic plants' research and supervised the lab experiments executed in UBC's Land and Food Systems department.

Pictures that are presented here were all taken by the author during the trip to Brazil, Colombia, and Costa Rica.

Parts of chapters 2, 3, 4, 5, and 6 have been published in [Torkaman, P., Veiga, M.M., de Andrade Lima, L.R.P., Oliveira, L.A., Motta, J.S., Jesus, J.L. and Lavkulich, L.M., 2021. Leaching gold with cassava: An option to eliminate mercury use in artisanal gold mining. Journal of Cleaner Production, 311, p.127531]. I was the lead investigator, responsible for concept formation, data collection, analysis, and manuscript composition. Marcello Veiga was involved in concept formation, supervised laboratory experiments, and contributed to manuscript edits. Luiz R.P. de Andrade Lima, Jaciene L. Jesus, and Joselito S. Motta coordinated the field trips and laboratory experiments in Brazil. Leslie Lavkulich was involved throughout the project in concept formation and manuscript editions.

Parts of chapters 2, 3, 4, 5, and 6 have been published in [Torkaman, P. and Veiga, M.M., 2023. Comparing cyanidation with amalgamation of a Colombian artisanal gold mining sample: Suggestion of a simplified zinc precipitation process. The Extractive Industries and Society, p.101208]. I was the lead investigator, responsible for all areas of concept formation, data collection, data analysis, and manuscript composition. Marcello Veiga was involved in concept formation and laboratory experiments and contributed to manuscript edits.

Parts of chapters 2, 3, 4, 5, and 6 have been presented as an oral presentation [Torkaman, P., Veiga, M.M. and Yoshimura, A., 2022. Alternatives to Eliminate the Use of Mercury in Artisanal Gold Mining. ICMGP 2022 – 15th International Conference on Mercury as a Global Pollutant: Why the Measures to Eliminate Hg in Artisanal Gold Mining Are Not Working. July 25-29, 2022 – Virtual Event]. I was the lead investigator, responsible for concept formation, data collection and analysis, and oral presentation. Marcello Veiga was involved in concept formation and laboratory experiments and contributed material supervision for the presentation. Akihiro Yoshimura was involved in concept formation and laboratory experiments.

Parts of chapters 2, 3, 4, 5, and 6 have been presented as an oral presentation [Veiga, M.M. and Torkaman, P., 2021. Alternatives to Eliminate the Use of Mercury in Artisanal Gold Mining. PlanetGOLD AGM Production: Technology Without Mercury virtual exhibition]. Marcello Veiga and I did the oral presentation. I was responsible for concept formation, data collection and analysis, and material preparation for presentation. Marcello Veiga was involved in concept formation and laboratory experiments and contributed to material preparation and supervision for the presentation.

Parts of chapters 2, 3, 4, 5, and 6 have been submitted to different journals as [Torkaman, P., Veiga, M.M., Yoshimura A., and Lavkulich, L.M., 2023. Dimethyl Sulfoxide, An Organic Lixiviant for Gold Leaching] and [Torkaman, P., Veiga, M.M., Lavkulich, L.M. and Kelin, B., 2023. Investigation of Techniques to Replace Amalgamation in Artisanal Gold Mining Operations].

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List of Abbreviations

AAS	Atomic Absorption Spectrometry
AGM	artisanal gold mining
AGM	artisanal and small-scale gold mining
CEGEP	Collége d'Enseignement Général et Professionnel
CICAN	Colleges and Institutes Canada
CAGR	Compound annual growth rate
DMSO	Dimethyl sulfoxide
FCA	Free Carrier
GMP	Global Mercury Project
GRG	Gravity Recoverable Gold
Kg	kilogram
NGO	non-governmental organization
OECD	Organization for Economic Co-operation and Development
PAX	Potassium Amyl Xanthate
TPD	tonnes per day
UN	United Nations
UNDP	United Nations Development Program
UNEP	United Nations Environmental Programme
UNIDO	United Nations Industrial Development Organization
UBC	University of British Columbia
XRD	X-ray diffraction

Acknowledgements

This thesis was not possible to be completed without the financial support of NSERC (RGPIN-2020-06125), China Gold International Resources Corp. and John Bell Foundation.

I want to thank my esteemed supervisor, Dr. Marcello Veiga, for his invaluable supervision, support, and tutelage during the course of my Ph.D. degree. You taught me to come out of my comfort zone, think critically, ask questions and be brave. Your friendship means the world to me. My gratitude extends to Dr. Les Lavkulich, who believed in me and made me feel like "the happiest girl on this planet" once I really needed that, and for his mentorship. I also thank Dr. Bern Klein, from my supervisory committee, for his thoughtful guidance and fruitful comments.

Special thanks to the Norman B. Keevil Institute of Mining Engineering and Land and Food Systems faculty and staff members for supporting me in undertaking my studies at the University of British Columbia.

I want to thank my friends, lab mates, colleagues, and research team for our cherished time together in the lab and social settings.

My sincere gratitude to the team of EMBRAPA Cassava and Fruticulture Center, Cruz das Almas, Bahia State, Brazil, especially to the director Dr. Francisco F. Laranjeira, as well as Dr. Luciana Alves Oliveira, Ms Jaciene L. Jesus and Mr. Joselito Motta for their assistance in the field trip, lab experiments with bitter cassava and hospitality in my first trip to Brazil. My gratitude also extends to Dr. Luiz Rogério P. de Andrade Lima from the Dept. of Materials Science and Technology of the Federal University of Bahia, Brazil in the first cassava leaching experiments we have conducted in his lab.

Additionally, I express gratitude to Dr. Akihiro Yoshimura from China University, Japan, for the inspiration of the DMSO tests with gold ores., as well as Dr. Bruce Marshall from UBC NBK Institute of Mining Eng. and Dr. Luis Gonzaga S. Sobral from the Brazilian Center of Mineral Technology, CETEM, Brazil, for their cooperation, influence on my experiment methods, and critiquing my results.

My appreciation also goes to the faculty and friends from the Federal University of Pernambuco, in particular, prof. Amanda Carvalho de Oliveira e prof. Aureo Octavio Del Vecchio Machado for the cassava leaching tests in their lab in my second trip to Brazil.

In addition, I thank Dr. Oscar Restrepo-Baena, Mr. Ferney Londono, friends, and staff of the National University of Colombia (Departamento de Materiales y Minerales, Facultad de Minas), Medellin, for their collaboration in my trip to Colombia and for assisting my tests with zinc precipitation and also for their fantastic hospitality.

Special thanks to Gaylord Chemical Company, L.L.C, in particular Mr. Mick Sadoudi for providing the DMSO samples for my research. I am also thankful to Newlox Gold Ventures Corp., for the hospitality in my trip to Costa Rica and Mineworx Technologies Ltd., in particular Mr Fabricio Maia, Ms Samanta Klein and Mr Evan Ben-Oliel for assisting me through different stages of this research.

My most significant appreciation goes to my family, my brother Pouriya, and my friends for their encouragement and support throughout my studies. I could not have done it without you. Thanks for listening to all my naggings and tolerating me through my hard times.

Dedication

To Mom & Dad.

To my beloved Mehdi.

To the artisanal miners around the world: I hope this research makes a slight difference in your lives.

Chapter 1: INTRODUCTION

This chapter is a summary of artisanal mining and the concerns regarding the history and evolution of these activities as a background to this thesis.

1.1 Statement of the Problem

In many countries, artisanal gold mining (AGM) uses elemental mercury for gold extraction (Esdaile and Chalker, 2018). The term artisanal gold mining is used for all the small, medium, large, informal, legal, and illegal processes that use rudimentary techniques for extracting gold from any secondary or primary mineral deposit (Veiga, 1997). The release of mercury from gold amalgamation causes severe environmental and health problems, especially for operators and people living around the processing facilities.

The Global Mercury Assessment (UNEP, 2018) reported that over 2000 tonnes of Hg are released annually to the environment (emissions to the atmosphere and discharges to land and water are estimated at 838 and 1206 tonnes/a, respectively) by over 20 million artisanal miners, representing the world's largest source of anthropogenic mercury pollution (Martinez et al., 2021). In addition, due to the recent high gold prices and Coronavirus outbreak, unemployment rates in developing countries have increased, pushing millions of people to informal gold mining activities (Hilson et al., 2021). This boom of artisanal mining has been increasing mercury use and, consequently, pollution.

The main focus of researchers and international agencies in the last 40 years regarding the problems of mercury associated with AGM has been the reduction of mercury by promoting gravity concentration with the amalgamation of concentrates and restricting mercury accessibility through legislation. Nevertheless, most interventions by governments, international agencies and researchers have been dedicated to monitoring mercury's environmental and health impacts, as well as, to bring procedures to legalize artisanal miners. A few projects are also dedicated to train the gold miners to adopt cleaner gold processing techniques (Veiga and Fadina, 2020). All these approaches are not resulting in major reductions in mercury use and losses in this sector.

Miners do not have the capital and skills to process the gold they mine so they rely on processing centers, which are the largest mercury polluters (Veiga and Fadina, 2020). Miners take their ore to these centers to be crushed, ground, and free gold particles amalgamated (rarely concentrated), paying nothing or a small fee for the service. The rudimentary processes used by these centers rarely extract more than 30% of the gold from the ore of their clients, who must leave the tailings in the centers' facilities as the principal payment. The centers' owners use cyanide to extract the residual gold from the Hg-contaminated tailings, exacerbating the pollution as mercury-cyanide complexes are discharged into the drainages (Marshall et al., 2020).

Miners and the owners of these centers must change their business model and adopt a coexistence approach to work fairly, splitting equally the revenues of the gold extraction and using cleaner gold extraction methods (Veiga and Fadina, 2020).

As suggested a priority must be given to stop the practice of amalgamation of the whole ore in ball mills. Concentration processes are critical to reducing mercury use in AGM. The amalgamation of gravity concentrates causes less mercury losses than the whole ore amalgamation in copper plates or small ball mills. Mercury loss in the amalgamation process of secondary ores (alluvial, colluvial, and eluvial) is at least ten times less when the primary ores are amalgamated due to lower gold grades and the need for pre-concentration. A concentrate has 10 times less mass than the whole ore. (Veiga and Gunsun, 2020, Esdaile and Chalker, 2018). Gold concentration should be emphasized as a key to reducing contaminants' emissions while increasing gold extraction for the miners. However, gold must be extracted from the concentrates and amalgamation is not efficient and still creates polluting consequences.

Hydrometallurgical methods to extract gold from concentrates without mercury must be simple and inexpensive to convince processing centers, small companies, or even skilled artisanal miners to adopt these methods and abandon amalgamation. The core of this thesis is to study the possible techniques to be adopted by these stakeholders.

1.2 Justification for this Research

World Health Organization (WHO, 2017) considers mercury one of the top ten chemicals of primary public health concern, while artisanal mining is the primary source of anthropogenic mercury (UNEP 2018). The gold amalgamation process in AGM has contributed to the mining sector's most significant environmental and human health problems for decades (Veiga et al., 2014b). Inhalation of mercury vapor by operators and communities residing around the processing centers is the main path of mercury intoxication. Mercury has harmful effects on the nervous, digestive, and immune systems, lungs, and kidneys and may be fatal (WHO, 2017). Although eliminating mercury use in AGM has been the center of attention of researchers, NGOs, international donors, and governments for the past four decades, no considerable progress has been made (Veiga and Fadina, 2020). The primary technological approach to the problem should be the introduction of fair business models into the processing centers where they would share equally the revenues of gold extraction with their clients, the miners. The artisanal mining sector is in emergent need of practical and, at the same time, economical solutions to stop utilizing mercury. With capital and more knowledge, these centers could adopt simple methods to eliminate mercury and increase gold extraction.

The challenge is to explore the metallurgical methods to extract gold from concentrates without mercury or complicated proprietary processes or reagents and, with efficient and affordable techniques. This research will partially fulfill this need by introducing alternative techniques for gold leaching at low cost and higher gold recoveries than amalgamation. The methods herein studied are easily performed with no need for detailed knowledge and training. Using a well-studied and high gold-grade ore from an artisanal mining operation in Colombia, this thesis followed a logical sequence of laboratory activities while searching for methods to replace amalgamation. The following steps and tests were performed and discussed:

1. Check how much gold can be extracted using the amalgamation process used by artisanal miners
2. Test an adaptation of the Merrill-Crowe method to eliminate the use filtration and vacuum, simplifying the cyanidation process
3. Test the use of bitter cassava to leach gold
4. Test the use of DMSO (dimethyl sulfoxide) to leach gold
5- Test the oxidative chloride process to leach gold

The anticipated outcomes of this Ph.D. research are as follows:

- Introducing a common plant, cassava, which contains cyanogenic compounds that can convert to cyanide in a straightforward process, as a source of cyanide for gold leaching process

- Development of a non-aqueous gold extraction process utilizing an organic compound, dimethyl sulfoxide (DMSO)
- Modification of the existing Merrill-Crowe process and test an adapted version that eliminates the need for filtration and vacuum for artisanal mining sector
- Examine halide leaching as a substitute for cyanide and mercury
- Comparison of the gold extraction potential of the introduced techniques with the existing whole ore amalgamation process.
- Suggest effective technical methods to eliminate mercury use in AGM

Research Questions

The research questions this study aims to answer are:

1. What can be a simple technical approach for gold extraction to assist artisanal operations so that they willingly stop using mercury?
2. What factors should be considered in developing an alternative gold processing method to make it acceptable by artisanal miners?
3. What other lixiviants can be utilized as gold extractant than mercury with higher efficiency?
4. How can it be possible to improve the existing gold extraction techniques for more straightforward and more affordable techniques?

1.3 Industry Significance

This research contributes to the artisanal mining sector and industrial mining companies.

For Artisanal Miners:

- Introduces alternative techniques for gold leaching to artisanal gold miners
- Provides economic benefits for both artisanal miners and processing centers
- Decreases the potential human health and environmental hazards of using mercury for gold extraction in artisanal mining,
- Addresses the global concerns of artisanal mining using mercury,

For Companies:

- Provide alternative lixiviants (local plants and organic chemicals) for conventional mining companies
- Development of simplified methods of gold extraction

1.4 Academic Significance

This research is significant because it focuses on one of the most challenging global issues of our time. Environmental and economic problems related to artisanal gold mining need to be studied in depth and practical solutions needed to provide which are the aims of this research.

Based on the literature on AGM, very little options have been generated to replace mercury and most of them are not practical for artisanal gold miners or simply based on gravity concentration methods followed by smelting. As a result, novel gold leaching methods, which investigated and provided by this research are of great importance and it takes the early steps for the further endeavors through resolving the global issues in artisanal mining sector.

1.5 Dissertation Chapters

I. Introduction

The Introduction includes a statement of the problem, a brief background about the artisanal mining sector, and its global impact on the environment and health. A discussion about the purpose and objectives of this research comes next. This chapter ends with a short discussion about the academic and applied contribution of the research.

II. Review of the Literature

The literature review chapter discusses the significant prior knowledge and concepts of artisanal mining and the efforts that have been made so far toward reducing and managing the human and environmental issues associated with mining activities. Different aspects of these issues and the key attributes are explained, followed by offered solutions by international communities and identified gaps. A list of gold leaching techniques investigated and suggested by this research and the scientific theory behind each offered method are also included in this chapter.

III. Methodology

This chapter includes the details and framework for the lab experiments for each investigated method. Information about each offered method's implementation, monitoring, and evaluation is mentioned.

IV. Results

This chapter brings all the results of the researcher's laboratory and field experiments in Canada, Brazil, Colombia, and Costa Rica. Data achieved by utilizing different experimental instruments and decision-making models are presented in this chapter.

V. Discussion

This chapter explains and evaluates the observations and data obtained during this study. Identify the weaknesses and limitations of each method and clarifies the unexpected results. Moreover, it contains the analysis of the data and how it relates to the arguments and research objectives mentioned in the previous chapters.

VI. Conclusion

The conclusion summarizes the findings of each technique investigated comparing and analyzing all the methods with the amalgamation process. It argues the possibilities of future cleaner methods to leach gold by revisiting the conceptual framework. Finally, it describes the significance of the research and provides recommendations for the research agenda.

Chapter 2: REVIEW OF THE LITERATURE

2.1 Definitions of Artisanal Mining

The history of gold mining goes back to 400 BC when all mining activities must have been known as ‘artisanal’; however, there is still no agreement about the definition. Many possible variables come into consideration to have an exact definition for this economic sector. Veiga (1997) stated that all low-tech manual operations, from individual ‘panners’ to larger groups for poverty alleviation, could be classified as the artisanal mining sector. Using unconventional and primitive mining techniques without having a long-term plan, whether formal or informal, legal or illegal, is another definition of artisanal gold mining (Hinton et al., 2003). There is little agreement about the term “artisanal and small-scale mining” in the literature and policy.

Frequently legislation of many developing countries uses the term “small-scale” interchangeably with “artisanal mining”, and the distinctions between the types of mining methods in each of these categories are often unclear (Veiga and Marshall, 2019). The term ASGM – Artisanal and Small-scale Gold Mining is preferentially used herein as AGM – Artisanal Gold Mining to refer to the miners using rudimentary techniques to mine and process gold ores, independently of the size of the operation.

The opposite of artisanal mining is “conventional” mining, referring to the activities of organized companies that may be large, medium, or even small but are legal and operating with appropriate technical methods. Some artisanal mining operations can be large, processing more than 2 million tonnes/a of, usually, secondary ores (alluvial, colluvial and, eluvial ores). An artisanal miner works based on survival instincts and does not use conventional geological exploration activities such as drilling and reserve definition (Veiga and Gunson, 2020).

The word “small” defines only the size of the operation and not necessarily the level of sophistication of a processing operation. According to the United Nations (UN) statement in 1972, operations on 50,000 metric tonnes/a of raw materials and the National Mineral Research Department (DNPM) in Brazil, between 10,000 t/a to 100,000 t/a of ore, are considered small-scale mining (Seccatore et al., 2014). While Veiga et al. (2014b) believe that it is not about the size of the operation, but the level of the technology applied that should be focused on the solutions for artisanal mining pollution.

2.2 Use of Mercury in Artisanal Gold Mining (AGM)

Mercury's use goes back to ancient times; burial ceremonies, dental amalgam, wall paints, cosmetics, fluorescent lamps, and treatment of syphilis were common uses. Mercury easily makes amalgams with most metals except iron and platinum (Veiga et al., 2014b).

Artisanal gold mining in more than 70 developing countries uses elemental mercury for gold extraction (Esdaile and Chalker, 2018). The use of mercury in AGM depends on the characteristics of the gold ore. In many countries, gold in primary ores, with high gold grades, is not concentrated. The ore is ground and amalgamated in copper plates covered with mercury or in small ball mills, known in Indonesia as "tromols", in Colombia as "cocos" and in Peru and Ecuador as "chanchas" (Veiga et al., 2006). Figure 2-1 outlines the unit operations involved in AGM gold extraction steps when processing primary ores. Usually, these steps are conducted in processing centers where miners have their gold extracted for free or by paying a nominal fee if they leave the tailings in the centers' facility.

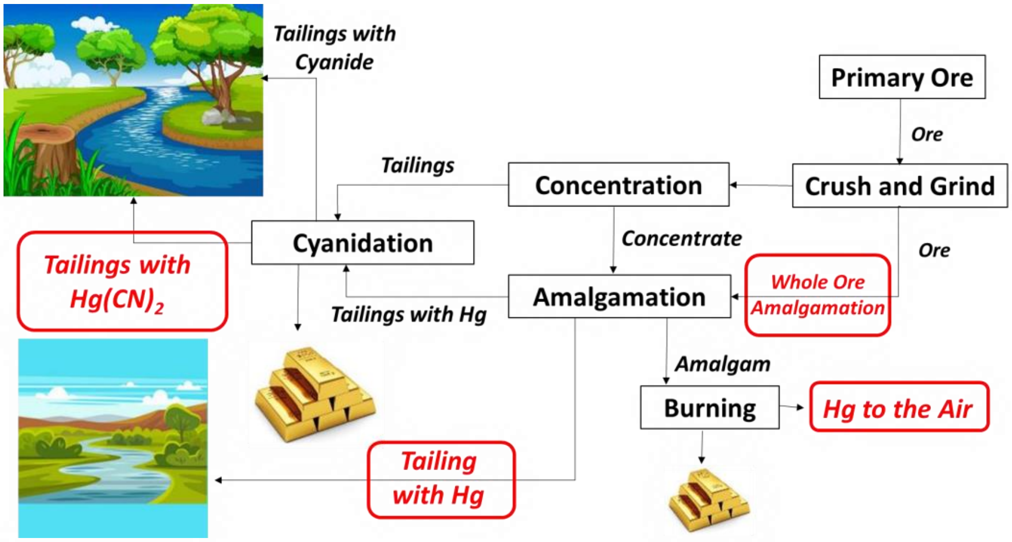

Figure 2-1. Steps involved in extracting gold from primary ores in processing centers

Riverbeds can contain alluvial gold deposits, while landslides can create colluvial deposits that contain particles of various sizes, with larger and heavier particles typically settling at the bottom of the mountain (Rajapakse, 2016). Eluvial deposits, on the other hand, are formed through weathering processes that occur in situ or through the accumulation of materials affected by gravity (Giuliani et al., 2020). The classification of gold deposits is complex, but there are two recognized types: primary and secondary. Primary deposits occur when gold precipitates during chemical reactions between hydrothermal mineralizing solutions and rocks in the Earth's crust, while secondary deposits form through weathering and erosion processes that result in the concentration of gold-bearing sediment in placer deposits (Boyle, 1979). Placer deposits can be found in different environments, such as marine or fluvial, depending on the depositional setting. Studies suggest that gold can be transported mechanically and chemically, which may explain the unusual size and purity of nuggets in some placer deposits (Boyle, 1979). The gold grades in secondary deposits can range from a few tenths of a gram per tonne (g/t) to several grams per tonne. The gold in primary ores is often concentrated in specific veins or mineralized zones, which can make it easier and more economical to extract. The gold grades in primary deposits can range from a few g/t to over 100 g/t, with some exceptionally rich deposits containing several thousand g/t It's important to note that these are general ranges and there can be significant variation from one deposit to another. The gold grades in any particular deposit will depend on a variety of factors, including the geological setting, the size and shape of the deposit, and the concentration and distribution of gold within the deposit. When secondary ores (alluvial, colluvial, or eluvial) are mined and processed, as these ores have low grades, artisanal miners previously concentrated the gold to amalgamate only the concentrates reducing the use of mercury. In these cases, the amalgamation of the whole ore is rare, but it can occur using copper-amalgamation plates (Veiga et al., 2014b).

For amalgamating the concentrates, mercury is mixed with the gold concentrate in a bowl, pan, or a small barrel and agitated for a specific time. Through this process, gold forms an amalgam. In order to eliminate the excess liquid mercury not bonded to gold, the amalgam is squeezed into a fabric. According to Pryor (1965), the amalgamation of mercury with gold does not form an alloy but deep sorption. In this regard, the more force applied in the amalgam filtration process, the more mercury is eliminated (Veiga et al., 2006). The three main types of gold amalgams are $AuHg_2$, Au_2Hg, and Au_3Hg (Taggart, 1945). Squeezing excess mercury manually in a piece of fabric, as usually done in AGM, results in an amalgam containing 40 - 50% mercury. Using the centrifugal force instead of the manual squeezing process results in an amalgam with 80% Au and 20% Hg

(Veiga et al., 2006). Once the amalgam is in hand, the artisanal miners heat it with a torch at a temperature above 460°C, vaporizing the mercury and leaving behind the gold (Santos, 2013).

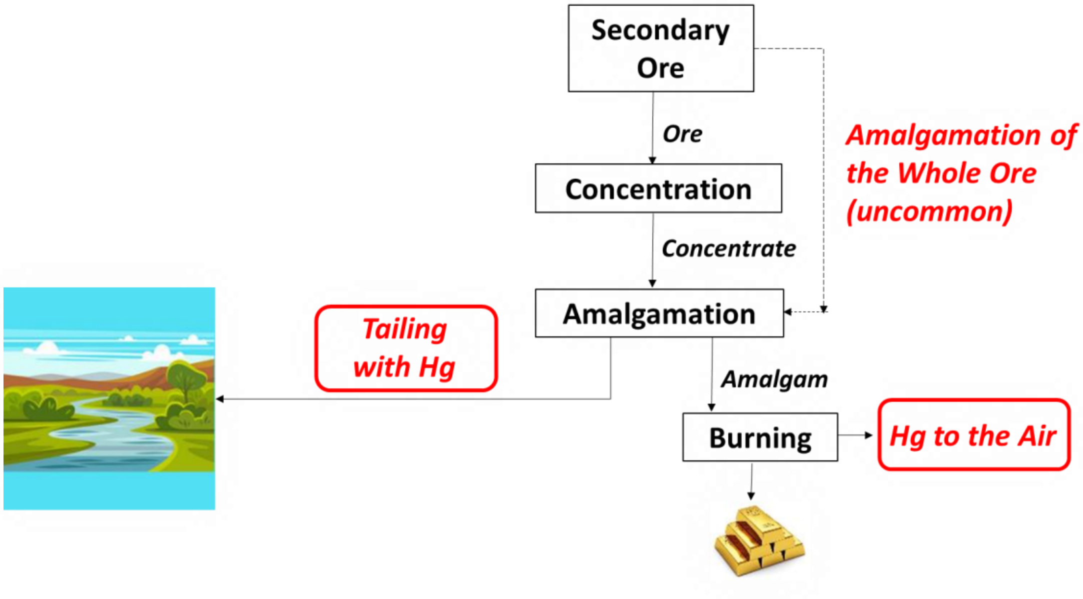

Figure 2-2. Steps involved in gold extraction from secondary ores

The final product of this process is a gold *doré* with residual mercury of 2 to 5% depending on the efficiency of the evaporation process (Veiga and Hinton, 2002, Veiga et al., 2014a). The evaporation of mercury depends on the temperature and length of time. In Sudan, miners use low-temperature bonfires to remove mercury from amalgams. The gold *doré* comes out with 20% mercury (Veiga et al., 2014b).

The amalgamation process of gold contributes to substantial release of mercury into the atmosphere resulting in severe health problems, especially to operators and people living around the processing facilities.

Mercury poisoning is a very critical human health issue in AGM communities. People in these communities can be affected by inhaling mercury vapor from heating the mercury-gold amalgam. Lungs can absorb mercury gas and transfer it to other organs. Acute exposure to mercury vapor can contribute to tremors, memory loss, respiratory distress, and even death (Park and Zheng, 2012). Elemental mercury can disturb the neurological function and fetal development process by passing the membranes, including the blood-brain barrier and the blood-placenta barrier (Esdaile and Chalker, 2018).

Oxidation of metallic mercury that is lost during the amalgamation process can reach water streams and produce soluble mercury species that eventually can be converted into methylmercury to bioaccumulate (Hinton and Veiga, 2008). Despite no concrete evidence of the methylation of metallic mercury from AGM and consequent bioaccumulation of methylmercury, this has been the main point to demonize the artisanal gold miners everywhere (Tchounwou et al., 2003, Gerson et al., 2018, Vasconcellos et al, 2021). The possibility of methylation of metallic mercury from AGM has also been raised by researchers (Mallas and Benedicto, 1986, Malm, 1998, Tromans et al., 1996, Barbosa et al., 2003, Olivero-Verbel et al., 2004, Hilson et al., 2007, Esdaile and Chalker, 2018) but no actual proof, such as isotopic mercury analyses of fish muscles, has been provided to confirm that the methylmercury in freshwater fish from artisanal mining areas comes preferentially from these operations (Veiga, 2022). The possibility of the contribution of mercury from other sources (e.g. dispersed industrial sources, forest fires, plants decomposition and release of Me-Hg compounds in hydroelectric reservoirs, erosion of river banks, etc.), together with the geochemical conditions of the environment, such as high concentration of dissolved organic acids in waters, have been also considered by scholars (Veiga et al., 1994, Tromans et al., 1996, Silva- Forsberg et al., 1999, Roulet et al., 2000, Fadini and Jardim, 2001, Jardim et al., 2010, Michelazzo et al., 2010, Pestana et al, 2019).

Women in AGM can be exposed to different sources of mercury. The main evidence is the mercury vapor emitted when amalgams are burned without filters or condensers. Women also frequently handle mercury in the amalgamation process, as this is a delicate and time-consuming task well performed by women (Hinton et al., 2006). Consequently, high levels of mercury are found in the bodies of women of reproductive age involved in AGM activities which can be transferred to the fetus (Esdaile and Chalker, 2018). That has been pointed out by some authors as the reason for the high incidence of physical and mental disabilities in children in the artisanal gold mining communities (Tchounwou et al., 2003; Park and Zheng, 2012).

In the last decade, developing practical non-mercury and low mercury loss technologies was significant in decreasing the dependence of artisanal miners on mercury (Metcalf and Veiga, 2012). A good example of the efforts towards decreasing mercury pollution from AGM was the idea of centralized processing centers, which first appeared in the 1990s in Zimbabwe (Veiga et al., 2014a). The purpose of developing these centers was to leave the step of processing the ore to the specialized operators at the centers. This step is supposed to be free or with a small fee for artisanal miners, but with the condition that they must leave the tailing at the center. As a result, miners do not need to process the ore themselves and purchase expensive equipment for gold extraction procedures. This ended with causing more social and pollution problems than it resolved, as the owners of these centers did not act appropriately. They use mercury for amalgamation of the whole ore with less than 30% of gold extraction, which is unfair to the miners, who must leave the tailings in the centers as part of the payment for the services. The centers leach the mercury-contaminated tailings with cyanide to recover the residual gold. This contributes to form very toxic mercury cyanide compounds that exacerbates the bioaccumulation of the pollutant in aquatic biota (Drace et al., 2016, Marshall et al., 2020). Seney et al., (2020) demonstrated in bioassays with rats, that mercury-cyanide complexes accumulate preferentially in the kidneys causing high toxic effects and they did not identify mercury in the brains of the mammals. Silva et al. (2023) found similar results using zebra fish as the toxicological subjects for experiments with $Hg(CN)_2$. They found the value of 0.53 mg/L of $Hg(CN)_2$ for the LC_{50} (lethal concentration to kill 50% of the fish) at 96 h of exposure and 100% mortality occurred at 0.64 mg/L. Lack of appropriate cyanide management and tailings with mercury, cyanide, and other heavy metals recklessly disposed in the environment, are problems associated with the processing centers.

Whole ore amalgamation and cyanidation of mercury-contaminated tailings in processing centers is the main problem to be resolved to reduce or eliminate mercury losses in AGM. About 15 parts of mercury are lost per part of gold produced when whole-ore amalgamation occurs in small ball mills (Cordy et al., 2011).

Most technical efforts to reduce the use of mercury must encourage miners and processing centers to avoid the use of mercury or, at least, amalgamate only gravity concentrates instead of the whole ore. The whole ore amalgamation continues to extract gold from primary ores, with high grades in Asian and Latin-American countries (Veiga and Gunson, 2020). The pollution is aggravated when the mercury-contaminated tailings are leached with cyanide.

The additional problem is that organizations of cyanide producers, such as the International Cyanide Management Institute (ICMI), hinder their products' sales to artisanal gold operations, including the rudimentary processing centers. Veiga et al. (2014a) observed that most of these centers acquire cyanide clandestinely or from non-ICMI members, such as Korean, Russian, and Chinese cyanide suppliers. Therefore, cyanide salts are not readily available in AGM sites and are costly, with prices on the mining sites ranging from US$ 3 to 5 /kg. Despite having more knowledge about cyanidation processes than artisanal miners, processing centers still do not respect environmental regulations, and most contaminated tailings are dumped into local rivers without treatment (Marshall et al., 2020).

Veiga and Fadina (2020) discussed that most initiatives the UN and other international agencies promote are to stop using amalgamation and cyanidation in processing centers. However, no feasible technical alternatives other than gravity concentration methods are suggested. Veiga and Gunson (2020) mentioned, in a significant review of the gravity concentration methods used by artisanal gold miners, that gravity concentration can reduce mercury use to less than 10% of the original mass when only concentrates are amalgamated. However, the processes to extract gold from the concentrates, in particular from the unliberated grains, are not so available for unskilled miners. When organized companies buy ores from artisanal miners, as observed in Colombia and Peru, the use of mercury is eliminated (Veiga et al., 2022). However, implementing business changes in artisanal mining is not so trivial due to 1) low enforcement of the laws from governments on processing centers (some legally established) to stop pollution, 2) no incentives for the processing centers to change their business model, 3) no alternatives for the miners to extract gold from their ores or concentrates, and 4) no affordable process, even for processing centers, to move away from cyanidation. On one side, the political and legal actions are not changing the processing centers' polluting methods. While on the other side, technical options to replace mercury are unclear for the governments, or project-sponsoring institutions. Consultants and companies are frequently offering several "new" techniques to replace gold amalgamation, which are either conventional gravity concentration pieces of equipment or hydrometallurgical methods to extract gold from concentrates. However, they are not financially attractive to miners who keep relying on processing centers to extract their gold by amalgamation, which is fast and affordable, but inefficient. Most of techniques brought to miners’ attention are based on proprietary lixiviants that bond the users to perpetual dependence on reagent supply or royalties to the technology owners (Veiga et al, 2014b).

An example of the impacts of mercury caused by processing centers can be seen in Colombia, which has a long history in AGM activities and was once responsible for the world's largest mercury consumer per capita (Cordy et al., 2011). In the 2010s, Colombia's artisanal gold mining sector had 200,000 miners officially producing 30 tonnes Au/a and losing over 130 tonnes/a of mercury to the environment (Cordy et al., 2011). Inefficiency in law implementation contributed to many informal and illegal miners in rural areas.

The Northeast part of Antioquia, Colombia, contains 17 mining towns and 15,000 and 30,000 artisanal gold miners. Processing centers are located adjacent to residences, schools, and stores, and miners take their ores to these processing centers. In the processing centers, mercury is added to the whole high-grade material without pre-concentration in small ball mills called "cocos." These steel ball mills are made locally and are able to process 50 to 70 kg of ore. This whole ore amalgamation process and burning the gold amalgam without any filtering/condensing system maximizes mercury losses. After extracting the gold by burning the amalgam, the tailings are leached with cyanide. Miners will only get the part extracted by amalgamation, and the substantial part of gold will remain in the tailings for the owners of processing centers (Veiga et al., 2018). The primary process processing centers use to recover residual gold from tailings is cyanidation to the tailings in vat leaching or agitated tanks, followed by gold precipitation with zinc shavings. Some centers use activated carbon to adsorb gold from the cyanide solution. After gold precipitation on the zinc shavings, the solution is pumped back for another round of leaching. Regarding the tailings grade, this leaching cycle can take from eight to thirty days. Miners check the zinc shavings visually for gold precipitation, and when the shavings do not turn black anymore, the leaching process has ended. The residual pulp and the gold-barren cyanide solution, still rich in zinc and mercury, are dumped into local creeks. Gold-loaded zinc shavings are burned at temperatures above 900 ^{o}C in open-gas furnaces to evaporate the zinc and obtain the gold. Zinc vapor with residual mercury precipitated in the cyanidation process is emitted into the environment (Velasquez et al., 2011).

Figure 2-3. Small ball mills,” Cocos”, in an urban processing center, Providencia, Colombia.

Mercury levels in the ambient air when mercury-contaminated materials are handled or burned can reach over 1 million ng Hg/m^3. Levels of 10,000 ng Hg/m^3 are typical in residential areas near places conducting gold amalgamation. When the WHO suggests a 1000 ng/m^3 limit for public exposure, the health effect risk is evident (Veiga and Baker, 2004; Cordy et al., 2011; Garcia et al., 2015).

The main possibility to eliminate the use of mercury would be to convert the processing centers into small, responsible processing companies, using cleaner methods, or keeping only cyanidation as the primary process. At this point, cyanide is the only feasible alternative for this sector in developing countries to replace mercury (Torkaman et al., 2021).

Over the past decade, other lixiviants have been introduced to substitute mercury and cyanide (Hilson and Monhemius, 2006; Vieira, 2006; Grayson, 2007). It is imperative to remove residual mercury before leaching contaminated tailings to avoid formation of Hg-cyanide complexes and to reduce the cyanide consumption in the hydrometallurgical operation. Methods to extract mercury before leaching with cyanide (Veiga et al., 1995) or to precipitate it in the cyanide solution have been investigated (Sandberg et al., 1984; Matlock et al., 2002. Veiga et al., 2014b, 911-Metallurgist, 2018).

2.3 Approaches to Eliminate Mercury Use in AGM

The following paragraphs categorize the actions taken to reduce or eliminate mercury in AGM.

2.3.1 Environment and Health Approach

Important approaches by academics, sponsoring agencies, and NGOs regarding mercury pollution by AGM activities, are surveying the levels of mercury in the environment and human bodies (Veiga and Fadina, 2020).

Monitoring mercury pollution emitted and released by artisanal gold mining activities has been the focus of many projects by governments, international agencies, NGOs and academic researchers. Only a few numbers of these monitoring projects propose solutions to eliminate mercury from AGM, mostly because the projects are not conducted with this objective and the researchers are rarely engineers with understanding of the whole gold extraction process (Veiga and Fadina, 2020).

Moreno-Brush et al. (2020) studied the fate of mercury released from AGM. They concluded that interpreting the mercury geochemical cycle is difficult due to the differences in hydrology, seasonality, sources of Hg, and nature of mining sites in tropical environments, so a standardized protocol is needed. In addition, there is an increasing trend in studies on mercury isotopic fingerprints, which can determine the source of pollution (natural or anthropogenic). An example is a UNIDO project on the isotopic analysis of highly mercury-contaminated Peruvian sediments, which revealed that the source was the dumped tailings of processing centers into the Ecuadorian river located 160 km upstream (Marshall et al., 2018; Schudel et al., 2019). Mercury speciation in fish can also benefit from the isotopic analysis to identify the sources of the pollutant (Veiga and Fadina, 2020).

Unfortunately, providing evidence of mercury intoxication for the miners does not change their mentalities and practices, and authorities do not implement the laws in most cases. Studies show that the person in charge of burning gold amalgam and the neighbors all get intoxicated with mercury (Boese-O'Reilly et al., 2003; Drasch et al., 2007). Steckling et al. (2014 & 2017) have conducted a thorough study on the chronic impacts of mercury vapor on artisanal miners and their communities and warned the public about the severity of the issue. Consequently, suitable treatment should be provided, and preventive measures must be recommended (Veiga and Fadina, 2020). However, most local doctors and other health workers cannot be helpful in this regard as they have no knowledge or ways to confirm that mercury is the main cause of health problems in mining community members.

For instance, in Colombia, the authorities provide diuretics for individuals burning amalgams with high levels of mercury in their urine. However, neurological symptoms are not confirmed in specific tests and when the levels of mercury in urine comes back to normal, the workers return to their polluting activities believing they are free of mercury in their bodies (Veiga and Baker, 2004).

Investigations on health and social aspects of mercury utilizing in AGM was increased substantially during 2010s but most monitoring programs have only the intention to highlight the problems without any suggestion how to mitigate it (Veiga and Fadina, 2020). These authors suggested that spending funds to prove the environmental contamination and human intoxication in AGM sites is not beneficial for reducing mercury use, as many authorities have limited access and capacity to implement solutions.

2.3.2 Legal Approach

2.3.2.1 Minamata Convention

The UN Minamata Convention on Mercury, a nations' agreement to protect human health and environment by reducing anthropogenic mercury pollution, has recognized the risks of mercury use in AGM and suggested that countries must control mercury trade while encouraging to investigate methods to eliminate mercury usage in this sector (UNEP, 2018). The Convention came into force in Aug. 2017 and currently has 138 parties, which are countries that ratified the Convention introducing laws or norms to control mercury trades (UNEP, 2022)

2.3.2.2 Formalization

The formalization of artisanal mining is a process that includes the establishment of legal and regulatory frameworks for mining activities, providing geological data of the area, legitimate access to the minerals for the miners, and capital, equipment, and technical assistance (Singo and Seguin, 2018).

The governments of countries with artisanal gold mining are willing to accept the adverse health, social, and environmental impacts and, on the contrary, want the sector to enter a virtuous circle of development, which contributes to the initiation of the formalization process (Pelon and Martel-

Jantin, 2006). They believe formalization is a way to have more control over artisanal mining activities and provide miners with a legal mining title for accessing credit and negotiating the area (Marshall and Veiga, 2017). Successful cases of formalization of AGM are rare. The reason is the government's lack of active engagement and constant support to artisanal miners (Hilson et al., 2019).

Pragmatically, no country currently has straightforward and simple regulations, and miners need to provide considerable documentation of requirements for legalization. Most of the policies only refer to the size of the operation in order to put taxes on artisanal miners (Veiga and Fadina, 2020).

For instance, in Peru, Law 27651 defines the regulations based on production capacity. It classifies the operations with more than 5000 tonnes per day (tpd) of ore as large-scale mines, while mines processing ores from 150 to 5000 tpd are medium-scale mine process (Marshall and Veiga, 2017). Peruvian artisanal miners need to provide all these documents to formalize, which will include a certificate of training; a certificate for proof of the absence of archeological remains; a valid permit for the use of explosives; and accreditation as an artisanal mining enterprise (Salo et al. 2016).

In Ecuador, three types of mining activities are defined in the mining law: artisanal, small, and large-scale (Vergara, 2009). By the law, small-scale mines can exploit up to 300 tpd, paying 5% tax, and operations above this capacity are classified as large-scale and subject to taxes as high as 50%. However, artisanal mining is defined as a manual activity only to make a living, without specifying the allowed size of processing (Marshall and Veiga, 2017). Echavarria (2014) studied the formalization process of Colombian artisanal miners and mentions that miners need to provide high levels of technical documents in order to be legalized. In addition, the government does not differentiate between the needs of artisanal miners and large-scale miners (Marshall and Veiga, 2017). According to Hilson (2016), in Africa, high levels of bureaucracy, high cost of the registration process and long processing time of permits application, prevent miners from formalizing their activities.

In Colombia, it has been reported that miners must follow over 380 administrative steps of legal requirements for formalization. The extreme bureaucratic process together with the lack of free mineral titles available to artisanal miners are the main hurdle for the effectiveness of the formalization process. In Latin America, less than 1% of the artisanal gold miners have their mineral titles fully legalized (Marshall and Veiga, 2017). In addition, legalization does not guarantee that the artisanal miners are operating in a clean way following all best practices (Veiga and Marshall, 2019).

Moreover, it is important to consider that the formalization process should provide miners with training and capital assistance from the governmental agencies. Without the necessary training, miners continue to use their inefficient rudimentary methods, contributing to pollution persistence. It must be noted that these education programs must be appropriate to each particular community and suit its needs, skills, and social relations (Marshall and Veiga, 2017).

Based on the studies in this area in developing countries, the current process of formalization of artisanal miners is on the way to failure and it needs fundamental adjustments such as reduction in taxes and in bureaucracy.

2.3.3 Technological Approach

Introducing new technologies, or modifying the ones already in use, by artisanal miners, is the fundamental of the technological approach associated with artisanal mining. This approach tries to offer a solution to eliminate or reduce the environmental and health contamination by developing changes in miners' behavior or methods. While new technologies should be able to be less harmful for both environment and people than the ones already being used by the miners, at the same time being profitable and simple to be operated by artisanal miners is of great importance.

Global Mercury Project (GMP), is one example of technical approach, executed from 2002 to 2008 by the United Nations Industrial Development Organization (UNIDO). The purpose of this project was to appraise artisanal miners about mercury emissions and releases, and introduce technical solutions in Brazil, Indonesia, Lao PDR, Sudan, Tanzania, and Zimbabwe. However, the outcome of this time and money-consuming project, was not successful and many miners did not utilize the methods they had learned (McDaniels et al., 2010).

The main cause for mercury losses in mining is amalgamation of the whole ore by miners, while concentration can reduce the mass to much less than 10% of the original mass to be amalgamated. Gold concentration is of great importance towards an efficient and economical processing following by chemical treatment methods as leaching, precipitation, and refining. Gravity concentration methods such as jigs, shaking tables, centrifuges, and sluice boxes are based on the high difference in weights between a gold and a typical gangue mineral, with the same size. (Gökelma et al, 2016). Gravity concentration provides a rich concentrate, but the gold still needs to be extracted from the concentrates. Amalgamation traps only the liberated grains of gold, whereas the leaching process dissolves all exposed particles of gold in a concentrate (Martinez et al., 2021).

Many international projects have been introducing different gravity concentration methods for the artisanal miners (Veiga and Gunson, 2020). A good example is a project in Colombia, which developed a series of homemade concentrators in order to be used by micro-miners with less than 2 tonnes of ore per day processing capacity. This project was sponsored by the Colleges and Institutes Canada (CICAN) and led by the Collége d'Enseignement Général et Professionnel (CEGEP) group from l'Abitibi-Témiscamingue, Rouyn- Noranda, Québec, (Veiga et al., 2018).

Another example of a well-promoted idea to eliminate mercury in AGM was the Borax Method. Borax, also known as sodium borate, is widely used in many detergents and household cleaning products. It is not toxic, and no chronic health effects have been reported (Appel and Na-Oy, 2012). In this suggested process, miners must concentrate gold by gravity methods to achieve a high-grade gold concentrate. The next step is to melt the gold with borax ($Na_2B_4O_7.10H_2O$), which forms a slag with oxides and silicates and results in the separation of gold. The reaction between borax and silicates involves the replacement of some of the silicon atoms in the silicate mineral with boron atoms from the borax. This results in the formation of a new compound that has a different structure and properties than the original silicate mineral (McIntosh, 2004).

In Tanzania, Appel and Jønsson (2010) replaced mercury with borax to produce gold from concentrates. They reported that borax was twice more efficient in gold extraction than mercury. In another study in the northern Philippines, Appel and Na-Oy (2012) achieved almost three times more gold extraction outcomes with the borax method than with mercury amalgamation. However, this process can only be used on concentrates with high grades of gold (>5% Au) and with no sulfides (Veiga and Gunson, 2020). When applied to concentrates with lower grades of gold, and sulfides, the gold extraction decreases as gold is lost with the slag (Veiga et al., 2014b). In addition, it is only suitable for miners producing small amounts of gold per day, since smelting of large amounts of concentrates requires an expensive furnace and skill to operate. Moreover, lack of accessibility and high prices of materials and equipment to use this method in the AGM regions are difficult hurdles to promote this method. In addition, the efforts to convince miners about the higher gold extraction rates of the Borax Method over mercury amalgamation, resulted in unsuccessful adaptability in the AGM sector (Zolnikov and Ramirez Ortiz, 2018).

2.4 Technologies Developed to Eliminate Mercury in AGM

Eliminating mercury use in artisanal mining needs gradual education of the miners, local support by projects and governments and sustainability in the implemented measures.

The main alternative to eliminate mercury use is to convert the technique of amalgamation and keep only cyanidation as the main process (Veiga et al., 2014a). Cyanide, in contrast to mercury, is not persistent in the environment and most toxic forms can be degraded by oxidation. Natural physical, chemical, and biological processes transform cyanide into other, less toxic chemicals. Free cyanide can also be attenuated through natural oxidation processes (Logsdon et al., 1999). The majority of conventional gold mining companies use cyanide to extract gold that requires forced destruction (oxidation) of the cyanide complexes from effluents (Habashi, 1969, Celep et al., 2009, Ogundare et al., 2014). Gould et al., (2012) studied the degradation of cyanide to thiocyanate, and further pathways for biodegradation of thiocyanate. Twenty strains of bacteria have been isolated that can transform thiocyanate to sulphate, ammonia (or nitrate) and carbon dioxide coming from genera such as *Bacillus, Acinetobacter, Pseudomonas* and *Thiobacillus* (Boucabeille et al., 1994; Hutchinson et al., 1965). Biodegradation test shows that ammonium thiocyanate is degraded 80% within 28 days, and in OECD countries thiocyanate is regarded as biodegradable (Wilson-Corral et al., 2012). As a result, although there is a concern about the use of cyanide that can create environmental and health problems (González Valoys et al., 2022) modern society can safely utilize substances that are potentially hazardous and have the ability to assess and manage the associated risks (Logsdon et al., 1999).

In gold processing, alternatives to replace cyanide, such as thiosulphate, thiourea, iodide, etc., have been studied (Hilson and Monhemius, 2006; Vieira, 2006; Grayson, 2007), but no relevant applications have been implemented in either conventional or artisanal operations. Most companies have great inertia and resistance to introducing new metallurgical methods on a large scale to replace well-established cyanidation processes. The artisanal miners and processing centers have neither skills nor capital to adopt methods that require more sophisticated chemical controls than the cyanidation currently uses.

The following sub-chapters reports on the relevant literature review of the processes investigated and reported in this thesis.

2.4.1 Cyanogenic Plants

Many plants contain glycosides that can be converted to cyanide by hydrolysis (Ballhorn, 2011). The plant does not contain cyanide, but it is generated as a plant defense mechanism to intruders. Cyanogenic glycosides are non-toxic substances intrinsically (Bolarinwa et al., 2016). The disruption of the plant cell structure coalesces the glycosides with the corresponding β-glucosidase enzymes, producing sugars, and cyanohydrin that spontaneously decomposes into hydrocyanic acid and a ketone (Bolarinwa et al., 2016). Hydrocyanic acid (HCN), also known as free cyanide, is not stable in solution at acidic or neutral pH and volatilize. Table 2-1 contains some of the plants that have cyanogenic glycosides in addition to levels of HCN that can generate in different parts of these plants.

Prunus family contains glycosides, prunasin, prulaurasin, and amygdalin, which are stored in the vacuole of the plant cell (Knight and Walter, 2002; Radostits et al., 2000). The chokecherry, on average generates 1430 mg of free cyanide/kg of fresh leaves. However, a sample of western chokecherry leaves is reported to produce around 3.68 mg of free cyanide/kg of fresh leaves (Knight and Walter, 2001; Radostits et al., 2000).

Table 2-1. Cyanide concentration in some tropical foods (Nartey, 1980)

Tropical Foodstuffs	mg HCN/kg
Bamboo/ Immature shoot tip	8000
Cassava (bitter)/ Dried Root Cortex	2450
Cassava (bitter)/ Leaves	310
Cassava (bitter)/ Whole Tubers	395
Cassava (sweet)/ Leaves	468
Cassava (sweet)/ Whole Tubers	462
Sorghum/ Whole immature plant	2500
Lima Beans from Burma	2100
Lima Beans from Java (colored)	3120
Lima Beans from Puerto Rico (black)	3000

In one Australian study, free cyanide-generating flaxseed reported 360– 390 mg/kg. Flax (*Linum usitatissimum*) has a high content of linolenic acid and dietary fiber and has the least toxicity among all cyanogenic foods, so it is considered an interesting plant (Chadha et al., 1995; Cunnane et al., 1993).

According to Ikediobi et al., (1988) four Nigerian varieties of sprouted sorghum were found to increase cyanogenic glycosides by 4000–7000% 2–6 days after sprouting. In addition, the authors stated that at least 99% of the glycosides are concentrated in the shoots and roots. In another study, 36 samples of fresh green sorghum were collected to estimate the cyanide content at various stages of growth. Results indicated that the concentration of free cyanide increased from about 6.98 mg/kg plant at the height of 46 cm to a maximum of about 25.4 mg free cyanide/kg plant at 80 cm of height. The cyanide decreases gradually to about 0.42 mg/kg at 180 cm in length (Al-Sultan, 2003).

Bamboo has over 1250 species and 75 genera across the world (family Poaceae). If these plants are not harvested at the right time once they have sprouted, they synthesize an acidic flavor, which contains the toxic cyanoglycoside, taxiphyllin. Disruption of plant cells results in the breaking down of taxiphyllin to cyanohydrins and sugars and consequently the production of hydrocyanic acid and aldehydes and ketones (Conn, 1979; Rosling, 1994). Fresh bamboo shoots generate levels of free cyanide as high as 25 mg /kg, while dried, canned, or boiled bamboo shoots produce about 5.3 mg of free cyanide/kg (Tang et al., 2008; Ding and Wang, 2018).

Lima bean's response to cell damage is the synthesis of toxic hydrogen cyanide (HCN) from cyanide-containing compounds within the plant (Jones, 1998; Ballhorn, 2008) as a defense mechanism. Raw lima beans produce 5.2 mg of free cyanide/kg (Adeniran et al., 2013).

Maize (*Zea mays*), also known as corn, is used widely as food in the most parts of the world. Nwaichis et al., (2013) conducted an experiment to determine the cyanide generated by the plant. They reported that raw maize (Zea mays) generates only 0.02 mg of free cyanide/kg of the plant.

Cassava (*Manihot esculenta Crantz*), is a root originally from the Amazon, that is currently extensively cultivated in tropical and subtropical regions of the world. There are 98 species of cassava, and 800 million people depend on it as a staple food (Rogers and Appan, 1973; Byju and Suja, 2020). Cassava is the third most important source of calories in the tropics, after rice and corn (Oke et al., 1990). While low consumption is reported in Europe, it is increasing as a result of the high rate of immigration of Africans (Kolind-Hansen and Brimer, 2010).

World cassava production was about 124 million tonnes in 1980 and has more than doubled to 292 million tonnes by 2017, of which Nigeria produced 20.4%, DRC 10.8%, Thailand 10.6%, Indonesia 6.52%, and Brazil 6.47% (Byju and Suja, 2020; Otekunrin and Swicka, 2019).

Farmers classify cassava roots based on their taste into "sweet or cool" and "bitter," which represents the inherent cyanogenic glycoside content and consequently determines the potential toxicity (Chiwona-Karltun et al., 2015). Tasting of the tip of the root reveals the bitterness and predicts the cultivator's glycoside levels (Chiwona-Karltun et al, 1998).

Prolonged consumption of bitter cassava can cause diabetes mellitus, hypothyroidism by iodine deficiency, and other neurological disorders such as konzo, a paralytic disease in the legs, commonly observed in African countries (FAO, 2011; Gbadebo and Oyesanya, 2005; Morrison et al., 2006; Bradbury, 2006). In addition, it is reported that chronic exposure to cyanide from cassava is associated with hypothyroidism and goiter in areas with low iodine intake (EFSA, 2019). Moreover, a hypothesis has been proposed that cyanide exposure through consumption of cassava could be associated with type 2 diabetes in malnourished populations, although more scientific evidence is needed (EFSA, 2019).

Cassava root tubers have a high amount of starch and little protein (less than 5% of the dry weight), while the leaves are rich in valuable proteins, minerals, and vitamins (Montagnac et al., 2009). High levels of cyanogenic glycosides were reported in both roots and leaves (linamarin and lotaustralin in a 20:1 ratio) of the bitter cassava cultivators (EFSA, 2019).

Cassava contains two cyanogenic glycosides: 95% linamarin and 5% lotaustralin. According to Jaszczak et.al, (2017) linamarin is present only in bitter cassava. The hydrolysis of linamarin by the available enzyme in the plant cells, linamarase, generates the HCN. Some varieties of bitter cassava can produce 1550 mg of free cyanide/kg fresh root (Burns et al., 2012). When the cassava root is crushed, the hydrolysis process starts generating HCN.

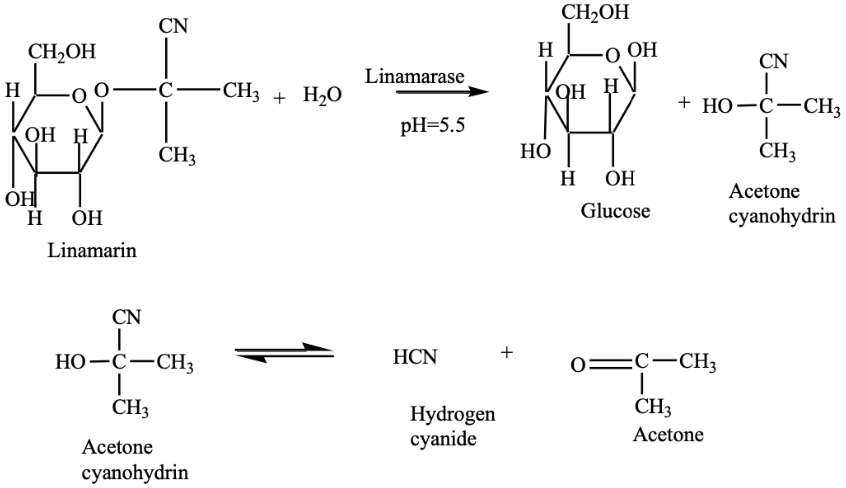

Figure 2-4. Hydrolysis of Linamarin (Wangari, 2013).

Nambisan and Sundaresan (1994) reported high levels of cyanogenic glycosides in cassava leaf, stem, and root peel tissues. It has been reported that cassava roots produce less free cyanide levels

(10- 500 mg/kg dry matter) (Siritunga and Sayre, 2003) than leaves (53-1000 mg/kg dry matter) (Wobeto et al., 2007). The center of the cassava roots produces less free cyanide (37 mg/kg) than the peripheral part of the root (135 mg/kg) and the root cortex (282 mg/kg) (Heuberger, 2005). According to Gomez and Valdivieso (1985) and Dufour (1988), low-cyanogenic cassava species have considerably lower linamarin concentration in the pulp than in the peel, while in high-cyanogenic types; linamarin is distributed more evenly throughout the entire root. The possibility of a correlation between the glycoside content of the peeled root and the leaves is low. It seems that leaves tend to contain higher concentrations of cyanogenic glycosides in both low- and high-cyanogenic varieties (Gomez and Valdivieso, 1985). Research on cassava roots revealed that the mean cyanogenic glycoside level is 29 mg free cyanide equivalent per kg of the wet root (range 1 – 123 mg/kg) in 132 roots from sweet varieties, while in 360 roots from bitter species the level of free cyanide generated was 153 mg/kg (range 22 – 661 mg/kg) (Chiwona-Karltun et al., 2004).

According to a WHO report, by Simeonova et al, (2004), bitter cassava dried root cortex, leaves and whole tuber can produce up to 2360, 300, and 380 mg of free cyanide/kg, respectively. The enzymatic reaction of cassava that generates free cyanide is based on the hydrolysis of linamarin, the main cyanogenic glycoside in bitter cassava (Bolarinwa et al., 2016).

During the current decade, growth in cassava production is likely to accelerate and cassava has emerged as a multipurpose crop in developing countries (Howeler et al., 2013). In Brazil alone, there are 1.5 million people involved in the production of flour using bitter cassava, as it is less expensive to cultivate than sweet cassava. In 2017, 706,652 tonnes of cassava flour produced by 355,207 flour mills ("casas de farinha") were registered, in which nearly 17% were situated in the Bahia State in rural areas (IBGE, 2017).

In order to prepare the flour, operators manually peel the cassava and crush it in a grinder (Figure 2-5 & 2-6). The paste is transferred to a cotton bag and pressed to remove the liquid that corresponds to 30-40% of the root weight. In this process, the glycosides are converted to free cyanide. The fluid "manipueira", which is the indigenous name for the liquid inside the cassava plant, is recklessly disposed of on the ground around the mills, and when fermented, creates a nasty odor, and attracts insects (Torkaman et al., 2021). Flour mills face a serious problem of disposing of large amounts of "manipueira" (300 L/tonne of the root) (Nitschke and Pastore, 2003), which represents a risk for domestic animals, and it is also a sanitation problem due to the fermentation of the liquid with consequent accumulation of mosquitos.

Later, the pressed material is heated on a large disk at 70-80°C to remove excess liquid and produce the flour. The flour producers prefer to plant bitter cassava as they have less value in the market than the edible sweet cassava. Anecdotally they believe that bitter cassava contributes to the flour with better taste. In Malawi, farmers reported that they cultivate mostly bitter varieties for three main reasons: to prevent human theft, lessen spoilage caused by animals and reduce the possibility of unplanned harvesting (Chiwona-Karltun et al., 1998). There are 5 to 10 people working in these local flourmills, while their average monthly salary is 200 US$ per person (Torkaman et al., 2021).

Figure 2-5. Cassava flour millers peeling bitter cassava, Cruz das Almas, Bahia, Brazil

Figure 2-6. Manufacturing cassava flour in Cruz das Almas, Brazil

The current research reported herein is targeted to leach gold from ore with a solution obtained from bitter cassava. “Manipueira”' usually represents 30% of the cassava root weight. In the case of bitter cassavas, it may be a source of cyanide for gold extraction that can be an option to replace mercury in AGM.

In the leaching process, the gold particles in the ore must be exposed to the free cyanide from the cassava liquid. In an oxidizing environment, created by intense agitation or addition of an oxidizing agent, gold forms a soluble complex with cyanide:

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^-$$

The stability of the free cyanide (HCN or CN^-) is pH-dependent. At lower pH, HCN (aq) is more dominant which continuously volatilizes as HCN (gas). In addition, HCN (aq) does not leach gold at a sufficiently fast rate to compete with the kinetics of CN^-. Maintaining the right pH level is crucial for efficient gold cyanidation, as high alkalinity can slow down the process. To balance the pH level and prevent the generation of hydrogen cyanide, it is recommended to keep it around 10.5 (Marsden and House, 2006). This will help accelerate the gold leaching process.

2.4.2 Dimethyl Sulfoxide

Utilizing aqueous solutions for dissolving gold has been extensively studied for decades (Marsden and House, 2006). However, a few nonaqueous solutions have been investigated for this purpose. Nakao and Sone (1996) introduced iodine–iodide–acetonitrile solution for the process of gold dissolution in the presence of heat. The advantage of this system is the possibility of reusing the leaching solvent, which contributes to less reagent consumption. Chloroform solutions of cetyltrimethylammonium bromide (CTAB) used for gold oxidation by Mortier et al. (2005) resulted in gold dispersion as nanoparticles in chloroform solution. Another study by Lin et al., (2010) investigated the mixtures of thionyl chloride ($SOCl_2$) and certain organic solvents/reagents (pyridine, N, N-dimethylformamide, and imidazole) to dissolve gold and recovery by roasting. High toxicity and flammability due to these mixtures' high vapor pressure inhibit their utilization on an industrial scale even though they have some advantages.

Abbot et al. (2003) raised the possibility of using Deep Eutectic Solvents (DES) to dissolve metal oxides. The difference in solubility of metal oxides in DESs provides the ability to utilize DESs for the selective recovery of metals. A DES is an ionic liquid consisting of two or three cheap and safe components with self-association, often through hydrogen bond interactions, to form an eutectic mixture with a lower melting point than each component (Zhang et al., 2012). In most cases, DES is mixed with a quaternary ammonium salt with metal salts, or a hydrogen bond donor can form a complex with the halide anion of the quaternary ammonium salt. The ability of DESs to donate or accept electrons or protons to form hydrogen bonds contributes to excellent dissolution capability (Zhang et al., 2012). Jenkin et al. (2016) proposed that ionic liquids could provide new environmentally friendly approaches to processing a variety of ores, particularly those that are difficult and energy-intensive to treat. In partnership with the University of Leicester, Argo Natural Resources announced that they developed a process using deep eutectic solvents to recover precious metals. The Argo team is commercializing DES for applications in metals recovery (Mining Global, 2019). The offered process by this company is a propriety process, and the price point for a laboratory test is around £1 Million.

Yoshimura et al. (2014) successfully used industrial-grade Dimethyl sulfoxide (DMSO) as a lixiviant for gold extraction from e-waste. DMSO is a water-free reagent, and FDA approved chemical, non-toxic, low-cost, biodegradable, and widely available. Regulatory authorities do not consider DMSO carcinogenic, used as a neutral solvent in the Ames mutagenicity tests. High concentrations exposure tests on organisms by contact, ingestion, or inhalation have shown low toxicity. DMSO includes the safest category of solvents, class 3, with low toxic potential (FDA, 2018). Due to the possibility of DMSO exposure through the handling or using process, skin contact with humans and animals has been widely studied. Results show that exposure to large dosages over extended periods contributed to negligible effects on the skin, like minor irritation, itching, burning, and low degrees of toxicity through skin adsorption (Gaylord Chemical, 2022).

This process is based on the solvation potential of both Cu (I) and Cu (II) ions in DMSO. As a result, adding $CuCl_2$ or $CuBr_2$ in DMSO causes Cu^{2+} ions to act as a potent oxidizing agent, contributing to oxidizing the gold while Cu^{2+} reduces to Cu^{+} until it reaches equilibrium (Yoshimura and Matsuno, 2016). The dissolved gold forms a complex with halogens (Marsden and House, 2006). The dissolution of gold in DMSO containing $CuCl_2$ occurs via the following reactions:

$$\mathrm{Au\ (s) + 3[CuCl_3] + 4Cl^- = [AuCl_4] + 3\ [CuCl_2]^-}$$

$$\mathrm{Au\ (s) + [CuCl_4]^{2-} = [AuCl_2]^- + [CuCl_2]^-}$$

Adding water to the DMSO changes the solution characteristics resulting in high redox potentials of gold in the mixture. DMSO and water do not form an azeotrope, making the separation process by simple distillation and allowing the solutions to be reused (Yoshimura et al., 2014). The same article suggested that the precipitation of copper can be prevented by adding an aqueous acid solution to the pregnant DMSO so that only gold will be selectively precipitated.

DMSO is a nontoxic polar solvent. It is widely used in pharmaceutical, electronic, and chemical fields such as solvent cleaning applications, paint stripping, and polymers' synthesis and processing. The USA, France, Japan, and China are the primary producers of DMSO. Major vendors/manufacturers in the market are Gaylord, Toray Fine Chemicals (TFC), Arkema, Hubei Xingfa, Shanxi Yangmei Fengxi, Yankuang Lunan Chemicals, Zhuzhou Hansen (QYResearch, 2020). As reported by Global Industry Analysis Inc (2022), during the COVID-19 crisis, the global market for Dimethyl Sulfoxide (DMSO), estimated at US$226.1 Million in the year 2020, is projected to reach a revised amount of US$341.7 Million by 2027. In 2023 the production of DMSO is estimated to be 129000 tonnes. The indicative pricing reported by Gaylord for larger quantities (>1,000 MT) is around $3.50/ lb FCA, Tuscaloosa (not freight inclusive) in the current market. However, this value depends on several factors, including packaging and volume requirements, etc. (Mentioned by the Gaylord Chemical Company Director in a conversation).

2.4.3 Merrill-Crowe Process in Pulp

After the gold in an ore or concentrate is exposed through a comminution process, the next step is to dissolve it, followed by precipitation (for example with zinc) or adsorption (e.g., activated carbon or resin). Zinc precipitation was one of the prevalent methods for the direct recovery of gold from clarified cyanide solutions, introduced in late 1980 (Miller, 1981). In the initial process, a gold-bearing cyanide solution gets in contact with a bed of zinc shavings. The method was not very successful regarding the quick change of zinc to passive condition, preventing further gold deposition. However, the process improved in a short time after first introduction to increase the process efficiency with approaches such as: addition of lead salts to the process in order to keep the zinc active for gold precipitation, substitution of zinc dust for zinc shavings to have more surface area to promote gold precipitation and reducing oxygen amount in the gold-bearing solution to inhibit zinc oxidation (Muhtadi et al., 1988). Utilizing clarified, de-aerated leaching solutions was the next step in modifying of this process, which is referred to Merrill-Crowe process after its pioneers (Muhtadi et al., 1988). This process is popular in conventional mining operations when the gold ore is rich in silver, usually to remove excess silver from the cyanide solution. When using activated carbon, silver hinders gold's adsorption on the carbon surface (Marsden and House, 2006). In Ecuador, small operations use zinc to remove excess silver followed by activated carbon to sequester the gold in solution (Velasquez et al., 2011). The chemistry behind the gold precipitation (cementation) process is that gold and silver metals are more noble than zinc. In other words, they prefer to be reduced to their native states as Au^0 and Ag^0 than remaining in the complex with CN (Muhtadi et al., 1988). Gold precipitation occurs according to the following reaction (Zadra et al., 1952):

$$2Au(CN)_2^- + Zn = 2Au + Zn(CN)_4^{2-}$$

While the gold is precipitating, the zinc combines with the cyanide to form a zinc-cyanide complex.

The Merrill-Crowe process requires low oxygen activity in the solution; otherwise, the precipitated gold reacts again with gold to solubilize it. Velasquez et al. (2011) observed that Ecuadorian processing centers conduct the zinc precipitation without using vacuum. This resulted in 6% of the gold already solubilized in the cyanide remaining in the solution. The process of obtaining gold in these centers takes a long time as the operators do not filter the solution, only counting on gravity to settle the solids to allow the siphon of the rich cyanide solution to PVC pipes filled with zinc shavings. The zinc-rich cyanide solution is re-circulated to the tanks to keep leaching the ore, and the process of decanting and siphoning the solution is repeated for five more days. Filtration equipment is an expensive piece of equipment for rudimentary processing centers.

Although the carbon adsorption process is widely used these days for the recovery of valuable metals, zinc precipitation is still preferred by artisanal processing centers over carbon adsorption when ore has a high amount of silver or in the presence of some species that can cause interference with carbon adsorption. Due to the costly carbon adsorption process, for small-size operations, zinc precipitation can be a more cost-effective option (Marsden and House, 2006).

Using aluminum for gold precipitation from alkaline cyanide solutions was initially proposed and patented by Moldenhauer in 1893 (Fleming, 1992). Although it has some advantages over zinc, the process has yet to be applied widely because of the more beneficial economics of zinc. Aluminum oxidizes rapidly in the presence of oxygen; as a result, deaeration of the solution is needed prior to the precipitation process (Marsden and House, 2006).

The overall stoichiometry of the gold precipitation reaction in the presence of Al is:

$$3Au(CN)_2^- + Al + 4OH^- = 3Au + 6CN^- + AlO_2^- + 2H_2O$$

$$AlO_2^- + 2H_2O = Al(OH)_3 + OH^-$$

The equation shows that the aluminum metal reduction is a three-electron reaction compared to zinc which is a two-electron reaction. Also, in the Al precipitation process, gold cyanide reduction yields 2 moles of cyanide for every mole of gold. In contrast, in the zinc precipitation reaction, zinc consumes 2 additional moles of cyanide for every mole of gold precipitated. Consequently, when Al is involved, gold precipitation effectively regenerates the cyanide.

A downside of using aluminum is that lime cannot be used for keeping the pH high as it generates highly insoluble calcium aluminate, which tends to foul filters and contaminates the final gold precipitate. When the pH > 12, the reaction favors the aluminate species, avoiding passivation of the aluminum surface by hydroxide layer formation. (Marsden and House, 2006). For gold extraction from solutions with minimal amount of silver, aluminum is less effective than zinc. However, it works well for the precipitation of silver, or both gold and silver, from pregnant solutions containing >50 mg/L silver (Marsden and House, 2006).

In this research, the next phase was to investigate modifying the Merrill-Crowe process by eliminating the solution filtration step to offer a simpler and faster method for artisanal miners. In other words, the recovery process was done in the pulp solution.

2.4.4 Chloride Process

In the late 19th century, the chloride process was prevalent before the cyanidation process. It was applied mainly for pre-treating refractory and carbonaceous ores in several plants throughout the United States in the 1980s (Marsden and House, 2006). The initial process was as follows; chlorine gas was pumped into a wooden tank containing ore with 6% moisture in a covered vat for a period of 12 to 18 hours. After the desired time, the extracted gold solution was poured into the bottom of the tank by opening the vat. The collected solution was sent to the precipitation vat for gold precipitation by adding iron sulfate. Silver chloride formed through the process was washed away by adding sodium hyposulfite, followed by calcium polysulfide. The generated silver sulfide was precipitated, roasted, and then melted with scrap iron and borax. Reported recoveries by this method were about 80% (Eissler, 1888).

Chlorine application is a proven method in gold-refining and electroplating processes (Feather et al., 1997; Viñals et al., 2006). The Wohlwill and the Miller processes are industrial-scale examples of gold refining with the chemical procedure.

The Wohlwill process occurs in an electrolytic cell where the impure *doré* bar plays the role of an anode, and thin sheets of pure gold (24K) are served as a cathode. Chloroauric acid ($HAuCl_4$) is an electrolyte responsible for passing electricity. Through the process, gold and other metals dissolve at the anode, and pure gold is plated onto the cathode with ion transfer by chloroauric acid. The process is complete when the anode is totally dissolved, and 99.999% pure gold is deposited at the cathode (Renner et al., 2000).

Miller's process is based on blowing pure chlorine gas through molten impure gold to generate reactions with metals and forming chloride compounds that float to the slag. By the end of the procedure, gold with 99.95% purity is obtained (Noyes, 1993). Successful refining procedures by this method motivated Vinals et al. (1995) to explore applying this technology in mineral processing by investigating the kinetics of aqueous leaching with chloride compounds of suspended gold particles. Engineers' primary problem in the 1800s was the corrosion in agitated steel tanks resulting from the leaching process.

In the 1990s, several patents based on the bromine/bromide systems were obtained, resulting in renewed interest in halides for gold leaching purposes (Pesic et al., 1992). Regarding the increasing refractory nature of ores and higher gold prices in recent years, a resurgence in the development of halide-based gold-leaching processes has resulted (Aylmore, 2005).

Halogens are very reactive to other ore minerals, especially sulfides. As a result, in the halide-leaching applications, reagent consumption would be very high if the ore contained significant sulfide minerals. In recent years, efforts have been focused on establishing ways to recover and recycle reagents to reduce costs effectively.

All halogen-based gold leaching procedures require high-oxidation conditions. The general equation explaining the reaction between gold with chlorine or bromine is (Aylmore, 2005):

$$2Au + 3X_2 + 2X^- = 2AuX_4^- \qquad X = Cl \text{ or } Br$$

The $AuCl_2^-$ complex is first formed, which rapidly gets oxidized to $AuCl_4^-$, as noted by Nesbitt et al. (1990) and Sun and Yen (1992). The stability of the Au(III)-chloride complex ($AuCl_4^-$) is influenced by the pH level of the solution, and the process necessitates high levels of chloride and chlorine, along with elevated temperature and increased ore surface area, as stated by Aylmore (2005). The complex is only stable at pH < 3.0 unless a sodium chloride concentration higher than 100 g/L is maintained. At a high pH value of 8, the hypochlorite ion (ClO^-) is the dominant oxychloride species, and the dissolution rate of the gold is very low.

In the early 1900s, cyanidation became widespread due to its benefits over chloride leaching. A faster extraction rate leaches silver and gold in the same step and using more straightforward equipment without the need to be corrosion-resistant are the advantages offered by the cyanidation process (Eissler, 1888). The gold-cyanide complex is very stable and does not decompose in most applications. However, the stability of the gold halide complex depends on the solution pH level, composition (regarding the halide concentration), solution potential, and the presence of reductants (such as metals and sulfidic minerals) in the ores.

A high solution potential is required to avoid the precipitation of metallic gold, which can be provided by a residual amount of oxidant in the process (Tran et al., 2001).

2.4.4.1 iGoli Extraction Process

iGoli is a simple and highly effective mercury-free gold extraction process developed in the 1990s by Mintek, a South African research center (Veiga, 2020). This method utilizes dilute hydrochloric acid (HCl) and sodium hypochlorite (NaOCl) to leach gold concentrate. Once the gold solution has been concentrated through the filtration process, sodium metabisulfite ($Na_2S_2O_5$) can be added to induce gold precipitation. This method, known as the iGoli process, has been utilized by some artisanal miners in South Africa. Artisanal and small-scale miners use sluice boxes, followed by panning, to concentrate the gold. Then apply the chlorine solution, a mixture of pool acid and bleach (NaOCl), to extract the gold from the concentrate. Gold and other metals, such as base metals and ferrous iron, dissolve in the chlorine environment. The next step is filtration to separate the gold-loaded solution and the pulp. Then sulfur dioxide, sodium metabisulphite, is introduced to reduce the gold ions present in the solution to a metallic gold powder. The liquid waste can be neutralized by adding lime/ limestone to destroy or precipitate all base metals and ferrometals available. The advantages of this process make it critical to artisanal and small-scale miners. It has high gold extraction delivering a very pure product. Solid waste is mostly environmentally friendly silica, and the liquid effluent can be treated easily. In an overview study, Krishnan et al. (2021) reported the chlorination process as a safe, economical method for gold extraction. It can substitute mercury use in AGM, resulting in less harm to miners and the environment. In addition, it has economic benefits due to its high recoveries, product purity, and simple waste management. Finally, refractory gold, which is very difficult to recover by other conventional ASM extraction methods, may be recovered by this method (Mahlatsi and Guest, 2003). Despite the advantages, some chemical skills are necessary for implementing this process as an amalgamation replacement. The method, as devised by the South Africans, had as a target the African micro-miners producing some few grams of concentrates per day and not tens or hundreds of kilograms a day, which would demand more infrastructure for the leaching, filtration, and precipitation processes. It is previously mentioned that the solutions offered so far to artisanal miners to change their technology and behavior were not wholly successful. Artisanal miners cannot invest in better costly equipment due to the lack of funds and skill and, many of the introduced methods cannot fulfill the artisanal miners' needs. The approach of this work is to present practical and affordable techniques for the artisanal mining sector. In the following chapter, the author's proposed methods lab procedure will be discussed in detail.

The reviewed literature sets the background for development of techniques for extracting gold in the next chapters subject to minimizing miners' health and environmental impacts.

Chapter 3: METHODOLOGY

3.1 Sample Used in this Study

A sample of a Colombian gold ore, mined by artisanal miners and kindly donated by the Gramalote Mine Project, was used for all the leaching tests. The Gramalote project is conducted by B2Gold which has a 50% interest in the project in joint venture with AngloGold Ashanti Limited with the other 50%.

The Colombian Central Cordillera is a mountain range that runs through the central part of Colombia, and it is known for its gold deposits. The gold deposits in the Central Cordillera are generally classified as mesothermal or epithermal, and they are typically not refractory (Shaw, 2000). Most of the gold in the Central Cordillera is not refractory, meaning that it can be extracted using traditional mining methods, including gravity concentration and cyanide leaching. This has led to the prevalence of artisanal gold mining in the region, with hundreds of thousands of small-scale miners operating in the area (Sierra Nevada Corporation, 2018).

The historical presence of artisanal gold miners in the area has been part of an engagement process of the project team. The sample was obtained from the La Maria site, which is an operation conducted by 18 artisanal miners within Gramalote mineral title with permits from the company. The site was visited in 2021 (Figure 3-1). The Gramalote Project team collected 40 kg of a representative sample and sent it to the University of British Columbia (UBC), Vancouver, Canada, for analysis and metallurgical test work.

Figure 3-1. La Maria mining site, San Roque, Colombia

About 20 kg of the run-of-mine La Maria head sample was crushed and ground in a lab disk mill to grain size below 0.13 mm. The ground ore was homogenized, and eight samples of 100 g were collected to send to the lab for a 30 g fire assay chemical analysis (Figure 3-2), followed by the dissolution of the bead with aqua regia and direct reading by Atomic Absorption Spectrometry (AAS) conducted by Met-Solve Analytical Services Inc., Vancouver, BC, Canada. The ore gold grade was also calculated based on the metallurgical balance of each test, i.e., based on the gold dissolved in each leaching test and the residual gold left in the tailings, after leaching.

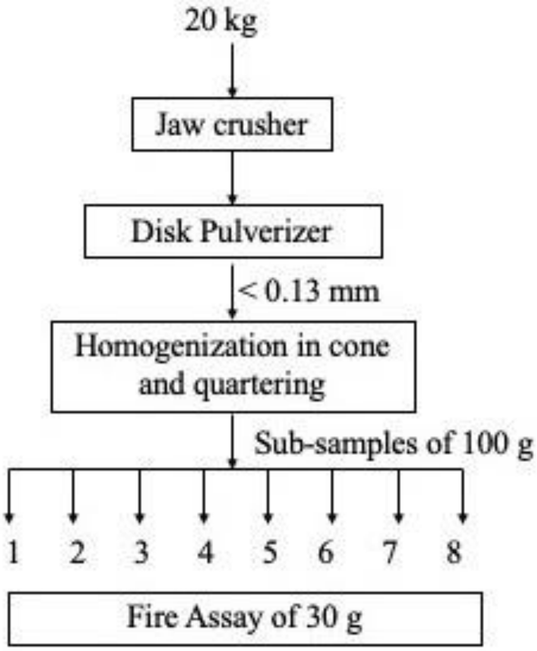

Figure 3-2. Sample Preparation Procedure

All laboratory tests of gold extraction were conducted with this La Maria head sample ground at 100% below 0.13 mm.

3.2 Different Types of Used Feedstocks

The La Maria ore sample may have been used as a source of gold in all tests. Chemicals such as NaCl (sodium chloride), HCl (hydrochloric acid), NaOH (sodium hydroxide), $Na_2S_2O_8$ (sodium persulfate), $Ca(OCl)_2$ (calcium hypochlorite) and HNO_3 (nitric acid) are commonly used in various chemical reactions, such as precipitation, acid-base reactions, and oxidation-reduction reactions.

These chemicals can be used to extract or separate compounds from the feedstocks or to modify their chemical properties.

$CuCl_2$, (copper (II) chloride) and $CuBr_2$ (copper (II) bromide), are chemical compounds used as oxidizing agents in the chemical reactions to dissolve gold with DMSO.

NaCN (Sodium cyanide) is a classical reagent used for all conventional gold mining companies in the extraction of gold from the ores. Due to its toxicity, it must be handled with extreme care and proper safety precautions, including wearing protective clothing, gloves, and goggles. Precaution was taken to destroy cyanide with hypochlorite before being safely discharged at the UBC tank for harmful reagents. A contracted company oversees final disposal of these reagents.

Zinc shavings and powder were used for gold precipitation from cyanide solution in the Modified Merrill-Crowe Process.

DMSO, or dimethyl sulfoxide, obtained from Gaylord Company is an organic compound widely used in paints and cosmetics due to its low toxicity.

K-3810 Cyanide CHEMets® Visual Test Kit Contents and Packaging is a colorimetric and portable kit for semi-quantitative analyses of free cyanide in a solution.
It's important to follow proper safety precautions when working with these compounds to avoid injury and environmental damage. This may include wearing protective clothing, gloves, and goggles, storing the compounds in appropriate containers away from incompatible materials, and ensuring proper ventilation in the workspace.

3.3 Cassava Solution as a Gold Leaching Lixiviant

3.3.1 Description of the Cassava Tests

A sample of "manipueira" was tested as a source of cyanide for gold extraction that may be an option to replace mercury in AGM. The first step of this study was to obtain a reliable analytical process to estimate the level of free cyanide in the liquid generated after cassava cell wall destruction. The next step was to conduct gold leaching tests utilizing the "manipueira" obtained from the Brazilian flour manufacturers in the Bahia State.

This had two steps:

- Step 1 - Extract and analyze cyanide from Cassava
- Step 2 - Leaching gold from the ore or concentrate by cyanide obtained from the step 1

Step 1- Investigation of hydrolysis of the glycosides:

As discussed earlier, when the cassava root is crushed, the hydrolysis process of linamarin, the cyanogenic glycoside starts producing sugars and cyanohydrin that spontaneously decomposes into hydrocyanic acid and a ketone. Hydrocyanic acid (HCN) is stable in solution at alkaline pH (above 10). The Brazilian flour shop operators squeeze the mashed cassava, releasing the "manipueira" containing HCN (aq) at pH 5.5 – 6, to the environment.

Several series of tests were conducted to investigate the hydrolysis of glycosides in cassava and generation of free cyanide. It was found out that time and pH are key parameters to improve the decomposition of the cyanohydrin into propane (acetone) and cyanide.

In conjunction with EMBRAPA Cassava and Fruticulture Center (Brazilian Agriculture Research Corporation) in Cruz das Almas, Bahia State, Brazil, "manipueira" was collected from a local flourmill for further analysis. The "manipueira" samples were collected in dark glass bottles just after the process of squeezing the cassava. In order to avoid evaporation of HCN and keep the predominant cyanide species as CN^-, 15 min after the collection, the original pH 5 to 6 of the "manipueira" was adjusted to 10.5 by adding NaOH solution to each sample. The transport of the samples from the field to the laboratory took 2 hours while the bottles were kept refrigerated in a cooler. In the laboratory, the "manipueira" was centrifuged at 40,000 rpm for 30 minutes to remove the suspended starch, generating a clear liquid. The "manipueira" ferments after one or two days in temperatures above 25^oC which could be observed by the smell coming from some unrefrigerated bottles.

Next step was to measure the amount of free cyanide in "manipueira". The visual colorimetric kit (K-3810) from Chemetrics Company was used for analysis the free cyanide levels in the "manipueira". The kit contains the chemicals barbituric acid, sodium hydroxide, isonicotinic acid, potassium phosphate, monobasic, and water. The reaction of these reagents with the free cyanide generated in the "manipueira" develops a blue color.

Figure 3-3. Color matching by utilizing colorimetric kit for analysis the free cyanide

Another analytical method used to determine the free cyanide in the "manipueira" was the Horiba cyanide ion electrode (model 8001). This cyanide ion electrode is used to measure the amount of free cyanide ions from 0.03 to 2,600 mg/L in alkaline pH (above 11). The electrode analyzes the free cyanide, in the "manipueira" by comparing the electrical potential generated by CN^- ions against the potential of a reference cell. A calibration curve with pure NaCN was derived and the readings of the electrode were interpolated in this curve. Several titration experiments were also conducted.

Liebig, in 1851 developed the first method of visual determination of cyanide by titration using silver nitrate, $AgNO_3$. Silver ions react with CN^- and form argentocyanide ion, $[Ag(CN)_2]^-$. After completion of the reaction, further addition of titrant results in the production of insoluble silver argentocyanide $Ag[Ag(CN)_2]$. The experiment endpoint is the formation of perpetual turbidity or the precipitate (Singh & Wasi, 1986):

$$Ag^{+} + 2CN^{-} \leftrightarrow [Ag(CN)_2]^{-}$$

$$[Ag(CN)_2]^{-} + Ag^{+} \rightarrow Ag[Ag(CN)_2]$$

Denigés 1895, modified the titration process by adding ammonium hydroxide (NH_4OH) prior to the titration and introducing potassium iodide (KI) as the indicator (Singh & Wasi, 1986). In the modified method, the endpoint is detected by the formation of silver iodide (AgI), a yellowish insoluble solid (Botz et al., 2013).

In 1944, Ryan and Culshaw introduced a modification to the titration process developed by Liebig, which involved the use of p-dimethylaminobenzylidenerhodanine ($C_{12}H_{12}N_2OS_2$) as an indicator. Rhodanine changes the color of the solution from yellow to pale pink due to the presence of excess silver ions once all the CN- has reacted with Ag+ (Breuer et al., 2011).

$$Rh(yellow)+Ag^{+}\rightarrow Rh-Ag(pink)$$

Titration with silver nitrate is a reliable method for analyzing free cyanide. The pH of the solution is kept at 11 by adding sodium hydroxide (NaOH) before titration to avoid the volatilization of hydrogen cyanide.

To determine the free cyanide content of “manipueira” with $AgNO_3$, the titrant and rhodanine as the indicator were utilized. In the process, a clean burette filled with $AgNO_3$ was set up, and each sample was titrated in the presence of rhodanine until its color changed from yellow to pale pink (Mousavi, 2018).

Step 2 - Investigation of the gold leaching process in the Laboratory

The gold leaching process was carried out in two series of tests:

1. 10 g of gold ore + 25 mL of partly clear “manipueira” (28.6% solid/liquid ratio, herein considered 30%)
2. 10 g of gold ore + 40 mL of partly clear “manipueira” (20% solid/liquid ratio)

For each gold leaching test, a sample of gold ore was mixed with “manipueira” at pH 10.5 (adjusted with NaOH) in a beaker. All the tests were conducted in duplicates. Samples were agitated in a shaker for certain periods of time between 8 to 48 hours. During the shaking time, pH decreased due to the fermentation reaction in the liquid. Therefore, pH was frequently checked and, if necessary, adjusted to 10.5 with NaOH solution. Once the leaching process was complete, the gold-rich solution was filtered (Whatman filter paper Grade 5: 2.5 µm), and solids were washed with distilled water to get the final solution. For each sample, gold was analyzed by Atomic Absorption Spectrometry (AAS). Each tailing (residue after teaching) was also analyzed by fire assay followed by AAS. The percentage of recovered gold was calculated based on the amount of extracted gold divided by the initial amount of gold in the sample. The analyses of the tailings provide useful information about the reliability of the metallurgical balance.

Based on the results of the previous experiments, another series of tests were conducted using another cassava variety identified in the interior of Pernambuco State, in Brazil. This cassava released a “manipueira” with 600 ppm of free cyanide.

3.3.2 Investigation of the Effects of Suspended Starch in Cassava Leaching Process

These series of tests were designed to study the interference and the possibility of preg-robbing by the cassava starch in the gold leaching process. Preg-robbing happens in the leaching process when the complex, $Au(CN)_2^-$, is removed from the solution by the ore components. The presence of carbonaceous matter in the ore, such as wood chips, organic carbon, or other impurities, such as elemental carbon, contributes to preg-robbing, which results in lower recovery in conventional cyanide leaching (Rees and Van Deventer, 2000).

Sweet cassava was used as a source of starch here. A series of leaching tests at different periods was done with pure CN solution and a mixture of CN and sweet cassava (acquired in a Vancouver supermarket). After peeling, the sweet cassava was blended and then squeezed through a piece of fabric, resulting in a solution that appeared cloudy due to the presence of starch. In one series of tests, 10 g of ore was leached with 40 mL of pure NaCN solution with 267 ppm of free CN concentration, and in the next series, with 40 mL of NaCN (267 ppm CN^-) + sweet cassava extract. pH was kept at 10.5 for all the tests. At the end of the desired time, samples were filtered (Whatman filter paper Grade 5: 2.5 µm), and final solutions were sent to the chemical lab for Au analysis.

3.4 DMSO, Organic Lixiviant for Gold Leaching

Gaylord Chemical, from the USA, the leading producer of DMSO in North America, generously provided Dimethyl sulfoxide (DMSO) commercial grade for these experiments.

The very first tests were conducted based on the experiments designed by Prof. Yoshimura at Chiba University, Japan, in conjunction with UBC. The mixture contained:10 mL of DMSO + 268.9 mg $CuCl_2$ +175 mg NaCl + 100 mg of La Maria ore, 7 hours of agitated leaching at 70 ^oC. The total gold extraction obtained in these tests contributed to further investigations with larger samples.

Each experiment included dissolving the assigned amounts of $CuCl_2$ and NaCl in DMSO (the amount of the reagent used in each experiment is dependent on the S: L ratio designed for the test) following by adding the 10 g of La Maria ore, which was constant in all the tests, agitation of each sample for the designed time (8 or 24 hours). Tables 3-1 and 3-2 show the variable values and their combinations for DMSO set of tests. At this phase of the experiments, the effect of temperature was not considered, thus all analyses were conducted at ambient temperature.

To explore the effect of temperature, the next series of experiments at 40 °C was applied. Higher temperatures would reduce the leaching time; however, additional costs and investment for the leaching tanks' heating process would be required. However, this temperature is typical in many tropical countries where artisanal gold miners work.

After the leaching process, each sample was filtered (Whatman filter paper Grade 5: 2.5 μm), and the residues were sent to a commercial analytical lab (MSA Labs) that attacked them with aqua regia and read gold by AAS. Due to the lack of AAS standards for DMSO solutions, only the residues, washed with pure DMSO after each test, were analyzed.

3.4.1 Yates Method

Yates Franck introduced Yates' algorithm in 1937. It is used to compute the estimates of the main effects and the interactions in a factorial experiment. For *k* binary coded variables, it is possible to run 2^k experiments to span all the combinatorial possibilities of variables states. In a more generalized scheme, however, one may ignore the effect of say p variables which leads to 2^{k-p} experiment runs (Riedwyl, 1998). This method enables analyzing data from a designed experiment and determining if any factors included will significantly affect the response under consideration. In chemical analysis, this algorithm can distinguish critical chemical components and the combinations that optimize gold extraction from the ore. It helps to study the effect of each factor and the effects of interactions between factors on the response variable (Box et al., 1978).

It was conducted to determine the most important chemical component(s) and conditions, as well as the combination(s) that will optimize gold extraction. To achieve this, the Yates model was used to arrive at the combination of experimental conditions for the four (4) variables (Solid-Liquid ratio, NaCl, $CuCl_2$ and, time) at 2 levels, culminating in a total of 16 experiments.

Table 3-1. Variables and levels of components in DMSO leaching experiments

Acronym	Variable	Levels	
S	S:L (ore:DMSO)	10% ($S_{0.1}$)	30% ($S_{0.3}$)
N	NaCl	0.6g (N_1)	1.16g (N_2)
C	$CuCl_2$	1.34g (C_1)	2.7g (C2)
T	Time	8h (T_1)	24h (T_2)

Table 3-2. Different combinations of variables in DMSO experiments

Sample ID	Combination	S:L (%)	Time (h)	NaCl (g)	$CuCl_2$ (g)
A1	$S_{0.3}$T2N2C2	30	8	1.16	2.7
A2	$S_{0.3}$T2N1C1	30	24	0.6	1.34
A3	$S_{0.3}$T2N2C1	30	24	1.16	1.34
A4	$S_{0.3}$T2N1C2	30	24	0.6	2.7
A5	$S_{0.1}$T1N1C2	10	8	0.6	2.7
A6	$S_{0.1}$T1N2C1	10	8	1.16	1.34
A7	$S_{0.1}$T1N2C2	10	8	1.16	2.7
A8	$S_{0.1}$T1N1C1	10	8	0.6	1.34
A9	$S_{0.3}$T1N1C1	30	8	0.6	1.34
A10	$S_{0.3}$T1N2C1	30	8	1.16	1.34
A11	$S_{0.3}$T1N2C2	30	8	1.16	2.7
A12	$S_{0.3}$T1N1C2	30	8	0.6	2.7
A13	$S_{0.1}$T2N2C2	10	24	1.16	2.7
A14	$S_{0.1}$T2N1C2	10	24	0.6	2.7
A15	$S_{0.1}$T2N1C1	10	24	0.6	1.34
A16	$S_{0.1}$T2N2C1	10	24	1.16	1.34

Additional gold leaching processes were carried out with 20 g of La Maria ore, using 0.82-3.27 g of $CuBr_2$, and 0.29-1.16 g of KBr in 100 mL DMSO for 12 h at 40 ℃. The gold precipitation process from the loaded DMSO solution was conducted by adding a weak acidic solution to the DMSO. The reason to keep the solution's pH low was to reduce the precipitation of other metals such as Cu or Fe (Yoshimura et al., 2014; Yoshimura and Matsuno, 2016).

The precipitation tests were conducted with 1.0 M H_2SO_4. In order to simplify the reagents to be more accessible at AGM sites, CH_3COOH (commercial vinegar), pure lemon juice with a pH of 2.0, and diluted lemon juice with a pH of 2.5 were used. The gold precipitation process involved agitation of the gold-loaded DMSO for 24 hours with a volume of 1 part of precipitation solution for 1 part of gold-loaded DMSO at room temperature. Table 3-3 summarizes the experimental conditions.

Table 3-3. Different combinations of variables using $CuBr_2$ and KBr in DMSO experiments

Sample ID	Ore (g)	DMSO (mL)	Time (h)	KBr (g)	$CuBr_2$ (g)	Acid Used for Precipitation
LM-1	20	100	12	1.16	3.27	Commercial vinegar
LM-2	20	100	12	0.58	1.64	H_2SO_4 (1.0 M)
LM-3	20	100	12	0.29	0.82	H_2SO_4 (1.0 M)
LM-4	20	100	12	0.58	1.64	diluted (half) lemon juice
LM-5	20	100	12	0.58	1.64	undiluted lemon juice

3.5 Modified Merrill-Crowe Process

The tests of the Modified Merrill-Crowe process used 1 liter of CN solution with 1 g/L of CN^- concentration made by dissolving 1.88 g of NaCN in one liter of distilled water. A 10 g sample of the La Maria head sample was leached with this CN solution for 24 hr. After the leaching process, the solution was divided into ten sub-samples. One sub-sample was filtered (Whatman filter paper Grade 5: 2.5 μm) to send for Au analysis. The pulp of each other sub-samples was agitated slowly for a specific time with a bag of zinc shavings inside. After the desired time, the zinc bags were removed, and the pulps were filtered (Whatman filter paper Grade 5: 2.5 μm). The final solutions were sent to the analytical laboratory for Au determination by AAS – Atomic Absorption Spectrometry.

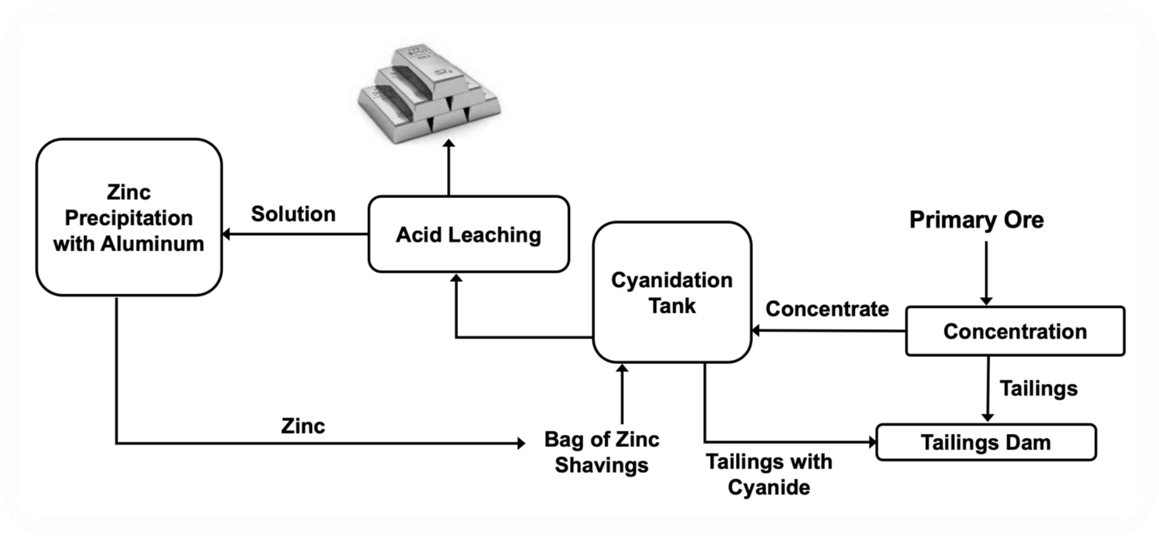

Figure 3-4. Scheme of gold precipitation by a bag of zinc shavings in the leaching tank

Another method investigated was the use of sintered zinc powder instead of zinc shavings bags. These blocks were made of zinc powder and table salt, and water in the proportion of one part of fine table salt and one part of fine zinc powder mixed in a small round mold. After consolidation, the block stayed in the water for a day to gradually dissolve the salt. The zinc block remained intact when it was sintered (Figure 3-3). This process has been developed and investigated at the Faculty of Mines of the National University of Colombia in Medellin.

Figure 3-5. Zinc powder sintered bloc

In another series of experiments, hanging bags with aluminum shavings (small foil pieces) were tested for gold precipitation. The process was the same as with zinc shavings. The pH was checked through the experiments to be 12.

3.6 Amalgamation Tests

A series of amalgamation tests were conducted in the laboratory using the same conditions as artisanal miners do in Colombia (whole ore amalgamation) to compare this method's efficiency with the ones studied earlier in the research. For the gold amalgamation with various amount of mercury and mixed with the ore in the following Hg to ore ratios of 1:50, 1:100, 1:200, 1:600. For all the tests S:L ratio was kept at 50% with the same amount of ore (10 g). All the tests were done at neutral pH. Duplicate samples were shaken for 2 hours. Afterwards, the samples were washed and filtered (Whatman filter paper Grade 5: 2.5 μm) while the gold amalgam was removed. Residues were left to dry. To determine the amount of gold that remained in the ore, 5 grams of each residue was ground and dissolved in 50 mL of hot aqua regia (40 mL HCl and 10 mL of HNO_3) for 3 hours followed by filtration (Whatman filter paper Grade 5: 2.5 μm). Each liquid sample was sent to the laboratory for Au and Hg analysis.

3.7 Chloride Gold Leaching Process

Gold leaching experiments were also designed using hydrochloric acid as the main lixiviant and different oxidizing agents.

In the first series of tests, sodium persulphate and calcium hypochlorite were applied to the same La Maria head sample. Calcium hypochlorite, $Ca(OCl)_2$, usually used to chlorinate swimming pools, contains 65% of active chlorine and when dissolved in water generates nascent chlorine. Calcium hypochlorite is also very stable and can be stored for long time (Askenaizer, 2003) and with a redox potential of nascent chlorine of 1.396 V ($Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$) (LibreTexts, 2022). The standard redox potential of sodium persulfate ($Na_2S_2O_8$) is 2.1 V (RedoxTech, 2023), which is higher than that of hypochlorite and hydrogen peroxide (1.763 V). Despite its strong oxidation potential, hydrogen peroxide was not tested as it is challenging to acquire and transport (H_2O_2 50% v/v) in developing countries. In addition, it decomposes quickly in hot climates.

The desired amount of oxidant was dissolved in a mixture of acid and water, followed by adding 5 g of oxidant. Each sample was agitated for 8 hours at room temperature. Details are described in Table 3-4.

Based on the preliminary results, $Na_2S_2O_8$ was chosen as the most appropriate oxidant for the next set of experiments. The impact of temperature was also studied in the next phase of experiments. In order to gold-chloride complexing conditions, an excess of chloride ions, 5 g of NaCl, was added to all samples.

Table 3-4.Values of the components of chloride leaching

Sample #	**Ore (g)**	**Oxidant Name**	**Oxidant (g)**	**HCl (mL)**	**H_2O (mL)**
1	20	$Ca(OCl)_2$	5	25	25
2	20	$Ca(OCl)_2$	5	25	25
3	20	$Ca(OCl)_2$	5	15	35
4	20	$Ca(OCl)_2$	5	15	35
5	20	$Na_2S_2O_8$	5	25	25
6	20	$Na_2S_2O_8$	5	25	25
7	20	$Na_2S_2O_8$	5	15	35
8	20	$Na_2S_2O_8$	5	15	35

Chapter 4: RESULTS

4.1 The La Maria Ore Grade

The eight sub-samples of the La Maria head sample analyzed by fire assay and AAS revealed a grade of 48.47 ± 6.52 (2 std) g Au/tonne of ore (ppm) (Figure 4-1). Additionally, 14 samples of cassava and NaCN leaching solutions and their respective residues were analyzed. The gold in solutions were read directly by AAS and the residues were dissolved with aqua regia, and the solutions analyzed by AAS. This obtained the feed gold grade by a metallurgical balance (Figure 4-2 and Table A-1, Appendix). The average concentration is 48.87 ± 6.30 (2 std) g of gold/tonne (ppm) of ore which is very similar to the concentration obtained by analyzing the ore samples by fire assay. The gold grade of 48.87 ppm was used for the calculations when the solution was not possible to be analyzed, such as in DMSO tests. The average copper grade of the head sample was 0.41%, and the average silver grade is 95 ppm. These results confirm the point mentioned by artisanal miners that the ore from La Maria usually has approximately two times more silver than gold. However, the price of gold is 71 times higher than silver.

A previous study of this same La Maria ore sample (Gonçalves et al., 2016) revealed that the cyanidation for 24 hours using a solution with 5 g/L (5000 ppm) of NaCN resulted in 97% gold and 71% silver extraction respectively. Additionally, a total of 99% gold extraction was achieved in 96 hours based on a calculated head of 45.26 g Au/t.

The mineralogy of a gravity concentrate, and a head sample obtained by X-ray diffraction revealed that quartz (the ore is from quartz veins) is dominant, and pyrite, chalcopyrite and amphibole are present in small amounts. The copper grade of the ore is 0.41% Cu, which translates to 1.19% of chalcopyrite.

The ore likely has no coarse gold nuggets, with medium-small size gold particles, very amenable to be concentrated by centrifugal process and/or flotation. This characteristic provides good homogenization, and the head sample grades analyzed and calculated based on metallurgical balances of each leaching experiment show consistent gold grade with minimal variation.

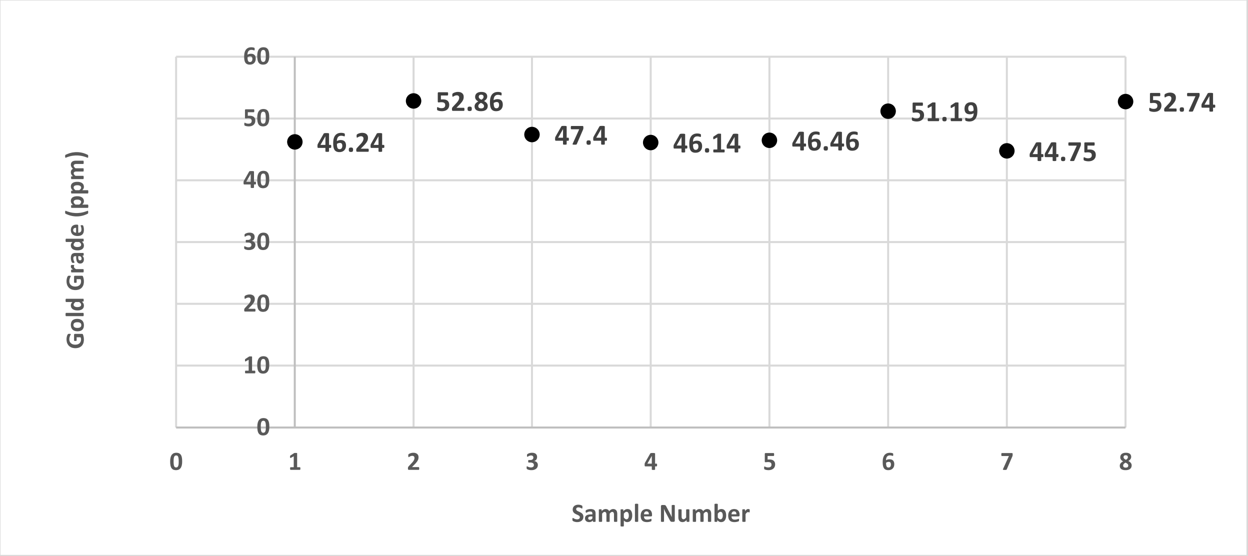

Figure 4-1. Gold grade in sub-samples (30g) by fire assay, average 48.47ppm Au

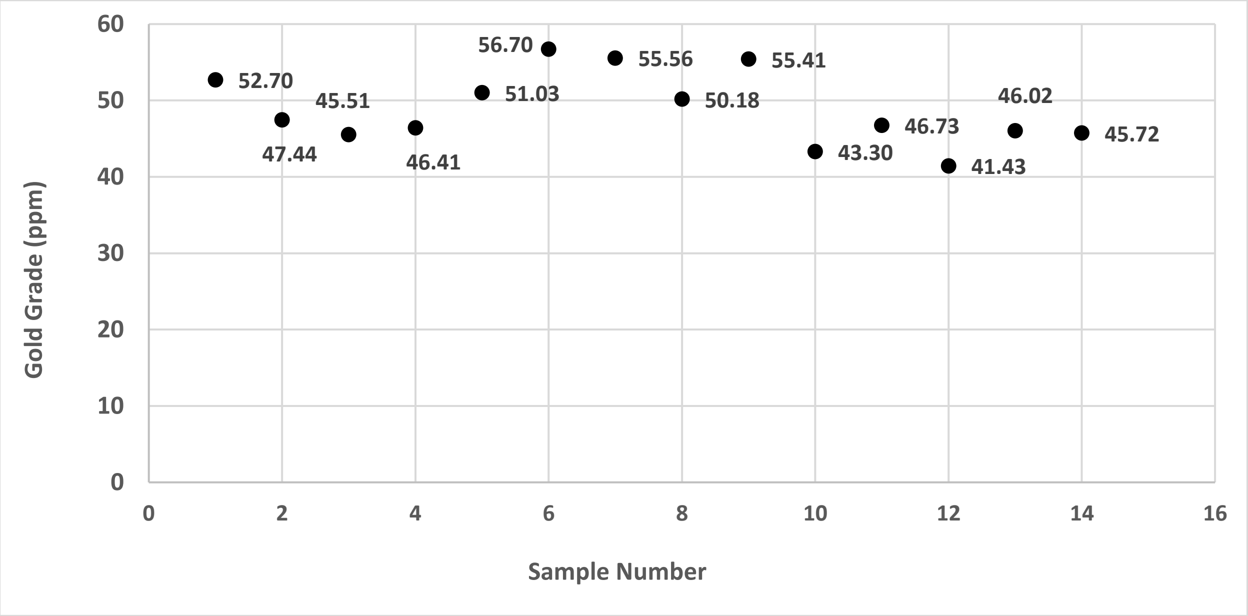

Figure 4-2. Gold grade in sub-samples (10g) by metallurgical balance, average 48.87ppm Au

4.2 Cassava

4.2.1 Investigation of Hydrolysis of the Glycosides

Free cyanide content in the "manipueira" sample measured by different methods are shown in Table 4-1. Assuming the data is approximately normally distributed, the probability of getting reliable results of free cyanide in the interval of 267± 80 ppm is about 95%.

Table 4-1 Summary of free cyanide analyses in "manipueira"

Method	Free cyanide (ppm)
HORIBA Cyanide Selective Electrode	286
Chemetrics Colorimetric Kit	210
Titration with $AgNO_3$ and Rhodanine (visual) natural pH 6	240
Titration with $AgNO_3$ and Rhodanine (visual) adjusting pH to 11	300
Automatic titration OI FS 3100 with Rhodanine	299
AVERAGE	267± 80 *

*NOTE: 2 std deviation

The colorimetric visual kit works based on the reaction of the available cyanide ions in the sample with chlorine to form cyanogen chloride (CNCl), which reacts with a stabilized isonicotinic-barbituric acid reagent to develop a blue-colored complex in proportion to the free cyanide concentration. The presence of sulfides, aldehydes, heavy metals, and thiocyanate can prevent obtaining accurate results. As the maximum reading of the kit is 1 ppm of free cyanide, it was required to dilute the "manipueira" sample before developing the color. When the "manipueira" sample was not diluted, a strong purple color was formed due to the high concentration of free cyanide. It was observed that the colorimetric reading was not affected when diluting occurs after the sample color development.

The ion-specific electrode is less practical than the colorimetric kits and frequently subject to instabilities. Constant calibrations are needed, as well as dilutions, to reduce the level of free cyanide in the analyzing solution.

Several titration experiments were also conducted. Titration with $AgNO_3$ and rhodanine (visual) at natural pH 6, titration with $AgNO_3$ and rhodanine (visual) adjusting pH to 11, in addition to automatic titration equipment OI FS 3100 with rhodanine. The end-point color with rhodanine is a salmon pink, which makes it easier to recognize it. The pH variation had little influence on the titration end point. The titration process, widely used in the mining industry, is a difficult task since the “manipueira”, even centrifuged, has a residue of starch in suspension. This makes difficult to observe the titration point.

As a result, the most practical method to analyze free cyanide in the “manipueira” is by the colorimetric method. This does not require clear “manipueira” since this may be diluted before or after the color development. Despite the semi-quantitative character of the method, which depends on the visual acuity of the analytical person to distinguish between hues of blue, the method is fast and practical for those miners to follow the concentration of free cyanide either in the “manipueira” or in the cyanidation process.

4.2.2 Investigation of the Gold Leaching Process with Cassava Juice

The results of the gold extractions in the experiments conducted with the La Maria ore leached with “manipueira” are shown in Tables 4-2 and 4-3. Parameters that play a key role in the experiments were S:L ratio (the amount of ore to “manipueira”), pH, and leaching time. Tests with 30% solids (10 g of ore + 25 mL of “manipueira”) resulted in 34% of gold extraction in 18 hours and 36% in 48 hours. While, decreasing the percentage of solids to 20%, resulting in higher and promising 36% gold extraction in 8 hours, 46% in 18 hours and 50.9% in 24 hours.

The ore was also leached with pure NaCN solution with the same cyanide concentration (267 mg/L of free cyanide) as the “manipueira” at pH 10.5 for comparison. Gold extracted in 24 h, was 70% for S/L = 30%, and 77% with S/L = 20% (Tables 4-2 & 4-3).

Table 4-2. Results of gold leaching tests with cassava (267 ppm CN^- & S/L: 30%)

Sample (no)	Time in the shaker (h)	Calculated Au Extraction (%)
1	18	33.3
1	18	35.7
2	24	28.5
2	24	39.3
3	42	35.7
3	42	29.7
4	48	38.3
4	48	33.3
Only NaCN	24	70.0

Table 4-3. Results of gold leaching tests with cassava (267 ppm CN^- & S/L: 20%)

Sample (no)	Time in the shaker (h)	Gold Extraction (%)
1	8	47.2
1	8	25.0
2	18	43.0
2	18	48.3
3	24	50.9
3	24	45.9
4	30	28.7
4	30	24.8
Only NaCN	24	77.0

In another investigation, in cooperation with the Federal University of Pernambuco, Brazil (UFPE), a variety of cassava that releases 600 ppm free cyanide was tested for leaching gold from the same ground La Maria head sample. The results of the experiments are presented in the following Table 4-4. Results show that up to 82.4% of gold extraction can be achieved with the "manipueira" containing 600 ppm of CN^- in 24 hours.

Table 4-4. Results of gold leaching tests with cassava (600 ppm CN^-)

Sample (no)	S:L (%)	Time (h)	Gold Extraction (%)
1	20	24	61.35
2	20	24	77.43
3	10	24	82.40
4	10	24	66.56
5	10	18	60.20
6	10	18	67.69
7	10	8	76.63
8	10	8	73.01

4.2.3 Investigation of the Effect of Suspended Starch in the Leaching

Table 4-5 shows the percentage of gold dissolved from the ore by NaCN as a leaching solution versus a mixture of NaCN and sweet cassava starch. In all the tests, the initial concentration of the CN^- was 267 ppm which resembles the CN^- concentration in “manipueira”. In 24 hours, the average of gold extraction was 77% with pure NaCN solution while with addition of the sweet cassava “manipueira” the Au extraction dropped to 59%.

The results obtained from this series of tests are shown in Figure 4-3 for better visual comparison. Results show that the presence of starch in the leaching solution inhibits gold dissolution. As a result, to get the best gold extraction results with the cassava, finding a way to eliminate suspended starch seems critical. In addition, the reduction in gold dissolution after 24 hours provides good evidence of preg-robbing.

Table 4-5. Gold extraction (%) by pure NaCN (267 mg CN/L) vs mixture of NaCN and sweet cassava juice

Sample Description	Time (h)	Gold Extraction (%)
NaCN+ Sweet Cassava	8	40.0
NaCN+ Sweet Cassava	8	52.9
NaCN+ Sweet Cassava	24	48.0
NaCN+ Sweet Cassava	24	69.9
NaCN+ Sweet Cassava	48	57.5
NaCN+ Sweet Cassava	48	58.3
NaCN Solution	8	77.6
NaCN Solution	24	73.4
NaCN Solution	24	80.5
NaCN Solution	48	71.6
NaCN Solution	48	82.3

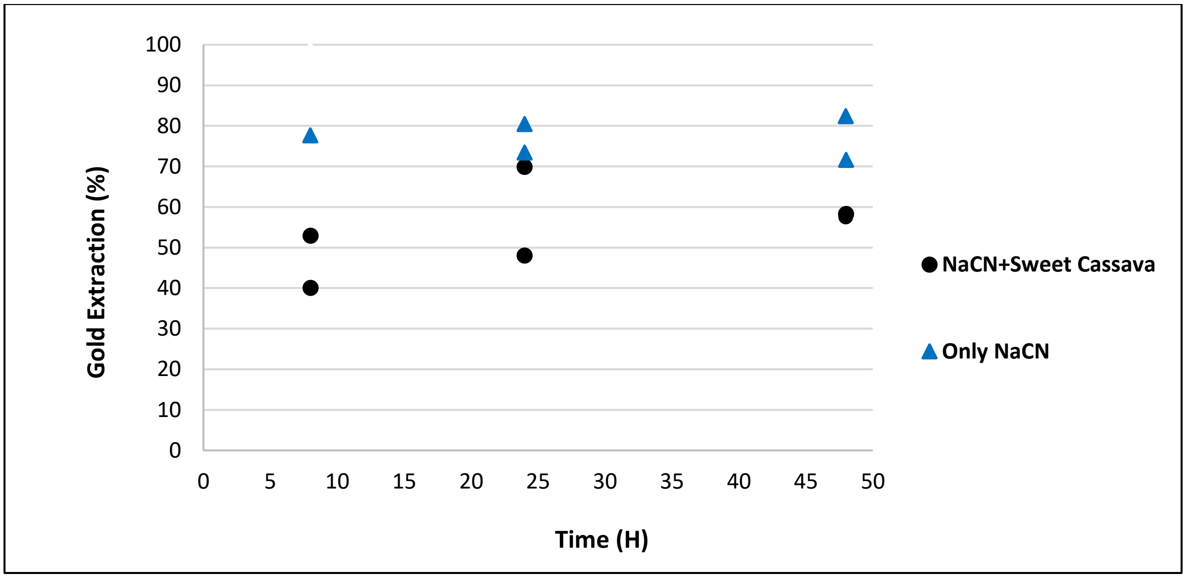

Figure 4-3. Gold extraction comparison of pure CN solution and CN-Cassava solution

4.3 DMSO TESTS

4.3.1 Gold Extraction

The gold dissolution in the DMSO of 10 g of La Maria ore was calculated based on the gold grade analyzed by fire-assay in all sixteen (16) residues obtained after filtration. The % of gold extracted was calculated considering the head sample grade of 48.87 ppm Au, as it was not possible to read the DMSO solutions in the Atomic Absorption Spectrometer due to matrix effects and being an organic compound that usually contaminates the AAS burner, and the commercial labs refused to analyze the Au-loaded DMSO. Table 4-6 shows the percentage of gold extracted by each combination of variables previously mentioned in Table 3-2. A13, A14, A15 and A16. This shows that the most effective combinations of variables regarding the gold extraction are with results of 94.68%, 93.72%, 91.28%, and 91.20%, respectively. In Table 4-7, the conditions of these tests are shown in detail.

Table 4-6. Results of the initial tests of gold extraction by DMSO

Sample ID	Au in residue (ppm)	% Gold extracted by DMSO
A1	24.67	49.52
A2	18.5	62.14
A3	9.85	79.84
A4	34.13	30.16
A5	6.69	86.31
A6	10.34	78.84
A7	9.45	80.66
A8	8.55	82.50
A9	4.93	89.91
A10	16.64	65.95
A11	19.61	59.87
A12	9.27	81.03
A13	2.6	94.68
A14	3.07	93.72
A15	4.26	91.28
A16	4.3	91.20

Table 4-7. Experimental conditions of highest Au recoveries in DMSO leaching tests

Sample ID	% Au extracted by DMSO	S:L (%)	NaCl (g)	$CuCl_2$ (g)	Time (h)
A13	94.68	10	1.16	2.7	24
A14	93.72	10	0.6	2.7	24
A15	91.28	10	0.6	1.34	24
A16	91.20	10	1.16	1.34	24

4.3.2 Yates Analysis

The Yates method, for the purpose of analyzing data obtained from the DMSO series of tests, can estimate the factor's effects and their relevant interactions (Box et al., 1978). The test conditions are detailed in (Table 3-2). After using the algorithm, Yates analysis generates the following outputs, which are presented in Table 4-8. Column 2 of this table represents the effect associated with each factor and interactions between the factors calculated by the model. In the 3rd column, the coefficient of each factor and combinations of them are shown which is based on the analysis equation:

Response (Y) = Constant + 0.5* (all factor and interaction estimates = Effects)
Coefficient = 0.5* Effects
Y (%Au extracted) = 76.11 - 11.31 (S) - 1.02 (N) - 4.10 (C) - 2.03 (T) + 0.01 (SN) - 5.56 (SC) - 7.37 (ST) + 0.23 (NC) + 5.78 (NT) – 2.93 (CT) + 0.33 (SNC) + 4.49 (SNT) - 2.99 (SCT) + 0.13 (NCT) - 0.27 (SNCT)

Y represents the predicated amount for the result, which generates the most adequate percent of gold extraction.

Third column in the Table 4-8 shows associated numbers calculated by the quantile function to make a normal distribution chart, Figure 4-4, of the effects. This figure also known as the normal probability plot, is a graphical method used in the Yates model to assess the goodness-of-fit of the model. The purpose of this chart is to visualize whether the residuals (the differences between the observed and expected values) follow a normal distribution, which is a key assumption of the Yates model. The chart can be used to identify outliers and assess the overall fit of the model. Outliers are indicated by points that fall far away from the straight line, indicating that they are unusual compared to the rest of the data. A curved or non-linear pattern in the points on the chart may indicate that the model does not fit the data well, suggesting that the Yates model may not be appropriate for this dataset.

Quantiles are cut points dividing the range of a probability distribution into continuous intervals with equal probabilities or dividing the observations in a sample.

Based on the effects calculated by the method, for each factor in Table 4-8, the Yates model can predict the results of the experiments.

Table 4-9 includes the analyzed and calculated gold extraction in the laboratory versus the predicted results by the Yates analysis. All the calculations for the predictions are based on the equation generated from the method mentioned above. In the Predict 1 column, the effect of all 10 factors observed in Figure 4-4 is considered in the calculations. The model's prediction shows an error of only 0.68% of the observed data.

To study the effect of each factor in more depth, the model predictions were designed so that in each run, one factor and its combination with other factors were ignored (see Table 4-9). Columns including Predict 2, Predict 3, Predict 4 and Predict 5 in this table are these predictions generated by the model while in Column 2, the laboratory gold extraction results are presented. For instance, in Predict 2, it was assumed that factor S and its interactions with other factors did not affect the gold extraction. As a result, numbers in column 4 (Predict 2, NO S) basically show the impact of factor S on the gold extraction percentage predicted by the Yates algorithm. In the next column, the percentage of error is calculated:

% Error = (ABSOULTE VALUE (Lab observation- Yates predication)/Lab observation) *100

The percentage of error in the Yates model represents the degree to which the model's predictions deviate from the actual values of the dependent variable. A high percentage of error for a given variable in the model indicates that this variable has a significant impact on the gold extraction results.

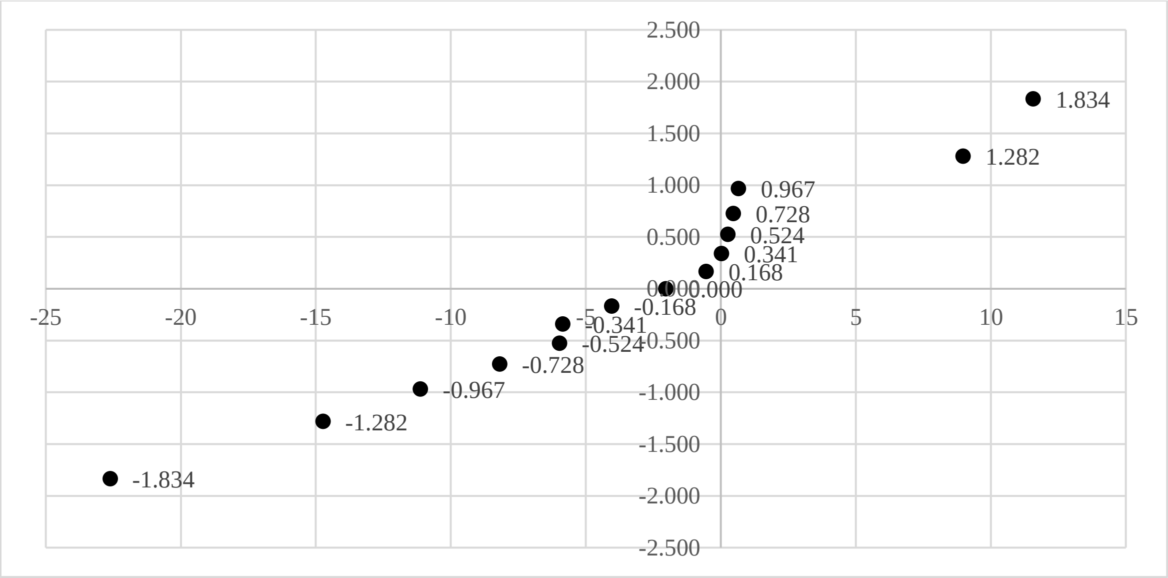

Figure 4-4. Effect of different factors on the results (Y axis: Quantile, X axis: Effect)

Table 4-8. Yates factors and coefficients used for DMSO experiments analysis

Factors	Effect	Coefficient	Quantile
S:L(S)	-22.62	-11.31	-1.834
NaCl(N)	-2.04	-1.02	-1.282
$CuCl_2$(C)	-8.19	-4.10	-0.967
Time(T)	-4.06	-2.03	-0.728
SN	0.02	0.01	-0.524
SC	-11.12	-5.56	-0.341
ST	-14.73	-7.37	-0.168
NC	0.46	0.23	0.000
NT	11.57	5.78	0.168
CT	-5.86	-2.93	0.341
SNC	0.65	0.33	0.524
SNT	8.98	4.49	0.728
SCT	-5.98	-2.99	0.967
NCT	0.26	0.13	1.282
SNCT	-0.54	-0.27	1.834

A higher percentage of error implies that the desired factor (S:L, time, and the amount of involved chemicals) has more effect on the gold extraction in the experiments. Regarding what was mentioned above, Predict 3 column shows the effect of factor N, Predict 4 column shows the effect of factor C and Predict 5 column shows the effect of factor T.

Figure 4-5 shows the gold extraction percentage obtained from laboratory experiments compared to the ones obtained from the Yates' model (Table 4-9, Predict 1 column). The Yates model predicted results were calculated using the Y formula mentioned earlier in this section considering all the variables involved in the process. Figure 4-5 shows a good correlation between predicted gold extractions and those observed in the laboratory tests, despite the calculated error being 9.97%.

Table 4-9. Comparison between gold extraction in the lab and Yates predictions

Au Extracted %	**Pred.1**	**Error %**	**Pred. 2 (NO S)**	**Error %**	**Pred. 3 (NO N)**	**Error %**	**Pred.4 (No C)**	**Error %**	**Pred.5 (NO T)**	**Error %**
82.5	88.62	1.52	86.21	4.50	80.67	2.22	84.40	2.30	86.89	5.32
89.91	77.64	5.45	86.21	4.12	77.93	13.32	85.48	4.93	76.03	15.44
78.84	87.36	1.46	72.41	8.16	80.67	2.32	79.76	1.17	85.03	7.85
65.95	75.34	25.41	72.41	9.80	77.93	18.17	62.92	4.59	72.89	10.52
86.31	92.34	1.55	83.67	3.06	83.47	3.29	84.40	2.21	90.01	4.29
81.03	58.04	19.28	83.67	3.26	70.45	13.06	85.48	5.49	55.59	31.40
80.66	89.48	1.80	70.27	12.88	83.47	3.48	79.76	1.12	87.75	8.79
59.87	56.3	6.35	70.27	17.37	70.45	17.67	62.92	5.09	54.69	8.65
91.28	85.36	1.59	76.71	15.96	91.23	0.05	92.50	1.34	86.89	4.81
62.14	73.3	6.10	76.71	23.45	70.97	14.21	46.14	25.75	76.03	22.35
91.2	82.5	1.46	85.51	6.24	91.23	0.03	93.02	2.00	85.03	6.77
79.84	71.56	19.60	85.51	7.10	70.97	11.11	64.66	19.01	72.89	8.70
93.72	87.48	1.21	61.93	33.92	94.27	0.59	92.50	1.30	90.01	3.96
30.16	54.26	55.47	61.93	105.34	39.81	32.00	46.14	52.98	55.59	84.32
94.86	86.22	1.34	72.17	23.92	94.27	0.62	93.02	1.94	87.75	7.50
49.52	51.96	9.96	72.17	45.74	39.81	19.61	64.66	30.57	54.69	10.44
AVERAGE		9.97		20.30		9.48		10.11		15.07

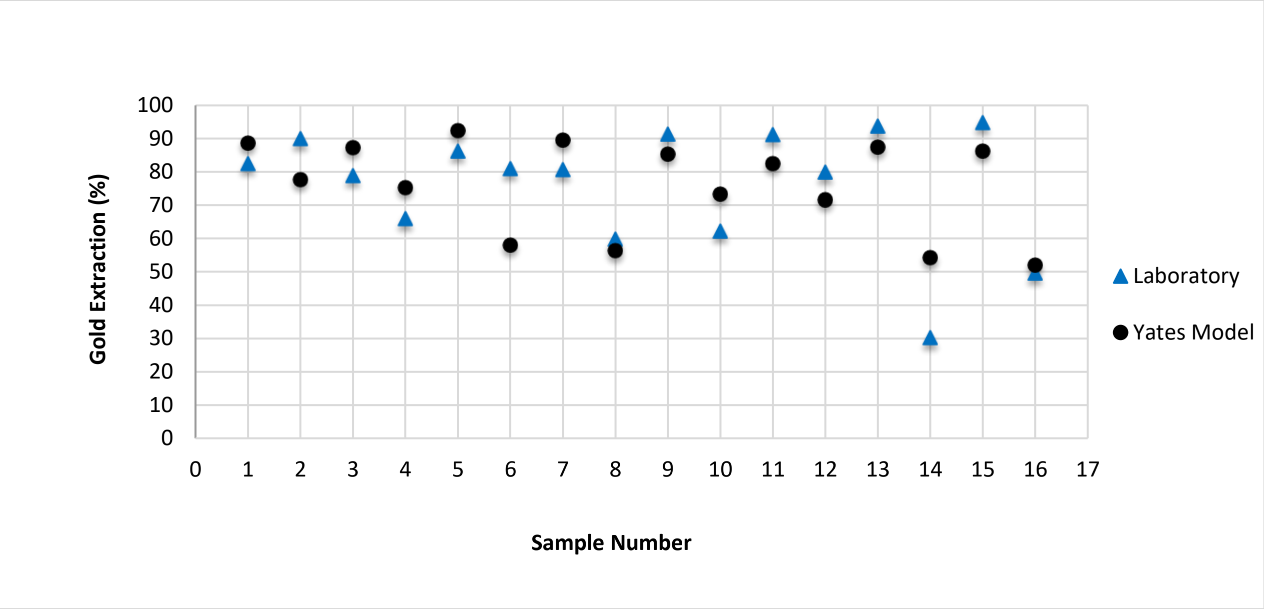

Figure 4-5. DMSO observed vs predicted results

The La Maria head sample was subjected to leaching at 40°C, and the results are presented in Table 4-10. The data shows that over 98% of gold was extracted after 2 hours of leaching. Furthermore, laboratory analysis revealed that gold extraction rates still exceeded 95% even at ambient temperature.

The gold content was extracted entirely from the La Maria samples by DMSO treatment at 40°C for 12 h with 0.28 g of $CuBr_2$ and 0.29g of KBr in 100 mL DMSO.

Table 4-10. Analytical conditions of highest gold extractions achieved by DMSO

Sample ID	**S:L (%)**	**Time (h)**	**Temperature**	**Au Extracted by DMSO (%)**
1	10	**2**	40 °C	98.81
2	10	**4**	40 °C	97.12
3	10	**6**	40 °C	97.36
4	10	**8**	40 °C	97.91
5	10	**2**	Ambient	96.50
6	10	**4**	Ambient	96.17
7	10	**6**	Ambient	95.42
8	10	**8**	Ambient	95.40

4.3.3 Gold Precipitation Tests from DMSO

The leaching tests with bromides at 40^{o}C resulted in complete (100%) extraction of gold from the La Maria ore. All the gold was leached in the presence of $CuBr_2$ and KBr (LM-3) (Table 3-3).

Table 4-11 includes the gold precipitation results from gold loaded-DMSO solution after the leaching process. Applying diluted H_2SO_4 (pH = 0) and lemon juice (containing citric acid, pH 2.0-2.5) recovered all or most of the dissolved gold. This result was the same as the previous study by Yoshimura et al. (2014) who used a pure Au sample. However, the recovered material contained other elements, such as copper and sulfur, from the partial attack of the DMSO to the 1.1% of chalcopyrite in the ore (Takatori et al., 2021). Table 4-11 confirms that 1M sulfuric acid and diluted lemon juice were the best reagents to precipitate the gold.

Table 4-11. Gold precipitation results from gold-loaded DMSO

Sample ID	Acid Used for Precipitation	Gold Precipitation (%)
LM-1	Commercial vinegar	25
LM-2	H_2SO_4 (1.0 M)	100
LM-3	H_2SO_4 (1.0 M)	89.6
LM-4	Diluted (half) lemon juice	100
LM-5	Undiluted lemon juice	100

The precipitation of gold by water addition without acid was also studied, but the gold extraction results were less than 60%.

DMSO, with a boiling point of 189 °C (Gaylord Chemical, DMSO Physical Properties), can be recycled by distilling the water at 100 °C. Vacuum distillation is a better option for low-temperature treatments. However, the boiling point of H_2SO_4 is 290 °C (Sigma Aldrich, SAFETY DATA SHEET of H_2SO_4) and the decomposition point of citric acid is 200 °C (Sigma Aldrich, SAFETY DATA SHEET of citric acid), respectively. As a result, these acidic contents will remain in DMSO. Further recycling tests are suggested.

4.4 Modified Merrill- Crowe Process

The gold extraction in the cyanidation tests with 1 g/L CN^- in 24 hours was 84%. Cyanidation of the same sample for 24 h using 5 g/L of CN contributed to 97% gold extraction (Gonçalves et al, 2016). It was not the intention of this research to increase gold extraction in the leaching process but to concentrate efforts to have high gold extraction in the modified Merrill-Crowe process (MMCP). The zinc cementation obtained 99.4% of gold precipitated in two hours (Figure 4-6) which is an outstanding result.

The theoretical mass ratio of zinc to gold in the Merrill Crowe process is 1.5:1, but due to the high concentration of silver and other metals in the cyanide solution, the recommended ratios of Zn:Au range from 5:l to 20:1 (Muhtadi et al., 1988). Zinc shavings have 500 times less surface area than powder (Marsden and House, 2006), but they are much easier to be handled in the MMCP.

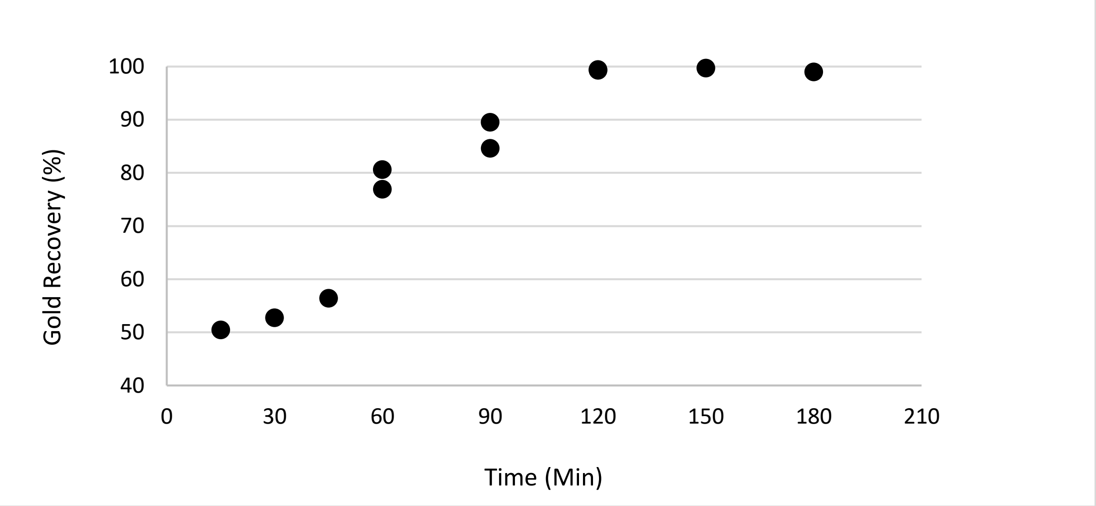

Figure 4-6. Gold recovered from solution with the MMCP (some points with duplicates)

The process of gold precipitation from cyanide solutions using a permeable fabric (this can be thin socks) with zinc shavings hung inside the cyanidation tank is simple and effective to produce gold in a short time. The cyanidation process needs high aeration, but zinc cementation is more effective in the absence of oxygen. The MMCP simplifies the gold production step once no filtration is needed, as the gold precipitation on the zinc occurs reducing to minimum the rate of the tank agitation. The gold-loaded zinc shavings can be leached with nitric or hydrochloric acids. Sulfuric acid can also be used, but in most developing countries, with the presence of artisanal miners, there are restrictions to purchasing sulfuric acid due to its possible use in cocaine production. Zinc can be recovered from the acidic solution by precipitation on aluminum foil.

The same gold precipitation process has been done with aluminum. A bag of scrambled aluminum pieces was inserted into the gold-loaded solution leached by cyanidation. Precipitation experiments were done with slow agitation. Results are promising as 91.68% of the gold was recovered in 2 hours of contact with slow agitation.

The main challenge of the MMCP is to have high agitation during the leaching process and slow agitation during the gold precipitation step. It is possible to adapt the impeller motor of the leaching tanks to have extremely low agitation during the cementation step or to turn on and off the motor for a few seconds every 10 to 15 minutes.

4.5 Amalgamation tests

Artisanal miners in Colombia use, on average, a Hg: ore ratio of 1:1400 in their "cocos" for whole ore amalgamation (Garcia et al., 2015). Using a much higher amount of mercury, i.e., the ratio of 1:50, the results have shown that the highest gold extraction by amalgamation was, on average, 17.4% (15.94% and duplicate 18.81%) (Figure 4-7). The gold extraction decreased drastically to approximately 8.7% when the Hg: ore ratio was 1:100. It is not possible to assert that all gold particles in this ground La Maria ore were liberated; therefore, amenable to be captured by mercury, but the grain size of the tests was compatible with the one used by the Colombian artisanal miners (P80 = 0.13 mm after grain size analysis of their amalgamation tailings) (Garcia et al., 2015).

The gold in this ore can easily be concentrated either by flotation or gravity concentration. The gold concentration with a Knelson laboratory centrifuge with the same head sample of La Maria ground 80% below 0.13 mm, resulted in 91% of gold extraction (five passes) with 9% of mass pull (the flowrate of solids reporting to the concentrate) and a combined grade of the concentrates of 536 ppm Au (Gonçalves et al., 2016, Veiga and Gunson, 2020). This exemplifies that most gold particles are either liberated or make the ore particles heavy enough to be concentrated by gravity methods at 80% of the sample below 0.13 mm. Consequently, concentrating the ore before performing the amalgamation or direct smelting could reduce the substantial amount of mercury loss (up to 48.6% of the original Hg according to Garcia et al., 2015) or even eliminate the amalgamation from the artisanal mining processes.

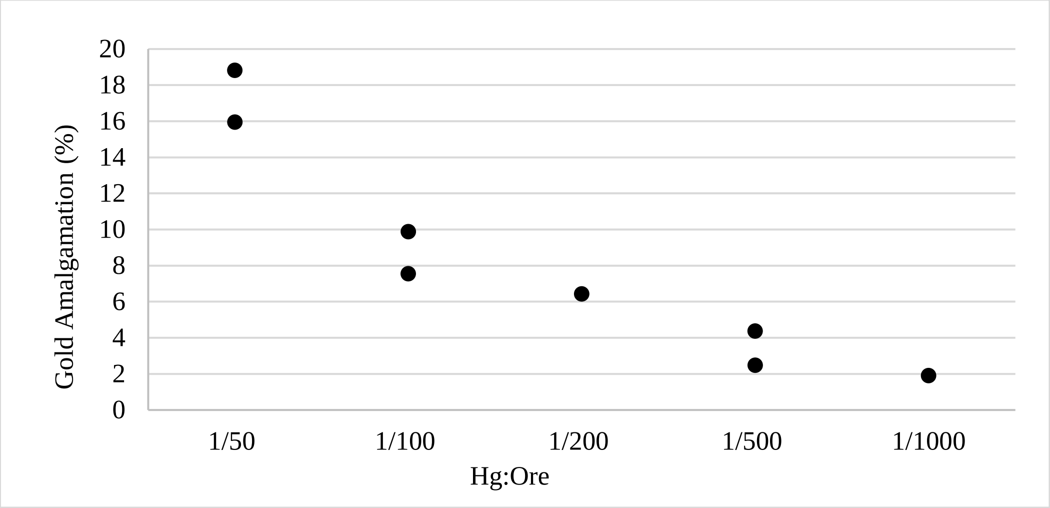

Figure 4-7. Gold amalgamation tests (some points with duplicates)

4.6 Chloride Leaching Process

Table 4-12 shows the experimental conditions and Table 4-13 shows the percentage of gold extracted from the oxidative chloride process on the La Maria ore sample. At room temperature and after 8 hours, sodium persulfate shows better results in terms of gold extraction. As a result, it is chosen for the next round of experiments.

Table 4-12. Experimental parameters of the gold chloride leaching tests

Sample #	Oxidant Name	Oxidant (g)	HCl concentration (%)
1	$Ca(OCl)_2$	5	50
2	$Ca(OCl)_2$	5	50
3	$Ca(OCl)_2$	5	30
4	$Ca(OCl)_2$	5	30
5	$Na_2S_2O_8$	5	50
6	$Na_2S_2O_8$	5	50
7	$Na_2S_2O_8$	5	30
8	$Na_2S_2O_8$	5	30

Sodium persulfate at room temperature can extract over 80% of gold in 8 hours. By applying 50°C to the process, this percentage increased to 100% (Table 4-14).

Table 4-13. Gold extraction results by chloride leaching application (5 g of oxidant)

Sample	Oxidant Name	Gold Extraction (%)
1	$Ca(OCl)_2$	16.78
2	$Ca(OCl)_2$	23.46
3	$Ca(OCl)_2$	35.45
4	$Ca(OCl)_2$	47.14
5	$Na_2S_2O_8$	56.08
6	$Na_2S_2O_8$	68.29
7	$Na_2S_2O_8$	41.12
8	$Na_2S_2O_8$	48.62

Table 4-14. Effect of temperature in chloride gold leaching with sodium persulphate

Sample	Temperature	Gold Extraction (%)
1	Room	83.90
2	Room	82.16
3	50°C	100.00
4	50°C	89.63

Chapter 5: DISSCUSSION

5.1 Free Cyanide Content Estimation

The results of all three methods, colorimetric, titration and ion specific electrode, used to determine free cyanide content in the “manipueira” sample from the Bahia State, Brazil provided similar and consistent results. Colorimetric kits are not very accurate as the cyanide concentration assessment is visual, but the results were not out of scale. The colorimetric kit has a visual scale from 0 to 1 ppm of free cyanide. For samples with higher free cyanide concentration, dilution is necessary to be in the color range. As mentioned above the analytical results do not change whether the dilution is performed before development of the color or after.

The colorimetric method is a fast-reliable method that can be used in the field to recognize high grade cyanide-producing cassavas.

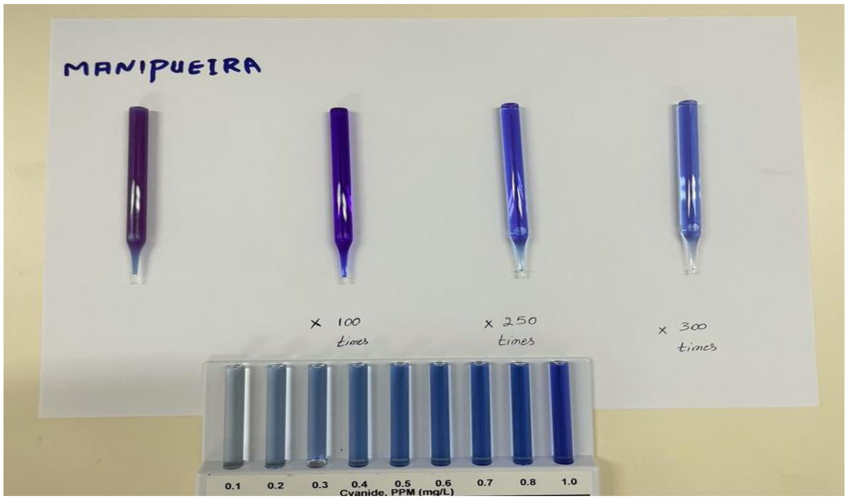

Figure 5-1. Gradual dilution of a “manipueira” sample to fit into the range of the kit

5.2 Gold Leaching with Cassava

The results of gold leaching tests show that up to 50.9% of gold can be extracted easily using cyanide generated in a cassava solution with 267 ppm of free cyanide in 24 hours. The solid-to-liquid ratio was a critical factor in the experiment as free cyanide is important for the purpose of gold leaching. Based on the results shown, a 10% reduction in this ratio can be achieved by adding more "manipueira" in the leaching process with the same amount of ore. This change contributed to a 10% increase in gold extraction in all test periods.

The gold in the ore is not refractory to dissolution with cyanide as shown by extractions above 77% in pure NaCN solution with a concentration of 267 ppm of free CN (Table 4-3). In order to confirm the low refractoriness of the ore, an additional cyanidation test of the feed sample was conducted in a rolling bottle with a high concentration of cyanide 5000 mg free cyanide/L, and the gold extraction reached more than 97% in 24 hours (Gonçalves et al., 2016). Another variety of cassava found in Pernambuco State, Brazil, contained 600 ppm of free cyanide, and this increased the gold extraction percentage to 82.4%. Consequently, the gold extraction efficiency can be increased by utilizing cassava varieties with higher cyanogenic glycoside levels, which contribute to higher free cyanide content. These types of cassava, according to the EMBRAPA Cassava and Fruticulture Center's experts, are more common in arid regions.

The possibility of using this "manipueira" with a higher concentration of free cyanide for gold leaching has been discussed with a Brazilian company, CIBUS, located in Salgueiro, Pernambuco State. This company processes up to 360 tonnes/day of bitter cassava extracting the starch for the food market (e.g., beer) as well as making flour (Figure 5-2). The company has the potential of producing up to 90 tonnes/day of "manipueira" that can be used in a small artisanal gold operation located 100 km from the cassava processing company. Field tests are being conducted at the Federal University of Pernambuco, the Dept of Mining Engineering, and UBC.

Gold leaching with highly accessible and low-cost cassava plants with the simple process presented here can financially benefit artisanal mining communities and cassava producers. The environmental impacts of substituting mercury in AGM activities cannot be disregarded.

Figure 5-2. CIBUS cassava processing center

5.3 Effect of Cassava Starch

The preg-robbing in the suspension and the reduction in gold extraction after 24 hours (Table 4-5 and Figure 4-3) could be caused by the presence of starch in the process. This may happen by the lack of exposure of gold particles to the solution. Suspended organics in the leaching solution may cause the passivation of gold particles, which prevents the proper leaching process and contributes to a lower gold extraction rate from the ore. In other words, starch contributes to the reabsorption of gold-cyanide complex followed by less gold extraction. Using a centrifuge, or flotation of the solution extracted from cassava, can separate these organic compounds, starch, from the solution.

As mentioned in the previous section, companies like CIBUS extract this starch and use or sell it for other purposes, such as flour and beer manufacturing. The preg-robbing effect of the starch needs further investigation.

5.4 DMSO

The percentage of gold extracted in DMSO tests ranged between 30.16 and 94.68%. The outcome of the tests shows that four of the possible sixteen combinations herein examined resulted in gold extraction of over 90%. From Table 4-7, it is evident that the S:L ratio and time are key factors that contribute to the high gold extraction.

In addition, predications by the Yates method confirms these results. As mentioned earlier, a higher percentage of error in the method implies that the desired factor has higher impact on the results of the experiments. Consequently, S:L ratio error percentage of 20.3% and time error percentage of 15% show the highest impact, respectively amongst other factors. As the amount of ore used in all the tests is the same, S:L ratio refers to the DMSO amount. Therefore, gold extraction from the ore in these series of tests depends mainly on the DMSO amount and time period.

The percentage of solids in the experiments had a significant impact on the gold extraction. The results showed that using 10% solids resulted in higher gold extractions than using 20%. Based on the analytical combinations and percent of gold recoveries, experimental conditions A13 and A15 were found to be the two most important factors. Among these, A13 yielded the highest gold extraction rate of 94.68%. The A15 condition with a solid-liquid ratio of 30%, on the other hand, is the same combination used in the previous research in Japan under the conditions of 100g of gold wire, 200 mL of DMSO, 13.4g of $CuCl_2$ and 5.85g of NaCl (Yoshimura and Matsuno, 2016). Higher S:L ratios should be investigated for optimum results in terms of industrial application. At the 40 °C temperature, with the same conditions as test A13, 98% of gold was extracted in 2 h of leaching. Even at the ambient temperature, gold extraction rates exceeded 95%. The DMSO leaching tests by utilizing bromides and temperature (40°C) yields 100% gold extraction.

The next step in this process was to assess the feasibility of gold precipitation. Adding sufficient water with low pH to the gold loaded DMSO solution resulted in gold precipitation. Water alone could precipitate 60% of the available gold in the DMSO solution after leaching, but copper precipitated as well. Applying a water-based solution with low pH can reduce the copper precipitation, obtaining a higher gold grade precipitate.

DMSO can react with some plastics, while $CuCl_2$ or $CuBr_2$ are corrosive in interaction with iron which is widely used in tanks in artisanal mining sites. Gaylord Chemical Company suggests that polyethylene, polypropylene, and ethylene-propylene rubber can be used for up to 50°C. Polytetrafluoroethylene (PTFE), Teflon grade, can also be used up to the atmospheric boiling point of DMSO. Mild steel works well enough, but DMSO discoloration occurs due to a slow corrosion rate, presumably due to dissolved/leached iron. 304 or 316 stainless steel or aluminum could be the best option, as the plant experience records show that over 10-year life can be expected with continuous exposure to DMSO, and it is expensive. Consequently, an appropriate selection of materials is required for utilizing DMSO at AGM sites.

The supply chain of the DMSO market was affected severely by the outbreak of COVID-19. The pandemic in 2020 and at the start of 2021 resulted in implementation of strict lockdown regulations across several nations. Consequently, the DMSO import, and export activities faced limitations and disruptions (QYResearch, 2020). Global dimethyl sulfoxide production is mainly in the USA, France, Japan, and China. In 2015, China was the leading producer of global dimethyl sulfoxide, with 45.66% DMSO production, while the USA was in second place with 28.63% global production share (QYResearch, 2021). The properties of electronic or higher-grade dimethyl sulfoxides produced in China are not as good as that produced abroad. China had many DMSO manufacturers; however, some discontinued or reduced their capacity in the past few years due to environmental issues and intense competition (QYResearch, 2021).

According to information provided in a conversation with Gaylord, the indicative pricing for larger quantities of over 1,000 metric tons (MT) of a particular product is approximately $3.50 per pound on a Free Carrier basis, with delivery taking place in Tuscaloosa, Alabama. It's worth noting that this price does not include any freight charges. However, it's important to keep in mind that pricing can be affected by a variety of factors, such as market conditions, supply and demand, and negotiations between the buyer and seller. Future Market Insights (2022) reported that the global demand for DMSO, throughout the projection period between 2022 and 2032, is predicted to increase at a CAGR of 5.4%, hitting a total of US$ 838.6 Million in 2032. This rapid expansion over the projected period can be due to 1) ongoing investigations on the application of DMSO in the pharmaceutical sector, 2) the growth in DMSO usage in the agrochemical industry due to its nontoxic and biodegradable features, 3) loosening the laws controlling the use of DMSO in recent years. The recent slow downward trend in the price is believed to be maintained in the future since an increase in the supply is predicted. Additionally, different brands will have to adjust their price with the market as competition intensifies.

5.5 Modified Merrill-Crowe Process (MMCP)

The goal in this study was to modify the existing Merrill- Crowe process to make it more accessible and affordable for AGM operations with no more prolonged need of costly filtration and vacuum equipment. In the classic Merrill-Crow process, a filter press increases labor costs for maintenance and energy consumption. The modified process requires powerful agitation during the cyanidation process (or addition of an oxidizing agent) and very slow agitation during the gold precipitation step, to avoid excess dissolved air in the solution. The process involves the introduction of a hanging fabric bag with zinc shavings into the pulp for at least two hours. The right time of cementation depends on the disposition of the bags in the leaching tank, agitation of the cyanide solution, and other operational parameters that must be tested in larger tanks (e.g., amount of gold and silver in solution, the surface area of zinc).

Gold precipitation on zinc yielded 99.4% recovery in two hours, while the same experiments with aluminum recovered 91.68% of the gold in the same period. This is due to the slower reaction of gold on the aluminum surface. Aluminum can be a good substitute for zinc in the gold cementation process when silver ores contain antimony and arsenic (Haque, 1987).

At the artisanal cyanidation operations in Ecuador, the Merrill Crowe process in agitated tanks have no filters, The processing centers leave the pulp decanting for 12 hours to siphon clear solution to a series of PVC pipes filled with zinc shavings. The solution is then recirculated to the tanks and the process repeated for 5 days. Gold precipitation on zinc shavings occurs at atmospheric pressure and on average leaves 6% of the gold in solution (Velasquez et al., 2011). Using the MMCP, the laboratory tests showed 99.4% of gold extraction in 2 hours. This method is a simple technique to improve the artisanal cyanidation process without any further investment.

5.6 Amalgamation Tests

Amalgamation is a simple process; but only liberated gold from the gangue can be trapped by mercury. The laboratory amalgamation process with the La Maria sample ground 80% below 0.13 mm in 2 hours, resulted in less than 19% gold extraction, even when the amount of mercury used in the laboratory was 28 times more than what is used by Colombian artisanal miners in their "cocos" (small ball mills) to amalgamate the whole ore in 2 hours. In comparison, the cyanidation process of the same sample with 1 g/L CN^- for 24 hours at ambient temperature resulted in 84% gold extraction.

The results are in agreement with the study by Veiga et al. (2009) that was designed to show Ecuadorian miners that with amalgamation of their gravity concentrates only 26% of the gold could be extracted, while cyanidation extracted more than 90%.

The low efficiency of gold extraction by amalgamation can be attributed to mercury oxidation and lack of liberation of gold particles (Rollien, 1936, Veiga and Gunson, 2020). The cyanidation process requires fine particles to bring the gold into the solution within a reasonable time, in contrast to amalgamation, which is based on surface reactions and the agglutination of gold grains. According to Wenqian and Poling (1983), gold amalgamation does not work effectively for free gold particles finer than 200 mesh (0.074 mm). Other authors also confirmed that very fine gold particles (below 0.07mm) cannot efficiently be amalgamated by Hg, while cyanidation works better with fine gold grains (< 0.2mm) (Macdonald, 1983, Hylander et al., 2007, Veiga et al., 2014b,). In addition, cyanidation can extract unliberated but exposed gold particles and amalgamation cannot.

The inefficiency of amalgamation is evident, and it has been brought to the attention of artisanal gold miners for decades. However, they insist on using mercury due to the simplicity of the process to obtain gold very quickly.

5.7 Chloride Leaching Process

In the experiments, chloride was used as a ligand to solvate Au(III) in the solution (Baghalha, 2007). In all the experiments, commercial hydrochloric acid with 37% concentration was used, which was diluted (50%) to make the process more affordable for artisanal miners. In the definition of the oxidizing agents, calcium hypochlorite and sodium persulfate were tested. The percentage of dissolved gold is much higher with the presence of sodium persulfate. Baghalha (2007) reported that due to the formation of the $CaOCl^+$ complex in solution, calcium hypochlorite produces slower gold-leaching kinetics compared to sodium hypochlorite. Consequently, in further experiments, only sodium persulfate was used in all the tests. At higher temperatures and by adding excess (5 grams) ligand (NaCl), gold extraction yields have been improved tremendously, and, in some cases, all the gold was extracted at 40^oC. Sodium persulfate is a white crystalline powder primarily used as a bleaching agent. It is soluble in water and can be stored at room temperature. As it is non-hygroscopic (less affinity for atmospheric water), it has a good shelf life and can be easily stored for long periods (Transparency Market Research, 2022). The average price of sodium persulphate and calcium hypochlorite is 900 USD/t and 1385 USD/t, respectively (Made-in-China, 2023).

This method resembles the iGoli process devised by MINTEK in South Africa, which is based on dissolving gold from gravity concentrates by utilizing hypochlorite in an acidic medium. Mahlatsi and Guest (2003) reported high gold recoveries (about 98%) demonstrating that it could be a good substitute for amalgamation processes for AGM. However, due to the complicated process and the need for technical knowledge, it was hard to convince miners to adopt it. The chloride leaching process presented here is a simplified version that can be considered as a practical option for AGM communities.

Utilizing diluted hydrochloric acid to dissolve gold from gravity or flotation concentrates with high grades of gold (say, for example, 200 ppm Au, and one tonne of such material would contain 200 grams of gold, which at the current price of around USD 57 per gram, would be worth approximately USD 11400) seems to be an affordable solution to avoid the use of cyanide. The price of commercial hydrochloric acid can vary approximately from USD 75- 250/tonne (ChemAnalyst, 2022; Alibaba, 2023) depending on the supplier and volume requirements, and it is usually available in most developing countries. The acid can be re-used or neutralized with $Ca(OH)_2$, which is usually widely available and inexpensive.

Chapter 6: CONCLUSION

6.1 Summary of the Results

Using the same sample, ore from the La Maria gold deposit with a grade of 48.87 ppm, currently mined by Colombian artisanal miners, enabled us to compare the extraction methods suggested in this research. The important results are outlined in Table 6-1.

Table 6-1. Gold extraction results achieved by each method studied in this research.

Gold extraction method	Time (h)	Temperature	Au Extracted (%)
Amalgamation	2	Ambient	19.0
NaCN (1000 ppm free CN)	24	Ambient	84.0
NaCN (267 ppm free CN)	24	Ambient	77.0
Cassava liquid (267 ppm free cyanide)	24	Ambient	50.9
Cassava liquid (600 ppm free cyanide)	24	Ambient	82.4
DMSO chloride	2	Ambient	96.5
DMSO chloride	2	40°C	98.8
DMSO bromide	12	40°C	100.0
HCl (50%) + $Na_2S_2O_8$	8	Ambient	83.9
HCl (50%) + $Na_2S_2O_8$	8	50°C	100

6.2 Cyanogenic Plants as Gold Leaching Lixiviants

The potential use of cyanogenic plants, such as bitter cassava, for gold leaching has been demonstrated, and future research could involve exploring other cyanogenic plants like bamboo. If local plants can replace the use of mercury in artisanal gold operations, it would be a significant step towards a more economic and efficient process in gold extraction methods for small-scale operations. The use of cassava extracts can have a positive environmental impact and eliminate exposure to mercury vapor. However, it is important to note that not all bitter cassavas produce "manipueira" with high levels of free cyanide, and species growing in dry regions usually produce higher cyanide levels.

The gold leaching process can also have a positive impact on the environment by using tailings of "manipueira" as a source of fertilizer for soils as "manipueira" is rich in nutrients like nitrogen, potassium, magnesium, phosphorous, calcium, and sulfur (EMBRAPA, 2011). This innovative strategy can make a positive impact on the economic, environmental, social and health aspects of artisanal and small-scale gold mining communities by substituting a renewable abundant resource, cassava extracts, for the highly toxic and environmentally persistent mercury. This substitution will also contribute to decreasing the potential health and environmental hazards caused by the "manipueira".

6.3 DMSO

Leaching gold from a gold ore with a non-aqueous reagent, DMSO, was investigated. This was usually called “organic aqua regia by Yoshimura and Matsuno (2016) due to its high capacity to dissolve gold in short time in the presence of chloride or bromide ions, and copper (II) ions acting as an oxidizing agent for gold. The gold precipitation process from the gold loaded can be done by adding an acidic solution such as lime juice.

DMSO can be recycled by distillation and reused in a repeating cycle. Therefore, a circulating system must be developed for gold extraction and precipitation. The results show that DMSO can be used as an innovative gold leaching agent in a straightforward and cost-effective process to substitute for cyanide and mercury in processing plants.

FDA has approved DMSO to have low acute and chronic toxicity for animal, plant, and aquatic life (Gaylord Chemical, 2022). The world-limited production of DMSO is a bottleneck to recommending this process to large operations. However, this process can potentially replace Hg and cyanide in leaching concentrates or high-grade ores in small plants working together with artisanal miners, but some knowledge and funds are needed to implement this process. The process's simplicity and low cost for equipment and reagent are the main positive points to suggest further investigations and larger pilot tests of this technique.

6.4 Modified Merrill-Crowe Process

One of the processes investigated in this study was to modify the existing Merrill- Crowe process to make it more affordable to small plants. The aim was to eliminate prolonged, costly filtration and vacuum equipment. The modified process requires powerful agitation during the cyanidation process and very slow agitation during the gold precipitation step. The process involves hanging a fabric bag with zinc or aluminum shavings into the pulp for at least two hours. The right cementation time depends on the bags' disposition in the leaching tank, agitation of the cyanide solution, and other operational parameters that must be tested (e.g., the amount of gold and silver in the solution and the surface area of zinc). This process can replace the inefficient gold precipitation using zinc shavings in PVC pipes, at atmospheric pressure, widely used in South America (Torkaman and Veiga, 2023).

6.5 Inefficiency of Gold Amalgamation Process

Although lab experiments have proven the inefficiency of mercury amalgamation, artisanal miners still prefer this method due to its time efficiency, simplicity, fast results, and inexpensive equipment. However, introducing new, efficient, and affordable processes to substitute amalgamation has not yet yielded any practical breakthroughs. Any new strategy must be inexpensive and more efficient than amalgamation and should consider site location, ore mineralogy, investment span, level of education, and motivation of miners. As artisanal miners increasingly depend on mercury, there is an urgent need to develop non-mercury technologies (Hilson and Pardie, 2006) or methods that reduce mercury loss (Metcalf and Veiga, 2012).

6.6 Chloride Leaching Process

Lab experiments have demonstrated that hydrochloric acid can extract 100% of gold within 8 hours at 50°C. This chloride process is a simple non-cyanide method that offers a faster reaction rate and less pollution, making it an attractive option where cyanide use is restricted by law or difficult to obtain. The International Cyanide Management Institute and other organizations have implemented programs to promote safe cyanide handling, which limits access for AGM communities. As a result, non-cyanide methods such as the chloride process may be a viable alternative for these miners. The chloride leaching process offers several environmental benefits.

Firstly, the process does not produce toxic hydrogen cyanide gas, which can be dangerous to handle and lead to severe environmental contamination in the event of a spill or leak. Secondly, chloride leaching can be carried out at lower temperatures and pressures, reducing energy consumption and greenhouse gas emissions. Additionally, using chloride as a leaching agent can minimize the waste generated during the process. Finally, the chloride leaching process can be used where cyanide use is restricted or prohibited, providing a safer and more sustainable alternative for gold extraction.

6.7 Limitations of the applicability of these techniques

Each technique has its own limitations, which are important to consider before implementing them in a particular setting. Here are some limitations of the techniques mentioned in the text:

1. Cassava plant effluent leaching: The cyanide concentration in the cassava plant effluent can vary widely depending on the type of cassava plant and the extraction method. In some cases, the cyanide concentration may be too low to effectively extract gold, while in other cases it may be too high (in arid regions) and pose a risk to human health and the environment.
2. DMSO leaching: DMSO is a reagent in demand for other industrial applications and there are a few producers in the world. This is a limitation of its use broadly in small plants and not yet suggested for large operations to leach gold concentrates. Additionally, the safety of DMSO is still a matter of debate and some studies have shown that it can be toxic to humans and the environment.
3. Zinc cementation: This technique may not be suitable for ores that contain high levels of base metals, as they can compete with gold for adsorption onto the zinc shavings. Additionally, the use of bags filled with zinc or aluminum may require additional maintenance and replacement costs. The legal access to cyanide by artisanal miners is also another problem as most countries have severe legislations for selling cyanide to rudimentary operations. Appropriate procedures must be in place to avoid accidents and misuse of cyanide (e.g., leaching Hg-contaminated tailings). The bureaucratic process to obtain permits to buy cyanide can be long.

4. Chloride application: This technique requires some heating, which can increase energy consumption and processing costs. Additionally, hydrochloric acid may not be available in all developing countries with artisanal miners and its cost to import might be high.

6.8 Final Remarks

All the processes investigated within this study have the potential to replace mercury (and cyanide in some cases). However, the application of these technologies, developed in the laboratory, is site-specific and must be brought to the attention of the miners and processing centers for field tests. About 90% of the almost 20 million worldwide artisanal miners genuinely operate at the artisanal level, processing less than two tonnes of ore daily (Veiga et al., 2018). To date, most of the projects have focused on offering environmental and technical solutions for these operations; however, they are not the primary polluters (Veiga et al., 2022). Processing centers are the main mercury polluters. They must change their business model and abandon the services of amalgamation (usually of the whole ore) for their clients, the miners and adopt a fair process to work together with artisanal miners providing better remuneration. The low extraction of gold with whole ore amalgamation (less than 20%) was proved in the laboratory using a sample with no-refractory gold. With amalgamation, leaving 80% of the gold in Hg-contaminated tailings to be leached with cyanide aggravating the polluting problem is unreasonable. Processing centers should be at the center of the changes to adopt cleaner and appropriate methods to coexist with artisanal miners. Coexistence offers more financial benefits for the artisanal miners and assists the private sector in actively reducing informality and pollution (Veiga et al., 2022). it is plausible to set up a processing center that utilizes the recommended techniques to eliminate the use of mercury. The use of cyanide-based leaching, DMSO leaching, zinc cementation, and chloride application have all shown promising results in terms of gold extraction rates.

The economic viability of the recommended techniques will depend on various factors such as the scale of operations, local regulations, and the cost of implementing the new techniques. However, it is generally known that the use of mercury-free techniques can significantly reduce the cost of gold production in the long term due to lower health and environmental risks and better gold recovery rates. The upfront cost of implementing the new techniques may be higher, but it can be offset by the long-term benefits of reduced health and environmental risks and higher gold recovery rates. Overall, the economic viability of the recommended techniques seems promising, especially in the long run.

Considering the diverse uses of gold, such as in jewelry, technology, and by central banks and investors, its crucial role in different points of the global economy seems to be growing, particularly in cycles of economic crises. This market diversity and nature result in ongoing gold demand as an investment and financial asset (WGC, 2022).

Due to the mentioned points and the increasing gold prices, there will be growing interest in worldwide exploration. Accordingly, more small- to medium-sized mines and processing centers are expected to develop and operate over the next decade. Poverty in rural areas of developing countries, low up-front investment, and a lack of alternative livelihoods draw more people to artisanal mining activities. The transformation of artisanal gold miners, as well as polluting processing centers, into responsible processors must be pursued. Alternative technologies are just a piece of this intricate puzzle involving political, social, legal, and economic decisions.

Therefore, environmental and economic problems related to artisanal gold mining need practical solutions. This research presents unconventional gold leaching processes to reduce the severe impacts of artisanal mining activities on humans and the environment. Particular attention was paid to evaluating alternatives for the gold amalgamation process. It is significant because it focuses on one of the time's most challenging global issues.

6.9 Suggested Additional Research

According to the author's experience and involvement in fieldworks at all the stages of this research, carrying out all the experiments in an artisanal mining sector under the best circumstances is logistically challenging, the other researchers are strongly encouraged to take the following steps:

- Further investigation in DMSO field tests and recycling process.
- Further cooperation with cassava processing centers (like CIBUS in Brazil) to analyze the cyanide levels of different varieties of cassava to: 1) identify cassava varieties with high free cyanide content and 2) work in collaboration with the artisanal mining sector and provide cassava liquid for their leaching process.

- Other cyanogenic plants like bamboo can be tested for cyanide extraction and then gold leaching.
- Field tests using zinc or aluminum shavings and zinc sintered blocks for the gold precipitation process.
- For the successful implementation of new technology, the presence of technical interveners, miners' education, financial aid, and understanding of the community are fundamental steps.

References

911-Metalurgist, 2018. Precipitation of Mercury in Cyanide Gold Leaching. https://www.911metallurgist.com/calcium-sulfide-precipitation-mercury-cyanide-leaching-gold-ores/

Abbott, A.P., Capper, G., Davies, D.L., Rasheed, R.K., Tambyrajah, V., 2003. Novel solvent properties of choline chloride/urea mixtures. *Chemical Communications*, 1, p.70-71.

Adeniran, H.A., Farinde, E.O., Obatolu, V.A., 2013. Effect of heat treatment and fermentation on anti-nutrients content of lima bean (*Phaseolus lunatus*) during production of daddawa analogue. *Annual Research & Review Biology*, 3(3), p.256-266. https://journalarrb.com/index.php/ARRB/article/view/24691

Alibaba, 2023. https://www.alibaba.com/showroom/hcl-acid.html

Al-Sultan, S.I., 2003. Sorghum halepenses and its cyanide content. *Pak. J. Nutr*, 2(3), p.123-124.

Alves, A.A.C., 2001. Cassava botany and physiology. *In*: *Cassava: Biology, Production and Utilization* (p. 67-89). Wallingford UK: Cabi.

Appel, P.W. and Jønsson, J.B., 2010. Borax–an alternative to mercury for gold extraction by small-scale miners: introducing the method in Tanzania. *GEUS Bulletin*, 20, p.87-90.

Appel, P.W. and Na-Oy, L., 2012. The Borax method of gold extraction for small-scale miners. *Journal of Health and Pollution*, 2(3), p.5-10.

Askenaizer, D., 2003. Drinking water quality and treatment. *In: Encyclopedia of Physical Science and* Technology. Vol. 4, p. 651-672. Ed. R.A. Meyers. 3rd Ed. Academic Press.

Aylmore, M.G., 2005. Alternative lixiviants to cyanide for leaching gold ores. *Developments in Mineral Processing*, 15, p.501-539.

Baghalha, M., 2007. Leaching of an oxide gold ore with chloride/hypochlorite solutions. *International Journal of Mineral Processing*, 82(4), p.178-186.

Ballhorn, D.J., 2011. Cyanogenic glycosides in nuts and seeds. *In*: *Nuts and Seeds in Health and Disease Prevention, Chap. 14,* p. 129-136. Academic Press.

Ballhorn, D.J., Kautz, S., Lion, U., Heil, M., 2008. Trade-offs between direct and indirect defences of lima bean (Phaseolus lunatus).J. *Ecology*, 96(5), p.971-980.

Barbosa, A.C., Souza, J.D., Dórea, J.G., Jardim, W.F., Fadini, P.S., 2003. Mercury biomagnification in a tropical black water, Rio Negro, Brazil. *Archives of Environmental Contamination and Toxicology*, 45(2), p.235-246.

Bolarinwa, I.F., Oke, M.O., Olaniyan, S.A., Ajala, A.S., 2016. A review of cyanogenic glycosides in edible plants. *In: Toxicology-New Aspects to This Scientific Conundrum*. Chap. 8, pp/ 179-191. INTECH Open Science. https://doi.org/10.5772/64886

Böse-O'Reilly, S., Drasch, G., Beinhoff, C., Maydl, S., Vosko, M.R., Roider, G., Dzaja, D., 2003. The Mt. Diwata study on the Philippines 2000—Treatment of mercury intoxicated inhabitants of a gold mining area with DMPS (2, 3-Dimercapto-1-propane-sulfonic acid, Dimaval®). *Science of the Total Environment*, 307(1-3), p.71-82.

Botz, M., Milosavljevic, E., Ward, I., 2013. Measurement of weak and dissociable (WAD) cyanide with a modified potentiometric titration. *Mining, Metallurgy & Exploration,* 30(4), p.197-204.

Boucabeille, C., Bories, A., Ollivier, P., Michel, G., 1994. Microbial degradation of metal complexed cyanides and thiocyanate from mining wastewaters. *Environmental Pollution*, 84(1), p.59-67.

Box, G.E., Hunter, W.H., Hunter, S., 1978. *Statistics for Experimenters* (Vol. 664). New York: John Wiley and Sons.

Boyle, R.W., 1979. The geochemistry of gold and its deposits. Geological Survey of Canada. Bulletin, 280, 584 p. https://publications.gc.ca/site/eng/9.817728/publication.html

Bradbury, J.H., 2006. Simple wetting method to reduce cyanogen content of cassava flour. J. *Food Composition and Analysis,* 19(4), p.388-393.

Brazilian Institute of Geography and Statistics (IBGE), 2017. Censo Agropecuário, Tabela 6961(in Portuguese). List of Agri Products Produced in Brazil; https://sidra.ibge.gov.br/tabela/6961.

Breuer, P.L., Sutcliffe, C.A., Meakin, R.L., 2011. Cyanide measurement by silver nitrate titration: Comparison of rhodanine and potentiometric end-points. *Hydrometallurgy,* 106(3-4), p.135-140.

Burns, A.E., Bradbury, J.H., Cavagnaro, T.R., Gleadow, R.M., 2012. Total cyanide content of cassava food products in Australia. J. *Food Composition and Analysis*, 25(1), p.79-82.

Byju, G. and Suja, G., 2020. Mineral nutrition of cassava. *Advances in Agronomy*, 159, p. 169-235.

Celep, O., Alp, İ., Deveci, H., Vicil, M., 2009. Characterization of refractory behaviour of complex gold/silver ore by diagnostic leaching. *Transactions of Nonferrous Metals Society of China*, 19(3), p.707-713.

Chadha, R.K., Lawrence, J.F., Ratnayake, W.M.N., 1995. Ion chromatographic determination of cyanide released from flaxseed under autohydrolysis conditions. *Food Additives & Contaminants*, 12(4), p.527-533.

ChemAnalyst, 2022. Hydrochloric Acid Price Trend and Forecast. https://www.chemanalyst.com/Pricing-data/hydrochloric-acid-61

Chiwona-Karltun, L., Brimer, L., Kalenga Saka, J.D., Mhone, A.R., Mkumbira, J., Johansson, L., Bokanga, M., Mahungu, N.M., Rosling, H., 2004. *Bitter* taste in cassava roots correlates with cyanogenic glucoside levels. *J. Science of Food and Agriculture,* 84(6), p.581-590.

Chiwona-Karltun, L., Mkumbira, J., Saka, J., Bovin, M., Mahungu, N.M., Rosling, H., 1998. The importance of being bitter—a qualitative study on cassava cultivar preference in Malawi. *Ecology of Food and Nutrition*, 37(3), p.219-245.

Chiwona-Karltun, L., Nyirenda, D., Mwansa, C.N., Kongor, J.E., Brimer, L., Haggblade, S., Afoakwa, E.O., 2015. Farmer preference, utilization, and biochemical composition of improved cassava (Manihot esculenta Crantz) varieties in southeastern Africa. *Economic Botany*, 69(1), p.42-56.

Conn, E.E., 1979. Biosynthesis of cyanogenic glycosides. *Naturwissenschaften*, 66(1), p.28-34.

Cordy, P., Veiga, M.M., Salih, I., Al-Saadi, S., Console, S., Garcia, O., Mesa, L.A., Velásquez-López, P.C., Roeser, M., 2011. Mercury contamination from artisanal gold mining in Antioquia, Colombia: The world's highest per capita mercury pollution. *Science of the Total Environment, 410,* p.154-160.

Cunnane, S.C., Ganguli, S., Menard, C., Liede, A.C., Hamadeh, M.J., Chen, Z.Y., Wolever, T.M., Jenkins, D.J., 1993. High α-linolenic acid flaxseed (Linum usitatissimum): some nutritional properties in humans. *British J. Nutrition*, 69(2), p.443-453.

Denigès, G., 1895. Sur une nouvelle méthode cyanimérique et sur les applications qui en dérivent. Première Partie: Principe de la méthode et applications directes. *Ann. Chim. Phys.*, 6, p.381-99.

Ding, M. and Wang, K., 2018. Determination of cyanide in bamboo shoots by microdiffusion combined with ion chromatography–pulsed amperometric detection. *Royal Society Open Science,* 5(4), p.172128.

Dinnebier, R.E. and Billinge, S.J., 2008 (editors). *Powder diffraction: theory and practice*. RSC Publishing, Cambridge. 582 p. ISBN (print): 978-0-85404-231-9.

Drace, K., Kiefer, A.M., Veiga, M.M., 2016. Cyanidation of mercury-contaminated tailings: potential health effects and environmental justice. *Current Environmental Health Reports*, 3, p.443-449.

Drasch, G., Boese-O'Reilly, S., Illig, S., 2007. Increase of renal excretion of organo-mercury compounds like methlymercury by DMPS (2, 3-Dimercapto-1-propanesulfonic acid, Dimaval®). *Clinical Toxicology, 45*(3), p.266-269.

Dufour, D.L., 1988. Cyanide content of cassava (*Manihot esculenta, Euphorbiaceae*) cultivars used by Tukanoan Indians in Northwest Amazonia. *Economic Botany*, 42(2), p.255-266.

Echavarria, C., 2014. What is legal? Formalising artisanal and small-scale mining in Colombia. *IIED, London and ARM, Colombia*, *79*.

Economia, A., 2014. Produccion de carbon, oro y níquel cayo en Colombia durante 2013 (in Spanish).

EFSA Panel on Contaminants in the Food Chain (CONTAM), Schrenk, D., Bignami, M., Bodin, L., Chipman, J.K., del Mazo, J., Grasl-Kraupp, B., Hogstrand, C., Hoogenboom, L., Leblanc, J.C. and Nebbia, C.S., 2019. Evaluation of the health risks related to the presence of cyanogenic glycosides in foods other than raw apricot kernels. *EFSA Journal*, 17(4), p.e05662.

Eissler, M., 1888. *Metallurgy of Gold.* Crosby Lockwood, Columbia Univ. London, 188 p.

EMBRAPA – Empresa Brasileira de Pesquisas Agro-pecuarias (2011). *Manipueira, a Precious Liquid*. https://www.embrapa.br/busca-de-noticias/-/noticia/18147209/manipueira-um-liquido-precioso (in Portuguese)

Esdaile, L.J. and Chalker, J.M., 2018. The mercury problem in artisanal and small-scale gold mining. *Chemistry–A European Journal*, 24(27), p.6905-6916.

Fadini, P.S. and Jardim, W.F., 2001. Is the Negro River Basin (Amazon) impacted by naturally occurring mercury?.*Science of the Total Environment*, 275(1-3), p.71-82.

FAO, 2011. Agricultural Organization of the United Nations. *FAO statistical yearbook 2005*-2006. https://www.fao.org/3/a0490m/a0490m00.htm

FDA, 2018. Q3C — Tables and List Guidance for Industry. https://www.fda.gov/media/133650/download

Feather, A., Sole, K.C., Bryson, L.J., 1997. Gold refining by solvent extraction-the Minataur Process. *J. Southern African Inst. Mining and Metallurgy*, 97(4), p.169-173.

Fleming, C.A., 1992. Hydrometallurgy of precious metals recovery. *Hydrometallurgy*, 30(1-3), p.127-162.

Future Market Insights, 2022, DiMethyl Sulfoxide (DMSO) Market by Raw Materials, Application & Region - Forecast 2022 – 2032. https://www.futuremarketinsights.com/reports/dimethyl-sulfoxide-dmso-market

García, O., Veiga, M.M., Cordy, P., Suescún, O.E., Molina, J.M., Roeser, M., 2015. Artisanal gold mining in Antioquia, Colombia: a successful case of mercury reduction. *J. Cleaner Production*, 90, p.244-252.

Gaylord Chemical, 2022. https://www.gaylordchemical.com/environmental-health-safety/

Gbadebo, A.M. and Oyesanya, T.M., 2005. Assessment of iodine deficiency and goitre incidence in parts of Yewa Area of Ogun State, Southwestern Nigeria. *Environmental Geochemistry and Health*, 27(5-6), p.491- 499.

Gerson, J.R., Driscoll, C.T., Hsu-Kim, H., Bernhardt, E.S., 2018. Senegalese artisanal gold mining leads to elevated total mercury and methylmercury concentrations in soils, sediments, and rivers. *Elementa: Science of the Anthropocene*, 6(11). https://online.ucpress.edu/elementa/article/doi/10.1525/elementa.274/112794/Senegalese-artisanal-gold-mining-leads-to-elevated

Giuliani, G., Groat, L.A., Fallick, A.E., Pignatelli, I., Pardieu, V., 2020. Ruby deposits: A review and geological classification. *Minerals*, 10(7), p.597.

Gökelma, M., Birich, A., Stopic, S., Friedrich, B., 2016 A Review on Alternative Gold Recovery Re-agents to Cyanide. *J. Materials Science Chemical Eng.*,4, p. 8-17.

Gómez, G. and Valdivieso, M., 1985. Cassava foliage: chemical composition, cyanide content and effect of drying on cyanide elimination. J. *Science of Food and Agriculture*, 36(6), p.433-441.

Gonçalves, A., et al., 2016. *In*: La Maria Mine and Processing Plant: Pre-feasibility Study. Ed. M. Veiga, project coordinator, Report from UBC Dept Mining Engineering to Gramalote Project, B2Gold, AngloGold Ashanti JV. 316p.

González-Valoys, A.C., Arrocha, J., Monteza-Destro, T., Vargas-Lombardo, M., Esbrí, J.M., Garcia-Ordiales, E., Jiménez-Ballesta, R., García-Navarro, F.J., Higueras, P., 2022. Environmental challenges related to cyanidation in Central American gold mining; the Remance mine (Panama). *J. Environmental Management*, 302, p.113979.

Gould, W.D., King, M., Mohapatra, B.R., Cameron, R.A., Kapoor, A., Koren, D.W., 2012. A critical review on destruction of thiocyanate in mining effluents. *Minerals Engineering*, 34, p.38-47.

Grayson,R., 2007. Fine gold extraction – alternatives to mercury and cyanide. *World Placer*, 7, p. 66-161.

Guinier, A., 2013. *X-Ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies*. Dover Publ. 641 p.

Güiza, L. and Aristizabal, J.D., 2013. Mercury and gold mining in Colombia: a failed state. *Universitas Scientiarum*, 18(1), p.33-49.

Habashi, F., 1969. *Principles of Extractive Metallurgy*: *Hydrometallurgy* (Vol. 2). CRC Press.

Hedley, N. and Tabachnick, H., 1968. Mineral Dressing Notes No. 23. *Chemistry of Cyanidation, American Cyanamid Company, New Jersey, USA*.

Haque, K.E., 1987. Gold leaching from refractory ores—literature survey. *Mineral Processing and Extractive Metallurgy Review*, 2(3), p.235-253.

Heuberger, C., 2005. *Cyanide Content of Cassava and Fermented Products with Focus on Attiéké and Attiéké Garba*. Doctoral dissertation, Swiss Federal Institute of Technology Zurich. ETH Zurich. https://www.research-collection.ethz.ch/handle/20.500.11850/74635

Hilson, A., Hilson, G., Dauda, S., 2019. Corporate Social Responsibility at African mines: Linking the past to the present. J. *Environmental Management*, 241, p.340-352.

Hilson, G., 2016. Farming, small-scale mining and rural livelihoods in Sub-Saharan Africa: A critical overview. *Extractive Industries and Society*, 3(2), p.547-563.

Hilson, G., Hilson, C.J., Pardie, S., 2007. Improving awareness of mercury pollution in small-scale gold mining communities: challenges and ways forward in rural Ghana. *Environmental Research*, 103(2), p.275-287.

Hilson, G., Monhemius, A.J., 2006. Alternatives to cyanide in the gold mining industry: what prospects for the future? *J. Cleaner Production* ,14(12-13), p. 1158-1167.

Hilson, G. and Pardie, S., 2006. Mercury: an agent of poverty in Ghana's small-scale gold-mining sector? *Resources Policy*, 31(2), p.106-116.

Hilson, G., Van Bockstael, S., Sauerwein, T., Hilson, A., McQuilken, J., 2021. Artisanal and small-scale mining, and COVID-19 in sub-Saharan Africa: A preliminary analysis. *World Development*, 139, p.105315.

Hinton, J.J., Hinton, B.E., Veiga, M.M., 2006. Women in Artisanal and Small-Scale Mining in Africa. *Women Miners in Developing Countries: Pit Women and Others*, Ch. 10, p.209-225. Ed. L.Lahiri-Dutt, M.MacIntyre.. ISBN-10:0 7546 4650 5. Ashgate Pub., Hants, UK.

Hinton, J.J. and Veiga, M.M., 2008. The influence of organic acids on mercury bioavailability: insight from an earthworm assessment protocol. *Environmental Bioindicators*, 3(1), p.47-67.

Hinton, J.J., Veiga, M.M., Veiga, A.T.C., 2003. Clean artisanal gold mining: a utopian approach?.*J. Cleaner Production*, 11(2), p.99-115.

Howeler, R., Lutaladio, N., Thomas, G., 2013. *Save and Grow Cassava. A Guide to Sustainable Production Intensification.* (No. FAO 633.6828 S266). FAO, Rome (Italy). https://agris.fao.org/agris-search/search.do?recordID=XF2013001064

Hutchinson, M., Johnstone, K.I., White, D., 1965. The taxonomy of certain thiobacilli. *Microbiology*, 41(3), p.357-366.

Hylander, L.D., Plath, D., Miranda, C.R., Lücke, S., Öhlander, J. Rivera, A.T.F., 2007. Comparison of Different Gold Recovery Methods with Regard to Pollution Control and Efficiency. *Clean*, 35(1), 52–61.

Ikediobi, C.O., Olugboji, O., Okoh, P.N., 1988. Cyanide profile of component parts of sorghum (Sorghum bicolor L. Moench) sprouts. *Food Chemistry*, 27(3), p.167-175.

Jardim, W.F., Bisinoti, M.C., Fadini, P.S., Silva, G.S., 2010. Mercury redox chemistry in the Negro River Basin, Amazon: the role of organic matter and solar light. *Aquatic Geochemistry*, 16(2), p.267-278.

Jaszczak, E., Polkowska, Ż., Narkowicz, S., Namieśnik, J., 2017. Cyanides in the environment—analysis—problems and challenges. *Environmental Science and Pollution Research*, 24(19), p.15929-15948.

Jenkin, G.R., Al-Bassam, A.Z., Harris, R.C., Abbott, A.P., Smith, D.J., Holwell, D.A., Chapman, R.J., Stanley, C.J., 2016. The application of deep eutectic solvent ionic liquids for environmentally friendly dissolution and recovery of precious metals. *Minerals Engineering*, 87, p.18-24.

Jones, D.A., 1998. Why are so many food plants cyanogenic?. *Phytochemistry*, 47(2), p.155-162.

Knight, A.P. and Walter, R.G., 2002. A guide to plant poisoning of animals in North America. *A Guide to Plant Poisoning of Animals in North America.* Teton NewMedia *ISBN 1893441113*

Kolind-Hansen, L. and Brimer, L., 2010. The retail market for fresh cassava root tubers in the European Union (EU): the case of Copenhagen, Denmark—a chemical food safety issue?. J. *Science of Food and Agriculture*, 90(2), p.252-256.

Krishnan, S., Zulkapli, N.S., Kamyab, H., Taib, S.M., Din, M.F.B.M., Abd Majid, Z., Chaiprapat, S., Kenzo, I., Ichikawa, Y., Nasrullah, M., Chelliapan, S., 2021. Current technologies for recovery of metals from industrial wastes: An overview. *Environmental Technology & Innovation*, 22, p.101525.

LibreTexts Chemistry, 2022. P2: Standard Reduction Potentials by Value. https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Electrochemistry_Tables/P2%3A_Standard_Reduction_Potentials_by_Value

Liebig, J., 1851. Process for determining the amount of prussic acid in the medical prussic acid, bitter almond and cherry-laural waters. *American Journal of Pharmacy (1835-1907)*, 14, p.253-255.

Lin, W., Zhang, R.W., Jang, S.S., Wong, C.P., Hong, J.I., 2010. “Organic aqua regia”—powerful liquids for dissolving noble metals. *Angewandte Chemie International Edition*, 49(43), p.7929-7932.

Logsdon, M.J., Hagelstein, K., Mudder, T., 1999. *The Management of Cyanide in Gold Extraction*. International Council on Metals and the Environment. Ottawas. 44 p, https://citeseerx.ist.psu.edu/document?repid=rep1&type=pdf&doi=43c2b874c19b6b11c9307a9dd4299f761edd18c2

Macdonald, E.H., 1983. *Alluvial Mining: the Geology, Technology, and Economics of Placers*. London: Chapman and Hall. 508 p.

Made-in-China, 2023. Sodium Persulphate. https://www.made-in-china.com/products-search/hot-china-products/Sodium_Persulfate.html.

Mahlatsi, S. and Guest, R.N., 2003. The iGoli mercury-free gold extraction process. Mintek.

Mallas, J. and Benedicto, N., 1986. Mercury and goldmining in the Brazilian Amazon. *Ambio*, 15(4), p.248-249.

Malm, O., 1998. Gold mining as a source of mercury exposure in the Brazilian Amazon. *Environmental research*, 77(2), p.73-78.

Marsden, J.O. and House, C.I., 2006. *The chemistry of Gold Extraction*. 2nd Ed. Society for Mining, Metallurgy, and Exploration Inc., Littleton, Colorado, 651 p.

Marshall, B.G. and Veiga, M.M., 2017. Formalization of artisanal miners: stop the train, we need to get off! *Extractive Industries and Society*, 4(2), p.300-303.

Marshall, B.G., Veiga, M.M., Silva, H.A., Guimarães, J.R.D., 2020. Cyanide Contamination of the Puyango-Tumbes River Caused by Artisanal Gold Mining in Portovelo-Zaruma, Ecuador. *Current Environmental Health Reports*, 7, p.303-310. https://doi.org/10.1007/s40572-020-00276-3.

Marshall, B.G., Veiga, M.M., Kaplan, R.J., Miserendino, R.A., Schudel, G., Bergquist, B.A., Guimarães, J.R., Sobral, L.G., Gonzalez-Mueller, C., 2018. Evidence of transboundary mercury and other pollutants in the Puyango-Tumbes River basin, Ecuador–Peru. *Environmental Science: Processes & Impacts*, 20(4), p.632-641.

Martinez, G., Restrepo-Baena, O.J., Veiga, M.M., 2021. The myth of gravity concentration to eliminate mercury use in artisanal gold mining. *Extractive Industries and Society*, 8(1), p.477-485.

Matlock, M.M., Howerton, B.S., Van Aelstyn, M.A., Nordstrom, F.L., Atwood, D.A., 2002. Advanced mercury removal from gold leachate solutions prior to gold and silver extraction: a field study from an active gold mine in Peru. *Environmental Science & Technology*, 36(7), p.1636-1639.

McDaniels, J., Chouinard, R., Veiga, M.M., 2010. Appraising the Global Mercury Project: an adaptive management approach to combating mercury pollution in small-scale gold mining. *Int. J. Environ. Pollut*., 41 (3/4), 242–258.

McIntosh, K.S., 2004. *The systems engineering of automated fire assay laboratories for the analysis of the precious metals*. Doctoral dissertation, Stellenbosch: University of Stellenbosch. 295 p. https://core.ac.uk/download/pdf/37342472.pdf.

Metcalf, S.M. and Veiga, M.M., 2012. Using street theatre to increase awareness of and reduce mercury pollution in the artisanal gold mining sector: a case from Zimbabwe. J. *Cleaner Production*, 37, p.179-184.

Michelazzo, P.A.M., Fostier, A.H., Magarelli, G., Santos, J.C., Carvalho Jr, J.A., 2010. Mercury emissions from forest burning in southern Amazon. *Geophysical Research Letters*, 37(9), L09809, doi:10.1029/2009GL042220. https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2009GL042220

Miller, J.D., 1981. Solution concentration and purification. *In*: *Metallurgical Treatises*, Ed J.K Tien and J.F. Elliot. Metallurgical Society of AIME. p.95-117. 643 p. https://openlibrary.org/works/OL17015221W/Metallurgical_treatises?edition=metallurgicaltre00usac

Mining Global, 2019. Argo Natural Resources: rethinking natural resources. https://www.miningglobal.com/technology/argo-natural-resources-rethinking-natural-resources

Moher, P., 2020. Health and Artisanal Gold Mining, *Human and Ecosystem Health*, Artisanal Gold Council. https://www.artisanalgold.org/publications/articles/health-and-artisanal-gold-mining/

Montagnac, J.A., Davis, C.R., Tanumihardjo, S.A., 2009. Nutritional value of cassava for use as a staple food and recent advances for improvement. *Comprehensive Reviews in Food Science and Food Safety*, 8(3), p.181-194.

Moreno-Brush, M., McLagan, D.S., Biester, H., 2020. Fate of mercury from artisanal and small-scale gold mining in tropical rivers: Hydrological and biogeochemical controls. A critical review. *Critical Reviews in Environmental Science and Technology*, 50(5), p.437-475.

Morrison, E.Y., Ragoobirsingh, D., Peter, S.A., 2006. The unitarian hypothesis for the aetiology of diabetes mellitus. *Medical Hypotheses*, 67(5), p.1115-1120.

Mortier, T., Persoons, A., Verbiest, T., 2005. Oxidation of solid gold in chloroform solutions of cetyltrimethylammonium bromide. *Inorganic Chemistry Communications*, 8(12), p.1075-1077.

Mousavi, A., 2018. Analysis of cyanide in mining waters. Lappeenranta University of Technology, School of Engineering Science. Chemical Engineering. 86 p. https://lutpub.lut.fi/bitstream/handle/10024/158936/Asra%20Mousavi%20thesis.pdf?sequence=1&isAllowed=y

Muhtadi, O. A., 1988. Metal extraction (recovery systems). *In*: *Introduction to Evaluation, Design and Operation of Precious Metal Heap Leaching Projects*. Ed. Dirk JA van Zyl, Ian PG Hutchison y Jean E. Kiel. Chap 8, p. 124-136. Society of Mining Engineers, Inc., Colorado. https://www.911metallurgist.com/blog/wp-content/uploads/2016/03/Merrill-Crowe-process.pdf

Nakao, Y. and Sone, K., 1996. Reversible dissolution/deposition of gold in iodine–iodide–acetonitrile systems. *Chemical Communications*, (8), p.897-898. https://doi.org/10.1039/CC9960000897

Nambisan, B. and Sundaresan, S., 1994. Distribution of linamarin and its metabolising enzymes in cassava tissues. *J. Science of Food and Agriculture*, 66(4), p.503-507

Nartey, F. 1980. Toxicological aspects of cyanogenesis in tropical foodstuffs .In: *Toxicology in the Tropics*. Eds Smith, R.L and Bababumni, E.A., Taylor & Francis Ltd, London, p. 53-73.

Nesbitt, C.C., Milosavljevic, E.B., Hendrix, J.L., 1990. Determination of the mechanism of the chlorination of gold in aqueous solutions. *Industrial & Engineering Chemistry Research*, 29(8), p.1696-1700.

Nitschke, M. and Pastore, G.M., 2003. Cassava flour wastewater as a substrate for biosurfactant production. In *Biotechnology for Fuels and Chemicals* (p. 295-301). Humana Press, Totowa, NJ. https://link.springer.com/chapter/10.1007/978-1-4612-0057-4_24

Noyes, R., 1993. *Pollution Prevention Technology Handbook*. Noyes Publications. 683 p.

Nwaichi, E.O., Onyeike, E.N., Ibigomie, C.E., 2013. Comparative Effects of Processing on the Cyanide Content of Manihot Esculenta, Gly-cine Max and Zea Mays. *Int J Food Sci Nutr Diet*, 2(1), p.15-18.

Olivero-Verbel, J., Johnson-Restrepo, B., Mendoza-Marín, C., Paz-Martinez, R., Olivero-Verbel, R., 2004. Mercury in the aquatic environment of the village of Caimito at the Mojana region, north of Colombia. *Water, Air, and Soil Pollution*,159(1), p.409-420.

Ogundare, O.D., Adeoye, M.O., Adetunji, A.R., Adewoye, O.O., 2014. Beneficiation and Characterization of Gold from Itagunmodi Gold Ore by Cyanidation. *J. Minerals and Materials Characterization and Engineering*, 2(04), p.300-307.

Oke, O.L., Redhead, J. and Hussain, M.A., 1990. *Roots, Tubers, Plantains, and Bananas in Human Nutrition*. FAO Food and Nutrition Series, n. 24, 145 p. https://www.fao.org/3/t0207e/t0207e00.htm

Otekunrin, O.A. and Sawicka, B., 2019. Cassava, a 21st Century Staple Crop: How can Nigeria Harness Its Enormous Trade Potentials? *Acta Scientific Agriculture,* 3(8). https://actascientific.com/ASAG/pdf/ASAG-03-0586.pdf

Park, J.D. and Zheng, W., 2012. Human exposure and health effects of inorganic and elemental mercury. *J. Preventive Medicine and Public Health,* 45(6), p.344-352.

Pecharsky, V.K. and Zavalij, P.Y., 2009. The powder diffraction pattern. *Fundamentals of Powder Diffraction and Structural Characterization of Materials,* p.151-202. Springer US: Boston, MA.

Pelon R. and Martel-Jantin B., 2006. Guidance notes on formalizing informal artisanal mining activity. A global review and comparative analysis of mining codes and policy approaches towards Artisanal and Small-scale Mining. Final report. BRGM/RP-54563-FR. 86 p., 2 fig., 8 tabl., 1 ap. http://infoterre.brgm.fr/rapports/RP-54563-FR.pdf

Pesic, B., Smith, B.D., Sergent, R.H., 1992, Dissolution of gold with bromine from refractory ores pre-oxidized by pressure oxidation. *In*: *EPD Cong. 1992* (p. 223-237).

Pestana, I.A., Azevedo, L.S., Bastos, W.R., Souza, C.M.M., 2019. The impact of hydroelectric dams on mercury dynamics in South America: A review. *Chemosphere,* 219, p.546-556.

Pryor, E., 1965. Mineral Processing; Elsevier: New York, NY, USA, p. 488.

QY Research, 2020. Global Dimethyl Sulfoxide (DMSO) Sales Market Report 2020. 139 p. https://www.qyresearch.com/index/detail/2195777/global-dimethyl-sulfoxide-dmso-sales-market

QY Research, 2021. Global Dimethyl Sulfoxide (DMSO) Market Insights and Forecast to 2027. 101 p. https://www.qyresearch.com/index/detail/2623978/global-dimethyl-sulfoxide-dmso-market-insights-and-forecast-to-2027

Radostits, O.M., Blood, D.C., Gay, C.C., Hinchcliff, K.W., 2000. Veterinary Medicine, A Textbook of the Diseases of Cattle, Sheep, Pigs, Goats and Horses. WB Saunders Company Ltd London, New York, Philadelphia, San Francisco, St. *Louis, Sydney,* pp 1632-1636.

Rajapakse, R.A., 2016. *Pile design and construction rules of thumb*. Butterworth-Heinemann. 378 p.

RedoxTech, 2023. Persulfate. https://www.redox-tech.com/persulfate/

Rees, K.L. and Van Deventer, J.S.J., 2000. Preg-robbing phenomena in the cyanidation of sulphide gold ores. *Hydrometallurgy,* 58(1), p.61-80.

Renner, H., Schlamp, G., Hollmann, D., Lüschow, H.M., Tews, P., Rothaut, J., Dermann, K., Knödler, A., Hecht, C., Schlott, M., Drieselmann, R., 2000. Gold, gold alloys, and gold compounds. *Ullmann's encyclopedia of industrial chemistry*. DOI:10.1002/14356007.a12_499

Riedwyl, H., 1998. Modifying and using Yates' algorithm. *Statistical Papers*, 39(1), p.41-60.

Rogers, D.J. and Appan, S.G., 1973. *Manihot Manihotoides* (*Euphorbiaceae*) flora neotropica. Monograph no. 13. https://www.jstor.org/stable/4393691.

Rollien, W,R., 1936, *The Effects of Lime on the Amalgamation of Gold*. Bachelor of Science in Metallurgical Engineering Thesis. Montana School of Mines, Butte, Montana, 30 p. http://digitalcommons.mtech.edu/bach_theses/66

Rosling, H., 1994. Measuring effects in humans of dietary cyanide exposure from cassava. *Acta Hortic*, 375, p.271-284. DOI: 10.17660/ActaHortic.1994.375.27.

Roulet, M., Lucotte, M., Canuel, R., Farella, N., Courcelles, M., Guimaraes, J.R., Mergler, D., Amorim, M., 2000. Increase in mercury contamination recorded in lacustrine sediments following deforestation in the central Amazon. *Chemical Geology*, 165(3-4), p.243-266.

Ryan, J.A. and Culshaw, G.W., 1944. The use of p-dimethylaminobenzylidene rhodanine as an indicator for the volumetric determination of cyanides. *Analyst*, 69(825), p.370-371.

Salo, M., Hiedanpää, J., Karlsson, T., Ávila, L.C., Kotilainen, J., Jounela, P., García, R.R., 2016. Local perspectives on the formalization of artisanal and small-scale mining in the Madre de Dios gold fields, Peru. *Extractive Ind, and Society*, 3(4), p.1058-1066.

Sandberg, R.G., Simpson, W.W., Staker, W.L., 1984. *Calcium Sulfide Precipitation of Mercury During Cyanide Leaching of Gold Ores* (Vol. 8907). US Department of the Interior, Bureau of Mines. https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwjbgK3M9bv-AhUrJTQIHQsSArQQFnoECAgQAQ&url=https%3A%2F%2Fstacks.cdc.gov%2Fview%2Fcdc%2F10340%2Fcdc_10340_DS1.pdf&usg=AOvVaw3CGnoq_3sHHCaA56K2nTuu

Santos, G. A. 2013. *Myths and Realities in Artisanal Gold Mining Mercury Contamination*. University of British Columbia. MASc thesis, Dept of Mining Engineering. https://open.library.ubc.ca/collections/ubctheses/24/items/1.0071961

Schudel, G., Kaplan, R., Miserendino, R.A., Veiga, M.M., Velasquez-López, P.C., Guimarães, J.R.D., Bergquist, B.A., 2019. Mercury isotopic signatures of tailings from artisanal and small-scale gold mining (AGM) in southwestern Ecuador. *Science of the Total Environment*, 686, p.301-310.

Seccatore, J., Veiga, M., Origliasso, C., Marin, T., Tomi, G., 2014. An estimation of the artisanal small-scale production of gold in the world. *Science of the Total Environment*, 496, p.662-667.

Seney, C.S., Bridges, C.C., Aljic, S., Moore, M.E., Orr, S.E., Barnes, M.C., Joshee, L., Uchakina, O.N., Bellott, B.J., McKallip, R.J., Drace, K., 2020. Reaction of cyanide with Hg0-contaminated gold mining tailings produces soluble mercuric cyanide complexes. *Chemical Research in Toxicology*, 33(11), p. 2834-2844.

Shaw, R.P., 2000. Gold mineralisation in Colombia. *In*: *4^{to} Simposio International del Oro (Lima). Volumen de presentaciones, CD-ROM, doc. 35e*.

Sierra Nevada Corporation. (2018). Artisanal and Small-Scale Mining (ASM) in Colombia. Technical report. Retrieved from https://www.sncorp.com/wp-content/uploads/2018/04/ASM-in-Colombia-Final-Report.pdf

Silva, H.A.M., Kasper, D. Marshall, B.G., Veiga, M.M., Guimaraes, J.R.D., 2023. Acute ecotoxicological effects of $Hg(CN)_2$ in *Danio rerio* (zebrafish). *Ecotoxicology*, https://doi.org/10.1007/s10646-023-02651-w

Silva-Forsberg, M.C., Forsberg, B.R., Zeidemann, V.K., 1999. Mercury contamination in humans linked to river chemistry in the Amazon Basin. *Ambio*, 28(6), p.519-521.

Simeonova, F.P. and Fishbein, L., 2004. *Hydrogen Cyanide and Cyanides: Human Health Aspects*. World Health Organization. 73 p. https://apps.who.int/iris/handle/10665/42942

Singh, H.B., Wasi, N., Mehra, M.C., 1986. Detection and determination of cyanide—A review. *International J. Environmental Analytical Chemistry*, 26(2), p.115-136.

Singo, P. and Seguin, K., 2018. Best Practices: Formalization and Due Diligence in Artisanal and Small-Scale Mining. Africa Portal. 24 p.https://www.africaportal.org/publications/best-practices-formalization-and-due-diligence-artisanal-and-small-scale-mining/

Siritunga, D. and Sayre, R.T., 2003. Generation of cyanogen-free transgenic cassava. *Planta*, 217(3), p.367-373.

Steckling, N., Bose-O’Reilly, S., Pinheiro, P., Plass, D., Shoko, D., Drasch, G., Bernaudat, L., Siebert, U., Hornberg, C., 2014. The burden of chronic mercury intoxication in artisanal small-scale gold mining in Zimbabwe: data availability and preliminary estimates. *Environmental Health*, 13(111), https://doi.org/10.1186/1476-069X-13-111.

Steckling, N., Tobollik, M., Plass, D., Hornberg, C., Ericson, B., Fuller, R., Böse-O'Reilly, S., 2017. Global burden of disease of mercury used in artisanal small-scale gold mining. *Annals of Global Health*, 83(2), p.234-247.

Sun, T.M. and Yen, W.T., 1992. Chemistry of gold dissolution in acidic hypochlorite solution. *In*: *ICHM'92, Proc. Second International Conference on Hydrometallurgy*, p. 475-480. International Academic Publishers.

Taggart, A.F., 1945. *Handbook of Mineral Dressing*. 1st Edition. John Wiley & Sons, New York. 1905 p. ISBN 10:0471843482 / ISBN 13:9780471843481

Takatori, K., Kato, H., Yoshimura, A., Matsuno, Y., 2021. Chalcopyrite Leaching in a Dimethyl Sulfoxide Solution Containing Copper Chloride. *Mining, Metallurgy & Exploration*, 38, p.1477-1485.

Tang, S.P.A., Kwong, K.P., Chung, W.C., Xiao, Y., 2008. Analysis of cyanide contents in some food plants and effects of processing on their levels. *Chin. J. Food Hyg*, 20, p.428-430.

Tchounwou, P.B., Ayensu, W.K., Ninashvili, N., Sutton, D., 2003. Environmental exposure to mercury and its toxicopathologic implications for public health. *Environmental Toxicology: An International Journal*, 18(3), p.149-175.

Torkaman, P., Veiga, M.M., Andrade Lima, L.R.P., Oliveira, L.A., Motta, J.S., Jesus, J.L. and Lavkulich, L.M., 2021. Leaching gold with cassava: An option to eliminate mercury use in artisanal gold mining. *J. Cleaner Production*, 311, p.127531

Torkaman, P. and Veiga, M.M., 2023. Comparing cyanidation with amalgamation of a Colombian artisanal gold mining sample: Suggestion of a simplified zinc precipitation process. *Extractive Industries and Society*, 13, p.01208.

Tran, T., Lee, K., Fernando, K., 2001. Halide as an alternative lixiviant for gold processing-an update. In *Cyanide: Social, Industrial and Economic Aspects as held at the 2001 TMS Annual Meeting* (p. 501-508).

Transparency Market Research, 2022. Sodium persulphate market. https://www.transparencymarketresearch.com/sodium-persulfate-market.html

Tromans, D., Meech, J.A., Veiga, M.M., 1996. Natural organics and environmental stability of mercury: Electrochemical considerations. *J. Electrochemical Society*, 143(6), p.L123.

United Nations Environment Programme, (UNEP), 2022. Minamata Convention on Mercury. https://www.mercuryconvention.org/en

United Nations Environmental, (UNEP), 2018. *Global Mercury Assessment 2018*. UNEP Geneva, Switzerland, https://www.unenvironment.org/resources/publication/global-mercury-assessment-2018).

United Nations Environmental Programme (UNEP), 2017. Minamata Convention on Mercury. UNEP Geneva, Switzerland. http://www.mercuryconvention.org/Portals/11/documents/meetings/COP1/English/1_29_e_report.pdf).

Vasconcellos, A.C.S.D., Hallwass, G., Bezerra, J.G., Aciole, A.N.S., Meneses, H.N.D.M., Lima, M.D.O., Jesus, I.M.D., Hacon, S.D.S., Basta, P.C., 2021. Health Risk Assessment of Mercury Exposure from Fish Consumption in Munduruku Indigenous Communities in the Brazilian Amazon. *International J. Environmental Research and Public Health*, 18(15), p.7940.

Veiga, M.M., 1997. *Introducing New Technologies for Abatement Of Global Mercury Pollution in Latin America*, 94 p. Rio de Janeiro, Brazil: CETEM/CNPq. http://artisanalmining.org/Repository/02/The_GMP_Files/processed%20files%20-%20iwlearn.net/Reports%20%28by%20country%29/introducing-new-technologies-for-abatement-of-global-mercury-pollution-in-latin-america.pdf

Veiga, M.M., 2020. *A Critical Review of Suitable Methods to Eliminate Mercury in Indonesia's Artisanal Gold Mining: Co-Existence is the solution*. Report to UNDP Indonesia, 48 p. https://www.goldismia.org/sites/default/files/2020-06/VEIGA%20-%20FINAL%20Report.pdf

Veiga, M.M., 2022. *Challenges to the Artisanal Gold Mining: The Mercury Problem*. Paper presented at PERUMIN, 35th Mining Conference, Arequipa, Peru, Sept 27, 2022. 9p. (in Spanish). https://perumin35.s3.us-east-2.amazonaws.com/media/04.Conferencias/Encuentro_Internacional/270922_Perumin-Marcello-Veiga_final.pdf.

Veiga, M.M., Angeloci, G., Hitch, M., Velasquez-López, P.C., 2014a. Processing centers in artisanal gold mining *J. Cleaner Production*, 64, p.535-544.

Veiga, M.M., Angeloci-Santos, G. and Meech, J.A., 2014b. Review of barriers to reduce mercury use in artisanal gold mining. *Extractive Ind. and Society,* 1(2), p.351- 361.

Veiga, M. and Baker, R., 2004. *Protocols for Environmental and Health Assessment of Mercury Released by Artisanal And Small-Scale Gold Miners*. GEF/UNDP/UNIDO Global Mercury Project. Vienna. 289 p., ISBN 92-1-106429-5, https://iwlearn.net/resolveuid/617e8a7184a7ec1e292a61c2319dc30f

Veiga, M.M. and Fadina, O., 2020. A review of the failed attempts to curb mercury use at artisanal gold mines and a proposed solution. *Extractive Industries and Society*, 7(3), p.1135-1146.

Veiga, M.M., and Gunson, A.J., 2020. Gravity Concentration in Artisanal Gold Mining. *Minerals* 10(11), 1026.

Veiga, M.M. and Hinton, J.J., 2002, February. Abandoned artisanal gold mines in the Brazilian Amazon: a legacy of mercury pollution. *Natural Resources Forum,* 26(1), p. 15-26.

Veiga, M.M. and Marshall, B.G., 2019. The Colombian artisanal mining sector: where formalization is a heavy burden. *Extractive Ind. And Society,* 6(1), 223-228.

Veiga, M.M., Masson, P., Perron, D., Laflamme, A.C., Gagnon, R., Jimenez, G., Marshall, B.G., 2018. An affordable solution for micro-miners in Colombia to process gold ores without mercury. *J. Cleaner Production*, 205, p.995-1005.

Veiga, M.M., Meech, J.A., Oñate, N., 1994. Mercury pollution from deforestation. *Nature*, 368, p.816-817.

Veiga, M.M., Metcalf, S., Baker, R.F., Klein, B., Davis, G., Bamber, A., Siegel, S., Singo, P., 2006. Manual for training artisanal and small-scale gold miners. Global Mercury Project. UNIDO, Vienna, Austria. https://iwlearn.net/documents/4896

Veiga, M.M., Nunes, D., Klein, B., Shandro, J.A., Velasquez, P.C., Sousa, R.N., 2009. Mill leaching: a viable substitute for mercury amalgamation in the artisanal gold mining sector? *Journal of Cleaner production,* 17(15), p.1373-1381.

Veiga, M.M., Tarra,J.A., Restrepo-Baena, O.J., Tomi, G., 2022. Coexistence of artisanal gold mining with companies in Latin America. *Extractive Industries and Society,* 12, p.101177.

Veiga, M.M., Veiga, A.T., Franco, L.L., Bonagamba, M., Meech, J.A., 1995. An integrated approach to mercurycontaminated sites. *Proc. Eco Urbs, 95,* p.51-53.

Velásquez-López, P.C., Veiga, M.M., Klein, B., Shandro, J.A., Hall, K., 2011. Cyanidation of mercury-rich tailings in artisanal and small-scale gold mining: identifying strategies to manage environmental risks in Southern Ecuador.J. *Cleaner Production*, 19(9-10), p.1125-1133.

Vergara, F., 2009. Ecuador Official Register, Year III, N. 517.

Vieira, R., 2006. Mercury-free gold mining technologies: possibilities for adoption in the Guianas. *J. Clean. Prod.* 14 (3–4), 448-454.

Viñals, J., Juan, E., Ruiz, M., Ferrando, E., Cruells, M., Roca, A., Casado, J., 2006. Leaching of gold and palladium with aqueous ozone in dilute chloride media. *Hydrometallurgy*, 81(2), p.142-151.

Viñals, J., Nunez, C., Herreros, O., 1995. Kinetics of the aqueous chlorination of gold in suspended particles. *Hydrometallurgy,* 38(2), p.125-147.

Wangari, M.F., 2013. Potential toxic levels of cyanide in cassava (Manihot esculenta Crantz) grown in some parts of Kenya. *Library Kenyatta University*.

Wenqian,W. and Poling, G.W., 1983. Methods for Recovering Fine Placer Gold. CIM - *Canadian Inst. Mining and Metallurgy Bulletin*, 76(860), p. 47-56.

WGC, 2022. World Gold Council Publications Archive. www.gold.org

WHO – World Health Organization, 2017. Mercury and Health. https://www.who.int/news-room/fact-sheets/detail/mercury-and-health.

Wilson-Corral, V., Anderson, C.W., Rodriguez-Lopez, M., 2012. Gold phytomining. A review of the relevance of this technology to mineral extraction in the 21st century. *J. Environmental Management*, 111, p.249-257.

Wobeto, C., Corrêa, A.D., Abreu, C.M.P.D., Santos, C.D.D. and Pereira, H.V., 2007. Antinutrients in the cassava (Manihot esculenta Crantz) leaf powder at three ages of the plant. *Food Science and Technology,* 27(1), p.108-112.

Yoshimura, A. and Matsuno, Y., 2016. A Novel Process for the Production of Gold Micrometer-Sized Particles from Secondary Sources. *Materials Transactions,* 57(3), p.357-361.

Yoshimura, A., Takai, M., Matsuno, Y., 2014. Novel process for recycling gold from secondary sources: Leaching of gold by dimethyl sulfoxide solutions containing copper bromide and precipitation with water. *Hydrometallurgy,* 49, p.177-182.

Zadra, J.B., Engel, A.L., Heinen, H.J., 1952. Process for recovering gold and silver from activated carbon by leaching and electrolysis, Report of Investigation 4843, United States Bureau of Mines.

Zhang, Q., Vigier, K.D.O., Royer, S., Jerome, F., 2012. Deep eutectic solvents: syntheses, properties, and applications. *Chemical Society Reviews,* 41(21), p.7108-7146.

Zolnikov, T.R. and Ortiz, D.R., 2018. A systematic review on the management and treatment of mercury in artisanal gold mining. *Science of the Total Environment*, 633, p.816-824.

Appendices

Appendix A: Geology of La Maria Mining Site

The study area is located in La Maria village, San Roque municipality, Antioquia department and can be accessed via a paved road from Providencia town, approximately 2 kilometers east. The proximity of the site to the eastern wall of Gramalote pit is about 300 meters, and the northern border of the tailing storage facility is roughly 250 meters away. The dominant lithology in the area is diorite and monzodiorite, with minor tonalite and dikes of dioritic to granodioritic and granitic composition. Hydrothermal alteration zones are structurally controlled, occurring in selvedges around veins ranging from a few millimeters up to 10cm. Three overlapping alteration zones including potassic, quartz-sericite, and quartz-carbonate-sericite are identified moving from fresh rock to mineralized veins over generally less than 20cm. Gold mineralization in La Maria is associated with structurally controlled quartz vein systems. Mineralized shear structures, characterized by a preferential orientation of 50º/60º and dipping 70º/80º east to southeast, show an association of pyrite, chalcopyrite, bornite, covellite, and galena in quartz veins with carbonate and occasionally chlorite and epidote. Based on the soil geochemistry, lithology, mineralization styles, and alteration, the Maria anomaly is considered to be the eastward continuation of the main Gramalote orebody.

Appendix B: La Maria Ore Analysis

The La Maria ore gold grade was estimated through a series of cyanide leaching tests. After the leaching process, the dissolved gold amount was read by AAS in each sample solution. The amount of gold left in each sample tailing was also obtained by the aqua regia process followed by AAS. By summing up these numbers, the gold grade was calculated for each sample.

Sample	Final Volume (mL)	Au in solution (mg)	Au residue (mg/kg)	Calculated Au Grade (ppm)
1	**120**	0.14	38.72	52.70
2	**172**	0.19	28.17	47.44
3	**146**	0.18	27.99	45.51
4	**124**	0.15	31.84	46.41
5	**121**	0.16	34.69	51.03
6	**74**	0.16	20.06	56.70
7	**71**	0.04	51.90	55.56
8	**99**	0.25	25.23	50.18
9	**124**	0.23	32.91	55.41
10	**93**	0.21	22.23	43.30
11	**97**	0.24	23.06	46.73
12	**109**	0.23	18.27	41.43
13	**105**	0.14	31.95	46.02
14	**75**	0.12	33.53	45.72
AVE				48.87

Table B-1. Analytical balance calculations obtained by AAS and aqua regia of 10g of La Maria sample

The ore's silver content was also analyzed through the fire assay process of a 30 g feed sample. The copper grade was obtained by dissolving another sub-sample in concentrated nitric acid, followed by AAS analysis.

The mineralogy of the sample was obtained by X-ray diffractometry (XRD). To enhance the detection of minerals by XRD, a gravity concentration using a laboratory Knelson centrifugal concentrator was also obtained after grinding the materials below 0.13 mm in a disk mill. The diffractometry yielded information about the crystal structure of the mineral which allows its identification (Dinnebier & Billinge, 2008; Guinier, 2013; Pecharsky & Zavalij, 2009).

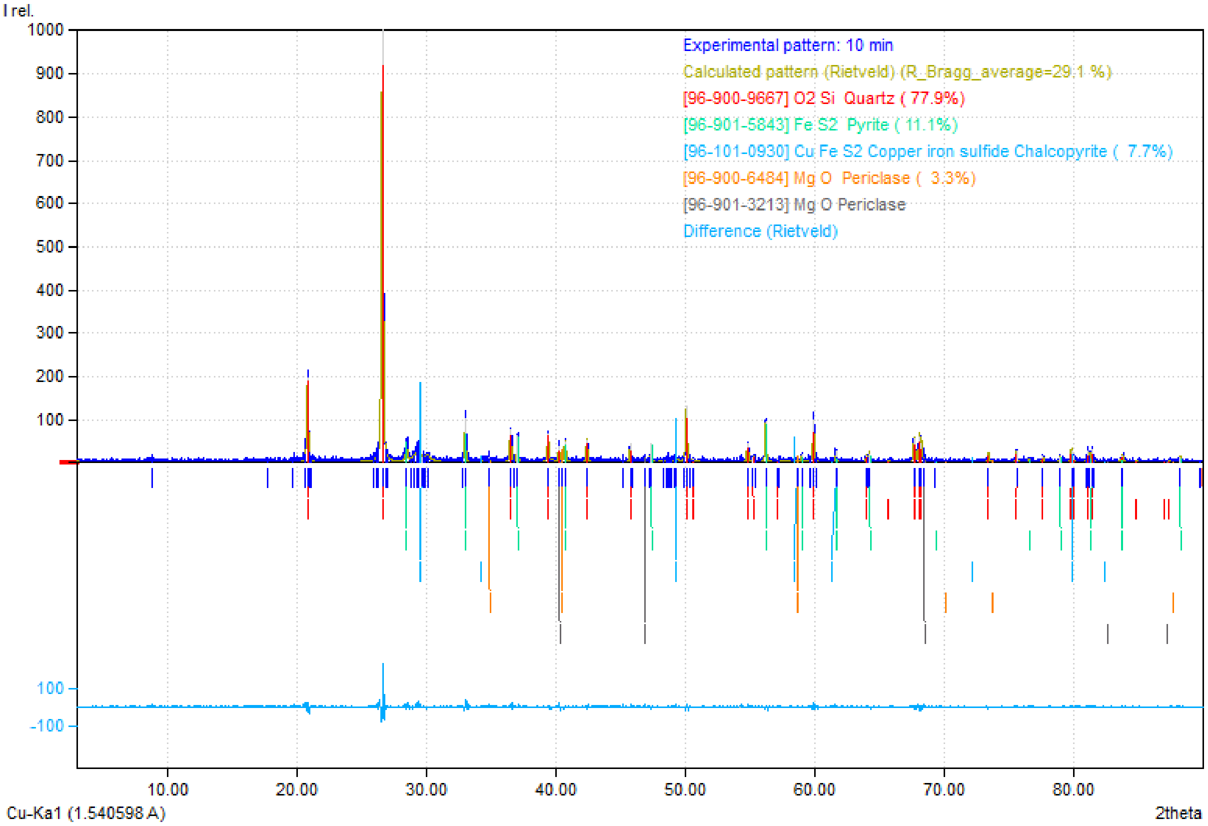

Figure B-1. X-Ray diffraction plot of a gravity concentrate of La Maria obtained by Knelson Centrifuge

Note: Periclase was used by the Rietveld software as a probable mineral, but it is very unlikely to be present.

Appendix C: Chemistry Behind the Aqua Regia Process

The chemistry behind using aqua regia for dissolving ore samples is mentioned below:

$$HNO_3(aq) + 3\ HCl(aq) \rightarrow NOCl(g) + Cl_2(g) + 2\ H_2O(l)$$

Mol of HCl = 36.5 g

3x Mol = 109.5 g

Mol of HNO_3 = 63 g

The grade of HCl and HNO_3 for laboratory use is 38% and 69%, respectively, so

109.5/0.38 = 288.16g of HCl and, 63/0.69 = 91.3g of HNO_3 were needed.

To obtain volumetric ratios:

HCl density = 1.2, so 288.16/1.2 = 240.13 mL

HNO_3 density = 1.51, so 91.3/1.51 = 60.46 mL

Then the volumetric ratio is 4 HCl to 1 HNO3 with commercial grades.

The gold dissolving process is:

$$Au(s) + 3HNO_3(ac) + 4HCl(ac) \rightarrow HAuCl_4(ac) + 3H_2O(l) + 3NO_2(g)$$

The premixed Aqua Regia was not used in this process, and HNO_3 was added incrementally and slowly to the HCl and ore sample mixture.

For the ore digestion process, consider using the solid-liquid ratio 1:10, i.e., for every gram of ore or tailing, prepare to use 10 mL of Aqua Regia.

1. Weigh ore/tailing in a beaker. Using, for example, 10 g.

2. Add all 80 mL of HCl to the beaker containing the ore and place on agitator w/heater.

The temperature should be set at 80°C, and the beaker should be covered.

3. Using a volumetric pipette, periodically over the 3 hours of leaching, add 20 mL of HNO_3 to the mixture till all HNO_3 is added. If the ore contains high sulfide amounts, more nitric acid can be added.

4. Leave the mixture on the agitator with the heater for 3 hours.

5. Remove from heat and allow cooling.

6. Filter the mixture (Whatman filter paper Grade 5: 2.5 µm), and wash/rinse the beaker and residue with distilled water.

7. Using high amounts of water for washing results in excessive dilution of the final solution, reducing the possibility of detecting gold in the solution. On the other hand, using too little water for washing results in the gold that is already dissolved will be impregnated in the filtered residue.

8. Collect and record the total volume of the filtrate. Use a volumetric balloon.

9. Read Au and Ag in an Atomic Absorption Spectrometer equipment.

10. The accurate weight of the material and the final volume are the most critical variables.