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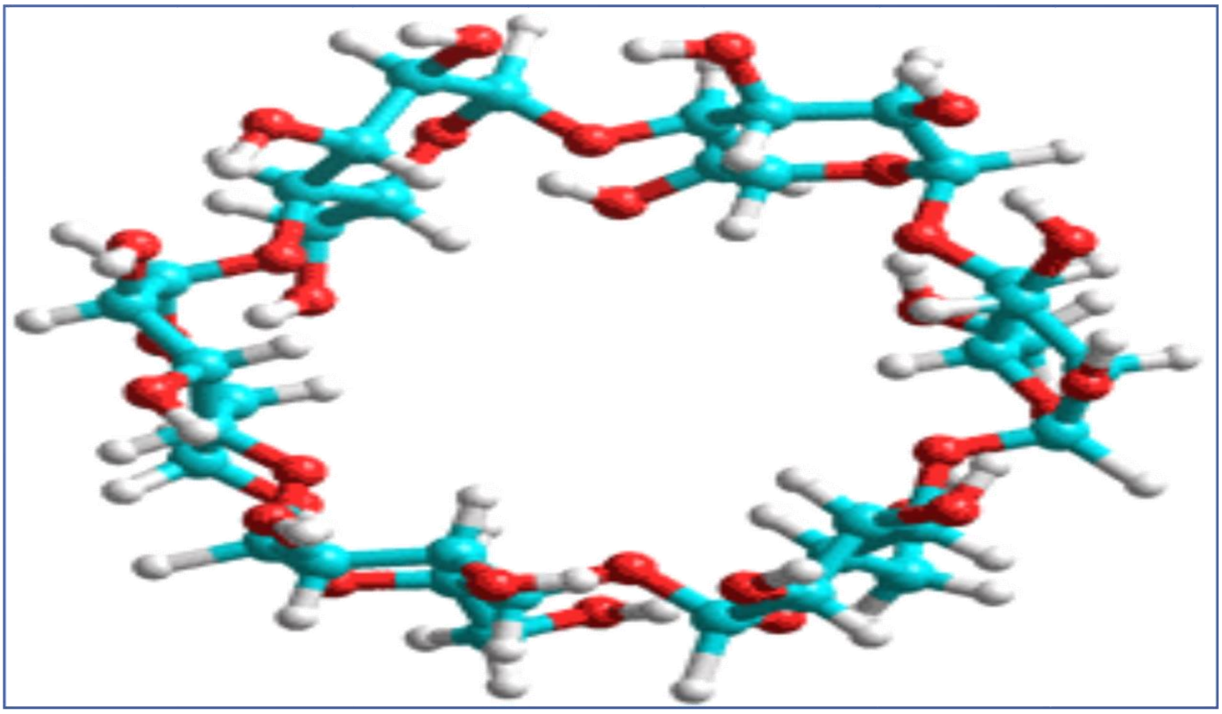
Handtekening

ANTON DE KOM UNIVERSITEIT VAN SURINAME
FACULTEIT DER TECHNOLOGISCHE WETENSCHAPPEN

Alpha cyclodextrine – an alternative to cyanide for gold extraction in the gold mining sector



A thesis submitted in fulfillment of the
requirements for the Degree of
BACHELOR OF SCIENCE IN
ENVIRONMENTAL SCIENCE

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Becker.

6 Mei 2022
Paramaribo, Suriname .

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PREFACE

This thesis is written in order to obtain the degree Bachelor of Science in Environmental Science (Orientation: Environmental Technology) at the Anton de Kom University of Suriname, Faculty of Technology. I was opportune to do my own research in my field of interest, with financial support from Waterforum Suriname and the Fernandes Group Social Foundation. The title of this thesis is: “ Alpha cyclodextrine – an alternative to cyanide for gold extraction in the gold mining sector”. Due to the COVID-19 situation this researched took from 2020 to 2022 to be complete, as the lab was closed during the period of March 2020 till July 2021. Through this research I got a better understanding of gold mining in Suriname.

Geneva Becker

Suriname, April 26th 2022

EXECUTIVE SUMMARY

Gold mining, alongside crude oil mining, is currently one of the most relevant sources of income for Suriname. Suriname's gold mineralization is produced by primary as well as secondary deposits. The primary deposits are commonly linked to quartz- and quartz carbonate veins while the secondary or placer gold occur as colluvial and alluvial deposits from weathered material in terraces of rivers and streams. Most of the gold deposits are found in the Marowijne Greenstone Belt in the eastern part of Suriname. Within the gold mining sector environmental problems from both the formal and informal sections of the gold sector are classified into two broad categories— physical effects (vegetation destruction, wastage of resources, and river siltation) and chemical effects (mainly pollution from mercury and cyanide). For this reason gold recovery using environmentally benign and sustainable chemical processes is a need of overriding importance in today's world.

Luckily, Lui et al made a discovery which heralds a greener host–guest procedure for gold recovery from gold-bearing scrap metals making use of alpha-cyclodextrin (α-CD), a cheap and environmentally friendly carbohydrate. This discovery prompted this research to verify the proposed method by Postdoc Zhichang Liu for gold recovery using alpha cyclodextrin. In addition this thesis researched the potential of the recovery of gold from Surinamese ore, with an attempt to reduce the use of cyanide and mercury in Suriname as to protect existing water resources.

Having that said an laboratory scale gold recovery was conducted by adopting the method described by Liu and his colleagues. For the gold ore recovery three monsters were prepared respectively the positive control consisting of 250 mg concentrated gold, the blank analysis consisting of 250 mg non gold ore and the lab control containing 1g (2.685 ppm) gold ore obtained from the site near New Koffie Kamp. The blank analysis was done to verify the reliability of the method, the lab control was carried out to find out if the method containing alpha-CD works for extracting gold out of Surinamese gold-ore and the the positive control was carried out to verify the recovery rate of gold using this method.

LIST of ABBREVIATIONS and SYNONYMS

CBvs	Centrale Bank van Suriname
ASGM	Artisanal and Small Scale Gold Mining
SSGM	Small-Scale Gold Mining
MIBC	Methyl Isobutyl Carbinol
FA	Fire Assaying
Ppm	Parts Per Million
AAS	Atomic Absorption Spectroscopy
M	Molarity
α-CD	Alpha-cyclodextrin
Hg	Mercury
CGTase	Cyclodextrin Glucosyl Transferase
CDs	Cyclodextrins
β-CD	Beta-cyclodextrin
Pt	Platinum
Fe	Iron
Ti	Titanium
Pt	Platinum
Pd	Palladium
µm	micro meters
mm	Mili meters
kg	Kilograms
CN^-	Cyanide ions
NaCN	Sodium cyanide
KCN	Potassium cyanide
$CaCN_2$.	Calcium cyanide
Ph	Potential of hydrogen
g/L	grams per liter
mg/L	Milligrams per liter

$Ca(OH)_2$	Calcium hydroxide or
NaOH	Sodium hydroxide
HCN	hydrogen cyanide
°C	Celsius degrees
KAuBr4	Potassium Tetra bromoaurate
HBR	Hydrogen bromide
HNO3	Nitric Acid
KOH	Potassium Hydroxide
Na2S2O5	Sodium metabisulfite
NOBr	Nitrosyl bromide
Br	Bromide
NO	Nitric Oxide
NO_2	Nitrogen Dioxide

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1.0 INTRODUCTION

In Suriname, a country situated in South America, gold mining activities take place at small and industrial scale. Multinationals such as IAMGOLD and NEWMONT make use of cyanide for gold mining, whereas the artisanal and small-scale gold miners use mercury to extract gold by “whole-ore amalgamation”. This is a technique which uses 10-25 g of mercury to produce 1 g of gold (Rasmus Køster-Rasmussen et al., 2016). In an attempt to reduce the damage from mercury pollution on people and the environment Suriname ratified the Minamata convention (Wet van 16 Maart 2018, houdende ratificatie van het Verdrag "Minamata Convention on Mercury. 2018). With the ratification of this convention on the 8th of March 2018, the use of mercury in Suriname is prohibited (STVS, 2018). This development lead some of the small-scale gold miners to use cyanide instead of mercury for the extraction of gold from ore (Luciano, Doest 2019).

As Fresh water resources are one of Suriname greatest treasures, environmental and health concerns over the use of cyanide necessitate the development of alternative methods. In particular concerns over environmental accidents such as the collapse of tailing dams and several other disasters with spills into rivers (ACT,n.d; Hilson and Monhemius, n.d).The 2017-2021 development plan acknowledges that the contamination of Surinamese water resources due to small scale gold mining is one of the most threatening issues in the development process. Policy makers also acknowledge that it is of paramount importance to keep the water sources as clean and pure as possible so that future generations can make optimal use of them.

Postdoc Zhichang Liu from Illinois ’Northwestern University coincidental discovered a proposed method for gold recovery. He combined two solutions at room temperature, one of which was a solution of a gold-containing organic salt named aureate (KAuBr4). The other solution contained alpha-cyclodextrin, a corn starch fragment consisting of six glucose units. This resulted in a one-dimensional supramolecular complex, with an extensive {[K (OH$_2$) 6] [AuBr4] (α-cyclodextrin) 2} n chain as seen in figure 1.0. Small needles of solid gold were also formed within a minute of merging the solutions. These needles were constructed from around 4,000 small gold threads with a diameter of approximately 1.3 nanometers *(Zhichang Liu et al., 2013).* This process is based on the second-sphere coordination of $[K(OH_2)6]^+$ and $[AuBr_4]^-$ by α-CD tori, as well as the electrostatic interactions between the ion pairs which facilitate the highly efficient formation and aggregation of the unique 1D cable-like superstructures which result in the highest co-precipitation yield for α·K·Br. Lui proposed this process as an environmentally friendly and cheaper alternative compared to cyanide, which can be implemented in the gold mining sector for gold extraction *(Zhichang Liu et al., 2016).*

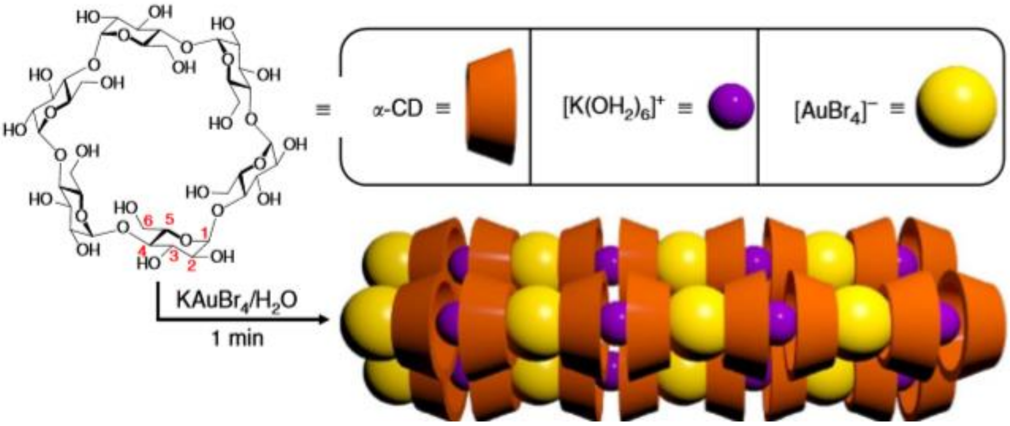


Figure 1.0 schematic representation of the self-assembly of alpha-Br (Zhichang Liu et al., 2013)

1.1 Problem statement

Suriname is a country blessed with clean freshwater resources. However, the gold mining sector contributes to a large part of ground and surface water pollution. As the use of mercury is prohibited extraction of gold is done by using cyanide in both the small-scale and industrial gold mining sector (Luciano, Doest 2019). Even though cyanide ions break down rapidly in sunlight, they have the potential to form cyanide compounds which may persist in the environment for some years. These compounds have the potential to leach into groundwater resulting in the contamination of these resources (Hilson and Monhemius, n.d.). Another concern is the occurrence of environmental accidents such as the collapse of tailing dams and several other disasters with spills into rivers (ACT,n.d; Hilson and Monhemius, n.d). As Suriname relies on groundwater to supply the drinking water industry, it is of paramount importance to keep them as clean and pure as possible. Recent studies tested an environmentally benign chemical processes for gold extraction using, a biologically reproducible product, alpha cyclodextrin (Lui et al., 2013; Anthony et al., 2020). For this reason this present study seeks to investigate the potential of alpha cyclodextrin for the extraction of gold. Therefore the current main question is as follows:

To what extent can the proposed method by Postdoc Zhichang Liu for gold recovery using cornstarch, containing the fragment alpha cyclodextrin, serve as an potential alternative in the gold recovery process in Suriname?

To answer the main question, the following sub research questions are formulated:

Sub research questions:

1. How does the gold mining process take place in Suriname?
2. What is cyanide and how can it influence the fresh and ground water resources in Suriname?
3. What is Mercury and how can it influence the fresh and ground water resources in Suriname?
4. To what extent will this method using cornstarch containing the alpha cyclodextrin fragment be environmental acceptable?
5. Which waste materials does the corn flour process produce?

1.2 Objective

The purpose of this thesis is to verify the proposed method by Postdoc Zhichang Liu for gold recovery using alpha cyclodextrin and to test its potential on the recovery of gold from Surinamese ore, with an attempt to reduce the use of cyanide and mercury in Suriname through a green gold mining process in order to protect existing water resources.

1.3 Relevance

Water is one of the essential elements of life. Humans do not only depend on an intake of water to replace the continual loss of body fluids, but also on food sources that in return depend on water to survive. Statics from The United Nations World Water Development Report state that the global water demand will continue to increase with 20 to 30 % above the current level of water use by 2050. Apart from population growth the availability of freshwater is put under pressure by economic growth, urbanization and pollution (UN Water, 2019). Without freshwater of adequate quality and quantity, sustainable development will not be possibele (Balance and Bartram, 1996). Suriname is amongst the countries with high fresh water availability. The country is believed to be ranked 6th among the countries that have superfluous water resources by the World Water Council Suriname. However this finite resource is being threathened by the effects of climate change. A study carried out for the World Wildlife Fund Guianas (2011), ‘Towards integrated water management in Suriname’, states that the production of surface and sub-soil water based on annual precipitation, is around 117 km^3. While The country used to benefit from a permanent and unlimited availability of fresh water, this situation seems to be compromised by the combined effect of higher demand and changed rainfall patterns which also affects the replenishment of groundwater (National Report for Suriname, 2013); (UNDP, 2016). Another potential threat to the freshwater resources is the pollution from cyanide and mercury resulting from the gold mining sector which happens to be one of the largest contributors to the country’s GDP. Due to the increasing global demand price of gold, it is not wise to put a stop to gold mining activities as they do contribute to the economical growth of the country and many people demand on the sector for a daily income (Wet van 16 Maart 2018, houdende ratificatie van het Verdrag "Minamata Convention on Mercury., 2018). To keep up the current standards of wellbeing and development a green gold mining technology is needed. In this research a sustainable technique for gold minning will be studied which will in return result in the conservation of the fresh water resources while also resulting in economical growth of Suriname.

1.4 Scope

The focus in this research lies on verifying and concluding if the findings of dhr. Zhichang Liu are significant by conducting literature study and lab testing.

1.5 Methods

In order to give an answer on the general question of this research, it will be divided into two phases.

1. In the first phase, literature study will be conducted to get a better understanding off the subject. This will be done by using searching engines such as; google scholar, Pubmed, Sciencedirect, Hinari en NCBI. Beside the searching engines books, journals and articles will also be used.

2. In the second phase a lab test with gold ore will be conducted to evaluate if the method of dhr. Zhichang Liu applies to the conditions in Suriname.

2.0 LITERATURE REVIEW

This chapter provides an overview of the gold resources and main processing methods in Suriname. In particular, the extraction of gold from gold ores, the impact of mercury and cyanide on the aquatic system and the method by doctor Lui are emphasized.

2.1 Cyclodextrins

Cyclodextrins also known as Schardinger dextrins, are relatively large molecules weighing between 1000 and 2000 molecular weight. They can be defined as naturally occurring cyclic oligosaccharides, consisting of six to twelve glycose units in a C-1 chair conformation, attached by α-(1,4) bonds. The outer surface of the cyclodextrins contains hydroxyl groups which are hydrophilic, whereas the inner cavity is hydrophobic. This phenomenon results in the encapsulation of hydrophobic parts of guest molecules by the hydrophobic center, while the hydroxyl groups at the edge of the CD allow the selector to interact with analytes through hydrogen bonding and dipole-dipole interactions. Depending on the number of glycoses building blocks, cyclodextrins can be distinguished into hexametric (α-cyclodextrin), heptameric (β-cyclodextrin), and octameric (γ-cyclodextrin) form. The most interesting property of cyclodextrins is their ability to form host-guest complexes with an abundant variety of organic and inorganic molecules (Di and Kerns, 2016; Giri , 2016; Dingenen, 2000). See figure 2.1 for an overview of the common cyclodextrines.

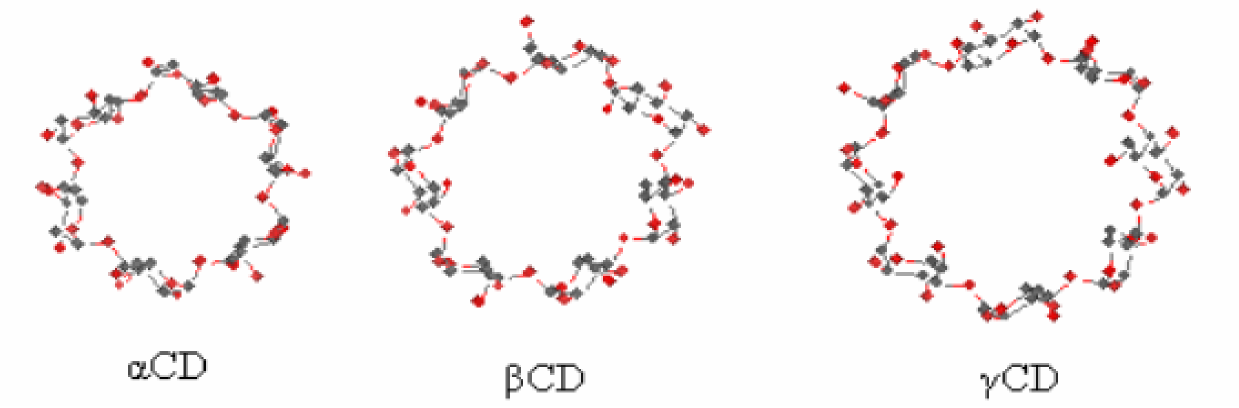


figure 2.1 Overview of the common cyclodextrines (Laboratory of Structural and Supramolecular Chemistry, n.d)

Various studies have shown that cyclodextrines are produced by the action cyclodextrin glucosyltransferase (CGTase) on starch substrates such as potatoes, corn, waxy corn and so on. The hydrolysis reaction is done at the optimum PH and temperature for the enzyme that is being used. Depending on the variability on the selected starch, CGT enzyme and processing conditions, the yields of alpha, beta and gamma cyclodextrins produced by treatment of starch with CGT will vary greatly. Some of the cyclodextrin transglycosylase (CGT) enzyme are; *B. macerans* amylase, *B. circulans*, *B. stearothermophilus*, *B. megaterium*, *B. ohbensis*, *B. klebsiella pneumoniae* and *B. micrococcus*. Out of this group of (CGT) enzymes it is known that the use of CGTase obtained from *B. macerans* will cause the production of of alpha- about 63% by weight; beta- about 30% by weight; and gamma- about 7% by weight of the total amount of cyclodextrin produced (Ammeraal,1986; Shieh& Hedges, 1994; N. Sharma& A. Baldi, 2016).

As a result of their complexation ability and other characteristics, cyclodextrins can be used in different application fields as shown in figure 2.2.

- Pharmaceutical industry (Tiwari, G., Tiwari, R., & Rai, A. K., 2010):
  In this field CDs have been used as complexing agents to increase the aqueous solubility of hydrophobic drugs as well as to increase their bioavailability and stability. They have also been used to reduce or prevent gastrointestinal or ocular irritation, reduce or eliminate unpleasant smells or tastes, prevent drug or drug additive interactions. They are even used to convert oils and liquid drugs into microcrystalline or amorphous powders.
- Biotechnology e.g wastewater treatment (Szejtli, 1990):
  The toxicity reducing effect of Beta-CD is based on the fact that the complexed guest molecules in the CD cavity are more likely to biological decomposition than in free, non-complexed form, resulting in the effective removal from the waste water.
- Food industry (Szente and Szejtli,2004):
  Beta-CD is used as flavor carrier and protector

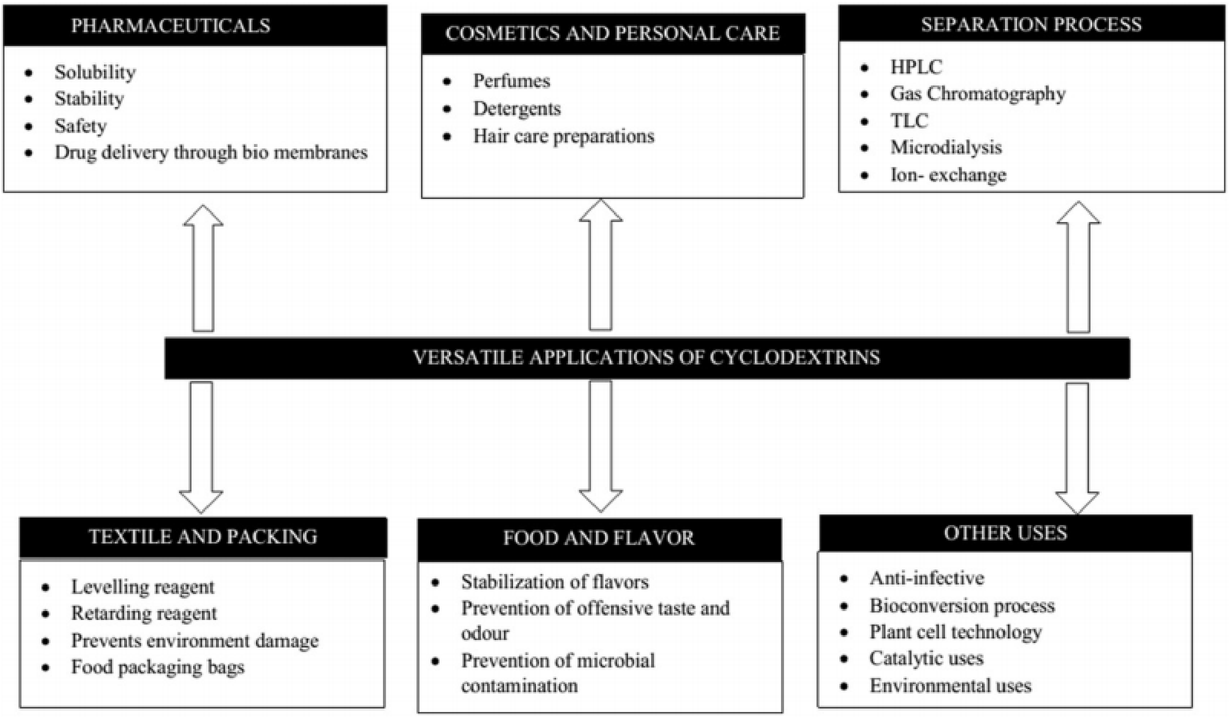


Figure 2.2 versatile applications of Cyclodextrins (N. Sharma & A. Baldi,2016)

2.1.1 Alpha-Cyclodextrin

alpha-Cyclodextrin (synonyms, cyclohexaamylose, cyclomaltohexaose, *alpha*-Schar-dinger dextrin) is a non-reducing cyclic saccharide consisting of six glucose units which are attached by *alpha*-1,4 bonds. Its annular structure provides a hydrophobic inner void which results in the formation of inclusion complexes with a wide range of non-polar organic molecules of appropriate size. The hydrophilic characteristics of the outer surface of the cyclic structure makes *alpha*-Cyclodextrins water-soluble. They are produced by enzymatic reaction of cyclodextrin glucosyltransferase (CGTase) on hydrolysed starch syrups. In the initial process of alpha-CD production, liquefied starch is treated with CGTase under controlled pH and temperature conditions. In the second step of the process the complex is removed and purified by dissolution in water followed by reperticipation. In the last step alpha-CD is obtained from the complexant by decantation and steam distillation, yielding a white powder alpha-CD with a purity of 98%.The hydrophobic and hydrophilic properties of respectively the center and the edge of *alpha*-cyclodextrin form the basis for its application in the food industry. Herein it is used as an ingredient for many food products such as bread, juices, chewing gum, food additives and dietary food supplement (Dr A.S. Prakash and Dr P.J. Abbott, n.d; Amar et al, 2016). Based on safety data, α-CD has been granted Generally Recognized as Safe (GRAS) status by the FDA (GRAS, 2016). According to test carried out by Doctor Prakash and Abbott, *alpha*-cyclodextrines have relatively low toxicity in animals. They are also less toxic than *beta*-cyclodextrin, for which studies of human tolerance are available. Due to that conclusion the statement was made that, as in laboratory animals, *alpha*-cyclodextrines would be fermented to innocuous metabolites before its absorption by humans (Dr A.S. Prakash and Dr P.J. Abbott, n.d).

2.2 Historical overview: The Suriname Gold Rush

Gold mining, alongside crude oil mining, is currently one of the most relevant sources of income for Suriname. In the middle of the 19th century this noble metal has gradually gained interest. In 1853 the German geologist Voltz determined that there was gold to be found in Central Suriname. Still a real gold rush did not start until gold was discovered in French Guyana in the 1860s. Followed by this discovery the first gold rush in Suriname started between 1870 and 1910 with the rise of the small-scale gold mining sector. Back then the workers in the goldfields were mainly creoles, the descendants of formal slaves. This gold rush was of a limited extend with low production. It was until 1907 where the industry reached its climax with a production of 1200 kg gold annually. Unfortunately, this only lasted for a few years as the production went downhill after 1910 to approximately 200 kg gold per year in the period 1930-1970 (Hoogbergen and Kruijt, 2014). The second boom started in the 1980th and continuous till date. It was triggered by the discovery of a large gold deposit at Serra Pelada in Brazil in 1980. From there on the gold rush spread to all neighboring countries (Mol et al., 2000; Ouboter, 2015). Since the internal war (1986 -1992) the existence of police force and government control was only symbolic in east Suriname. This led to the immigration of Brazilians (*garimperos*) from Amapá, the state lying between the Amazon and the (French Guiana) river border Oayapock, to the internal of Suriname and the boom of informal small-scale gold mining. At the same time, restrictions on Small-scale goldmining in Brazil drove thousands garimperos to the Guianas. The arrival of these Brazilians contributed to a culture of entrepreneurs aiming to reach high yielding rates, as fast as possible and without considering the damage the gold mining would do to the environment. They contributed to a mechanized and modernized small scale gold mining sector. Many young maroon men with limited employment options started to join them (Hoogbergen & Kruijt, 2014; GOMIAM, 2011). The production of gold which has gradually emerged as an important pillar in the Suriname economy, replaced bauxite as the primary export commodity from about 2004 (Crawford and Bliss, 2014). This long history of gold mining which started with small-scale artisanal extraction activities has recently seen the development of large-scale operations.

2.2.1 Gold deposits in Suriname

There are two types of gold deposits namely lode (primary) and placer (secondary) gold deposits. The primary or lode deposits are those veins of ore that are embedded in rocks and minerals. Gold is most often found in quartz rock. In order to recover gold from lodes, miners must blast, mill, or treat the rock with chemicals to recover the gold inside. Placer gold or secondary gold is gold of which a lode deposit is eroded by weather and environment factors, leaving the "heavier" minerals, like gold, to be transported down a stream or river (Hylsop,2015; The Shark Group, 2000). Placer gold can be divided in Eluvial gold, Colluvial gold and Alluvial gold. Alluvium is deposited by rivers or streams and consists of silt, sand, clay and gravel (Encyclopedia Britannica, n.d). The heavy eroded material, which is transported with the gold, becomes black sand on the bottom of riverbeds and depressions (Motes, 2017).

Suriname's gold mineralization is produced by primary as well as secondary deposits. The primary deposits are commonly linked to quartz- and quartz carbonate veins while the secondary or placer gold occur as colluvial and alluvial deposits from weathered material in terraces of rivers and streams. Most of the gold deposits are found in the Marowijne Greenstone Belt in the eastern part of Suriname, which contains three main metavolcanic–metasedimentary formations. These formations are the *Paramaka Formation*,the *Armina Formation* ,the *Rosebel Formation*. Conducted studies devided the gold deposits from recent exploration and mining activities in two major zones: one with an E–W orientation (including Rosebel, Nassau and Maripaston) and the other with a NW–SE tendency (including Sara Creek, Lely Mountains and Benzdorp) (Kioe-A-Sen et al., 2016; UNITED news,2015). Even though the majority of large-, medium- and small-scale operations take place in these areas in the eastern green-stone belt, gold also occurs in the Apoera area in west Suriname but only at a low scale (Kioe-A-Sen et al., 2016).

2.2.1.1 The E–W orientation: Rosebel, Nassau and Maripaston)

The Rosebel deposits , located in the Brokopondo District, has many characteristics that enable classification of the ores as an orogenic gold deposit. These deposits are hosted in the Armina and Rosebel Formations (Daoust et al., 2011).
The main gold mineralization consist of a quartz,carbonate,tourmaline,pyrite cluster. Except for primary deposits, secondary gold is also being mined at Rosebel. This secondary gold occurs as free coarse grains or is attached to iron (hydro)oxides. Merian project is hosted in the Armina Formation where gold mineralization is related with quartz veins and linked sulphides consist mostly of pyrite.
The Nassau Plateau is hosted in the Paramaka Formation where both primary and placer gold has been found. Geological research of gold mineralization in this plateau have not been intensively studied, but studies suggest that gold found in mafic rocks are associated with Pt, Fe, P and Ti, as well as native mercury (Kioe-A-Sen et al., 2016).

2.2.1.2 The NW–SE orientation: Sara Creek, Lely Mountains, Benzdorp and Sela Creek

The Sara Creek, Lely Mountains, Benzdorp and Sela Creek are known as working areas for small scale goldminners as shown in figure 2.3. Sara Creek has long been known for extensive mining of placer gold from saprolitic materials and quartz veins, while the geology of the Lely Mountains consists of mining of alluvial gravels and colluvial material. The Benzdorp area is hosted in the Paramaka Formation. Gold mineralisation in this area has not been established with certainty yet, but locally extracted gold linked with copper has might hint at a copper–gold porphyry-type deposit. At the Sela Creek area gold is targeted in saprolitic materials consisting of metavolcanics and metasedimentary rocks (Kioe-A-Sen et al., 2016). The high demand price for gold during the last decades have triggered a gold rush across the country, which resulted in the destruction of thousands of hectares of pristine rainforest and the contamination of major rivers with toxic materials (ACT, n.d).

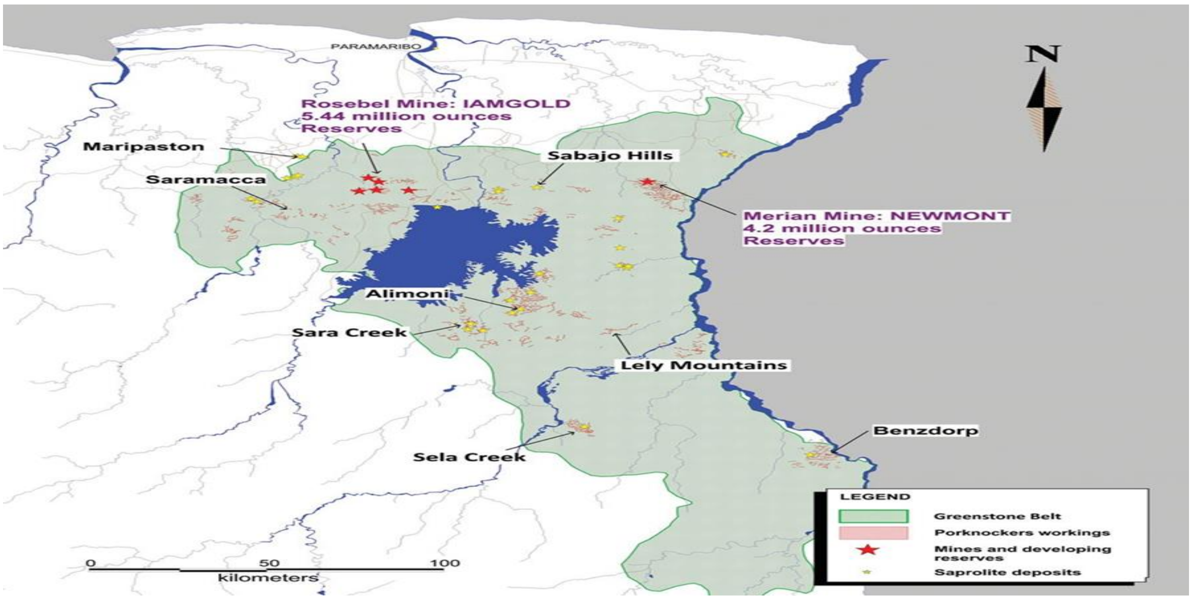


Figure 2.3 the main gold deposits in the greenstone belt

2.3 Small scale Gold Mining

The small-scale gold mining sector has emerged over the past decades as the main engine for economic growth for the people living in tribal communities. It is often characterized by its informality as a result of the civil war, lack of government control in the interior and an outdated legislation. Due to its informal nature, merely a small group directly benefits from the revenues of this sector. With an effort to stimulate and regulate the gold sector and restore confidence in Suriname’s currency by rebuilding international monetary reserves, the CBvs launched a purchasing program in 1994. The first attempt by the CBvs to regulate this sector was by directly buying gold from SSGM. This task was later transferred to gold buying companies (CBvs,2014). Every person who sells his or her gold automatically pays royalties and other government fees (Heemskerk &Duijves, 2011). The government’s attempt to regulate this sector included starting a Gold Sector Planning Program in 2011 to restore the authority of the central government in the interior and to legalize all illegal activities (CBvs, 2014). This economic sector produces about two thirds of the nation’s gold. In 2015 the amount of gold produced by ASM accounted for 18.9 tonnes (Heemskerk et al., 2016). However, this sector also gained attention as the main driver for deforestation and other environmental problems in context to mercury contamination and the pollution of freshwater. Most of the small-scale mining activities are informal (Seccatore & de Theije, 2017).

Till date the exact amount of people in the mining sector is unknown most likely to the widespread informal nature of the sector. Still estimates put that figure at about 12-15 thousand (Heemskerk et al., 2016). Mostly all Suriname nationals active in gold mining are maroons, tribal people of African descendants. They used to mine for gold when they needed cash to purchase important resources, but today small-scale gold mining is their primary source of income. This is the consequence of high poverty rates in rural areas, increased economic instability and the internal 1986-1992 civil war. Study carried out by Heemskerk in 2002 showed that the maroons make this choice of occupation, because of the lack of employment opportunities in their community to sustain their family (Heemskerk&Kooye, 2003). Even while most miners are Brazilian migrants, the maroons have maintained control over gold mining in Suriname. The migrants often work for maroons or else pay them 10% concession fees for the right to mine on their territories (Heemskerk, 2001).

2.3.1 Methods used in Small-scale gold mining

Small-scale gold miners in Suriname work on dredges in rivers, pan river-sediments and mine tailings, and use hydraulic machines of different degrees of power. The most familiar mining methods used by miners in Suriname are based on gravity concentration. The most common extraction process in Suriname are:

- ❖ Hydraulic pumps (spoiti soigi)

  Hydraulic gold mining is by far the most common gold mining method used by SSGM. First miners start by exploring possible sites, often near the site of another miner who is known or believed to have hit a good location. To be sure if a site is suitable the rudimentary prospecting method is applied. This method consists of digging one or several holes of about 2 m deep. The contents are washed with a batea, a circular metal pan with a pointed bottom. If gold is encountered, a site is deemed suitable. After site selection, a forest area of about one ha is cleared from trees (Heemskerk& Kooye,2003). A generator powered mining machine is placed at the prepare site and empowers about two to three hoses. One or two power hoses divert high pressure water to remove first the top layer of sand or clay and later the gold bearing layer of soil, creating a slurry. The soil-water slurry is pumped through the suction hose into a sluice-box. This piece of mining equipment consists of a series of tilted wooden boxes outlined with carpet consisting of plastic fibers. When the slurry flows down the sluice, gold and other heavy minerals are trapped in the fibers of the carpets. The lining of the sluice box consists of a type of carpet with plastic fibers. The mine tailings usually gravel, sand, and clay from which gold has been (partly) removed, flow into either an abandoned mining pit or adjacent forest (Heemskerk, Negulic&Duijves, 2016). After two or three weeks of work, the sluice-box is ‘washed’. Gold is recovered by washing the screen and the mat with water, while adding mercury which chemically binds with gold but not with the other heavy minerals that have been retained. Gold and mercury combine in a ratio of 1:1 to form an amalgam. At last mercury is separated from the gold by evaporation. Most miners simply heat the gold mercury amalgam in a batea, instead of using a closed system which is both cost-effective and healthier (Heemskerk& Kooye,2003).

- Hydraulic mining with screen (Sur: isri daal)

In locations with a lot of pebbles and stones, ASGM teams use a large vertical screen panel. This method is based on the separation of larger rocks from the finer material through sieving. After site selection the top and gold containing layer is excavated. Another excavator places the ore on top of the sieve. Next two spurting hoses spray the material through the sieve. The sluice-box is placed behind the sieve on the ground to catch the gold and heavy metals (Heemskerk, Negulic&Duijves, 2016).

- Ground sluicing (Sur: Sumaje)

This method can be practiced to mine colluvial deposits, alluvials, or tailings in teams of two or alone. About one to three small hydraulic pumps are placed on a hill. As the topsoil layer is loosened up with a pickaxe or shovel by an individual, a spurting hose is used to create a slurry. This slurry subsequently runs downhill onto the mats, which are placed on a piece of board in a narrow trough. Observations suggest that this system is mostly used by the local people (Heemskerk, Negulic&Duijves, 2016).

- Long tom

  This method is a slightly more advanced variation on ground sluicing which makes use of the long tom, a long narrow sluice box. The box is lined with a mat, which is held in place with riffles. Loosened ore is placed on top of the highest end of the long tom with a shovel. In order to separate the larger material from the finer material, water is spurted in the box pushing the ore through the sieve on the bottom of the box. Mercury is usually placed just below the sieve, where the water spins. Observations suggest that this system is very rare mostly used by local people (Heemskerk, Negulic&Duijves, 2016).

- Crushing and grinding (Comminution) This method is used to increase the separation of gold from other particles, which increases the amalgamation rate of gold with mercury, and thus increases the gold yielding. Ore is crushed mechanically using a hammer mill. All material leaving the crusher must first past through an amalgamation box containing mercury. The box will usually have multiple compartments in which material accumulates. Mercury and gold precipitate in the box as the lighter material is washed over the containing sides of the box. The overflow of these boxes typically flows onto sluices for further treatment of gold concentrations (Heemskerk, Negulic&Duijves, 2016).

- Panning

  Panning is used for prospecting, but also occasionally as the primary means of gold concentration. As a primary income source, panners (Sur: baté-mans) seek out rich tailings and creeks. This method is the preferred by gold miners who take and wash the ore of others, usually the local people (Heemskerk, Negulic&Duijves, 2016).

- Metal detectors (pew-pew)

  This method is based on the detection of gold particles. Depending on the power of the device, more and larger gold particles can be found. As a primary income source, pewpew operators often target either the tailings or stockpiles of other operations, which sometimes causes conflict with mine operators (Heemskerk, Negulic&Duijves, 2016).

- Mining on river dredges

  This method is based on the regular hydraulic mining on land with the exception that mercury is not placed in the sluice box rather in the concentration phase. Dredges or rafts are used to mine river sediments by ASGM in Suriname. This can be both manually as mechanically operated. The smaller type, locally named ponton or pondo, is operated manually. First a suction hose is moved across the river bottom by divers who may stay under water for about 4 hours at a time. Through this hose the slurry is pumped to a sluice, which is situated on the raft as the tailings flow into the river. A larger and more advanced version of this system is the skaljan. In this system, the suction hose is mechanically operated from the dredge and does not need divers. While the investment in an automated river raft is relatively high (0.5-1 mln. USD), the earnings also tend to be considerably higher than in land-based operations (Heemskerk, Negulic&Duijves, 2016).

2.3.1 Effects of mercury use on aquatic systems

Environmental problems from both the formal and informal sections of the gold sector are classified into two broad categories— physical effects (vegetation destruction, wastage of resources, and river siltation) and chemical effects (mainly pollution from mercury and cyanide) (Maponga and Ngorima, 2003). Mercury is recognized as a substance producing significant adverse neurological and other health effects, with concerns expressed about its harmful effects on infants and unborn children. The ASGM sector is the largest contributor of anthropogenic mercury emissions to the environment. It accounts for as much as 1,000t of mercury releases to the atmosphere every year. In this sector elementary mercury is used to extract gold from sediments as an amalgam. Amalgamation recovers gold in its native or ‘free’ form. This process can be applied for already-liberated elementary gold with a grain size ranging between 20–50 µm and 2 mm. The amalgam is then heated to evaporate the mercury and isolate the gold (Esdaile & Chalker, 2018; Kippenberg, 2017; Maponga and Ngorima, 2003). Worldwide the minimum amount of mercury needed to amalgamate gold is 1:1. Findings of formal studies based on interviews with ASG miners in Suriname, give a 3.33:1 mercury to gold ratio. This means that for every 1 kg of gold produced, 3.3 kg of mercury is emitted to the environment (Heemskerk et al., 2016). In Suriname almost all ASM operations rely on gravity concentration and mercury amalgamation of sediments. The most common gold mining method involve sluicing with or without excavator (Heemskerk& Duijves, 2017). Within this sector, the amalgamation process, tailings processing, and gold recovery from the amalgam result in considerable release of mercury into the environment. Two primary sources of these emissions are from tailings discharge to land and water as well as mercury gas emissions during the burning of the metallic mercury from the amalgamated gold. After the mercury gas emissions enter the atmosphere, they oxidize and are deposited into nearby or far waterways by wet or dry deposition. Another way how elemental mercury enters the aquatic systems is after gravity separation when the tailings consisting of considerable amounts of mercury flow into the forest or directly back into the creeks (Esdaile & Chalker, 2018). Figure 2.4 and 2.5 gives an overview of the pathways of Mercury in the environment.

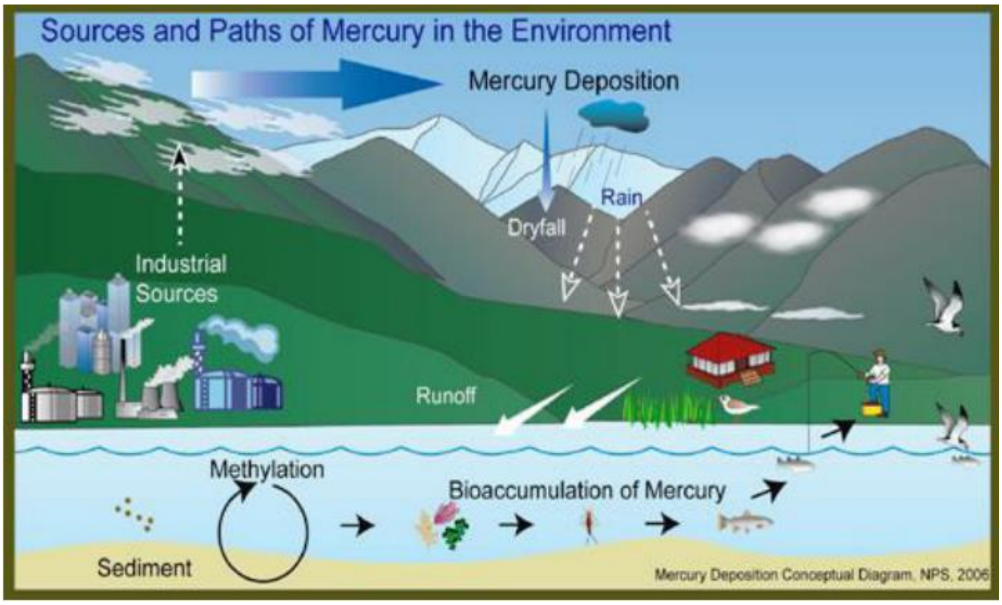


Figure 2.4: Sources and Paths of Mercury in the Environment (NPS,2005)

When this happens, the methylation process of elemental mercury by bacteria into methylmercury starts. The rate at what this process takes place depends on the availability of sulfate-reducing bacteria in anoxic environment. Part of the mercury may be bound to sediment particles, especially to the clayish fraction. Methylmercury is an inorganic compound which is the most poisonous form of mercury (Ouboter, 2015). It can enter the food chain and bioaccumulate causing a lot of health disorders, all of which amount to the following main effects (UNITED news, 2015):

- Allergic reactions resulting in rash, fatigue and headaches, lung irritation, eye irritation, vomiting and diarrhea.
- Disturbance of the nervous system.
- DNA damage and chromosomal damage.
- Damage to brain functions that causes degradation of learning capacity, memory loss, personality changes, deafness, facial changes and uncoordinated muscle movements.
- Negative reproductive effects, such as sperm damage, birth defects and miscarriages

2.3.2 The consequences of mercury use for the environment

The release of mercury from tailings into soil and water is a serious hazard to the environment near mines and communities near these mines, but also in Urban areas. Mercury pollution in Urban areas is due to gold shops. Gold isolated after heating the amalgam usually contains up to 5 % residual mercury by mass. Gold shops owners purchase the gold and process it further to remove mercury through distillation. Some gold shops also process the full mercury–gold amalgam resulting in the emission of mercury vapour in high population centers (Esdaile and Chalker,2018). Given this information the broad range of environmental effects are (UNITED news,2015):

- Disruption of local community hunting and fishing areas.
- Certain fish are poisoned by mercury and die, or the reproductive system fails, causing the fish to disappear from the creek and disrupt the food chain in that area.
- The remaining fish are contaminated with mercury and pose a danger to human health.
- Decrease in the natural value of the area
- Loss of soil fertility and productivity.
- Water pollution

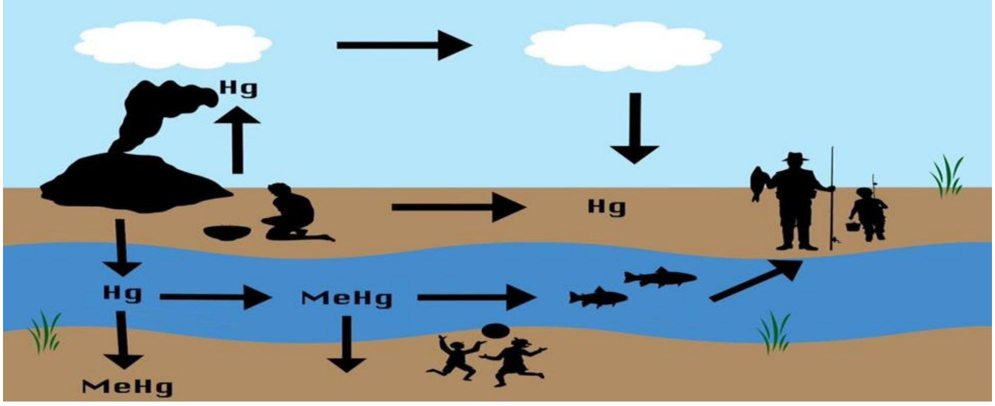
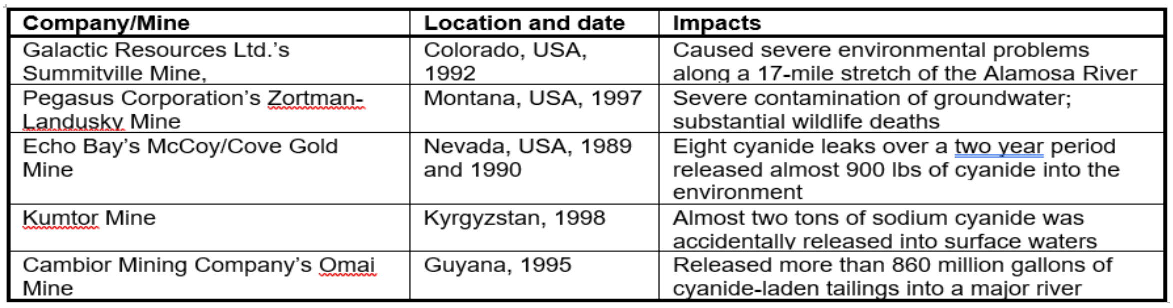


Figure 2.5 Sources and pathways of mercury in the environment (Agostini et al., n.d)

2.4 Industrial Scale gold mining in Suriname

The presence of industrial gold mining is very common in Suriname and is frequently referred to as being more contained, controlled, and less destructive to the environment than small-scale mining. Two large-scale gold mining subsectors operating in Suriname are Rosebel Goldmines N.V. and Newmont Suriname LLC, with the first commencing into commercial goldmining in 2004 and the latter in 2016 (Stichting Plan bureau Suriname, 2018). RGM is in the district Brokopondo in the northeastern part of Suriname of which five percent is owned by the government of Suriname and 95 percent owned by the Canadian company IAMGOLD. The arrangements between RGM and the government are noted in a separate mineral agreement. Regarding royalty payments, this agreement distinguishes between ordinary royalties of 2.25 percent paid in pure gold over the amount exported and extraordinary royalties of 6.5 percent. The government receives 2 percent, and the other 0.25 percent goes into a fund designated for the development of natural resources. In case the gold price rises above US$425 per troy ounce, the extra ordinary royalties can be paid in cash. RGM also pays income tax of 36 percent of net profits and 25 percent tax on wages (CBvs, 2014). Newmont Suriname, previously known as Surgold, is owned by the US-based mining corporation Newmont Corp, which owns and operates the open-pit Merian Gold Project. It is located 66km south of Moengo. The company entered an agreement with Staatsolie Maatschappij Suriname N.V. (Staatsolie) which grants the latter a 25% interest in the project (bnamericas, 2019).

In contrast to ASGM these Multinational Companies make use of the cyanidation process for the extraction of gold from ore. Since cyanide is a toxic compound, cyanide-containing effluents cannot be discharged into the environment without being subjected to treatment to reduce their cyanide contents to very low levels (0.1 mg of CN2 per liter) (Dumestre etal., 1997). This requires the application of a set of chemicals and solar energy to degrade cyanide containing tailings, which are contained in dams. Even though the industrial sector is more formal and causes less destruction to the environment, caution must be taken in the significant risk of eventual dam break of the tailing ponds as such events took place worldwide. In most of these cases, cyanide from processing operations has entered the environment either by leakage through tears or punctures in protective heap leach liners, or by spillage from overflowing solution ponds or tailings storage areas. Such an event recently took place in Suriname’s neighboring country, Guyana, in the Omai mine where millions m^3 of cyanide-laced tailings and wastewater leached into the Omai and Essequibo rivers (ACT,n.d; Hilson and Monhemius, n.d).(See figure 2.6 for an overview cyanide spills and resulting impacts).



Company/Mine	Location and date	Impacts
Galactic Resources Ltd.'s Summitville Mine,	Colorado, USA, 1992	Caused severe environmental problems along a 17-mile stretch of the Alamosa River
Pegasus Corporation's Zortman-Landusky Mine	Montana, USA, 1997	Severe contamination of groundwater; substantial wildlife deaths
Echo Bay's McCoy/Cove Gold Mine	Nevada, USA, 1989 and 1990	Eight cyanide leaks over a two year period released almost 900 lbs of cyanide into the environment
Kumtor Mine	Kyrgyzstan, 1998	Almost two tons of sodium cyanide was accidentally released into surface waters
Cambior Mining Company's Omai Mine	Guyana, 1995	Released more than 860 million gallons of cyanide-laden tailings into a major river

figure 2.6 Overview of cyanide related mine accidents (Hilson and Monhemius, n.d)

2.4.1 Cyanides in the environment

Inorganic Cyanides and nitrile compounds can naturally occur in nature through the synthesis of cyanide by some organisms as fungi, bacteria and algae. They also play a vital role in the evolution of life on Earth as an important form of nitrogen for microorganisms, fungi and plants.   Cyanides are very poisonous compounds and can be lethal if exposed in high concentrations. Despite this given it is extensively used in many industries such as the large-scale gold mining industry (Gupta et al., 2010; Dash et al., 2009; Ebbs, 2004). Cyanide has been used as a leach agent at gold mines for over one century, because of its high efficiency and relatively low cost. The process of obtaining gold from Ores using this chemical is called "cyanidation". The active agents in this process are cyanide ions (CN^-), which dissolve the gold contained in the ore by complexation forming a solution from which gold can later be extracted (Lui etal.,2013). Even while cyanide does not belong to the group of persistent toxins, it poses a serious health threat to a wide range of ecological entities. the CN^- ion tends to react readily with innumerable chemical agents and molecules to form hundreds of different compounds, many of which are lethal to organisms. If exposed to in large quantities, cyanide can cause immediate dead to animals and humans. It binds to the iron-carrying enzymes required for cells to use oxygen, thus inhibiting bodily tissues from extracting oxygen from the blood. In return the body exhibits symptoms of oxygen starvation and suffocation. Symptoms of cyanide poisoning include irregular heartbeat, convulsions, chest pains and vomiting (Hilson and Monhemius, n.d.).

2.4.2 Cyanide leaching

Leaching is a solid-liquid mass transfer process, where the constituents of the ore are dissolved into a solution using varying reagents including water, acids, alkalis, and salts. Currently cyanidation is the main industrial gold leaching process. The cyanide salts that are mostly used in the industry as a source of cyanide, are sodium cyanide (NaCN), potassium cyanide (KCN), and calcium cyanide (Ca(CN)2). Gold leaching using cyanide is typically affected by the following factors: cyanide and oxygen concentration, temperature, pH, agitation, surface area of exposed gold and the presence of other ions in solution (Syed,2012; Azizi et al., 2021 and Altinkaya et al., 2020) . Maximum gold extraction can be achieved in a 0.005% free CN- concentration or 0.01% NaCN, in the presence of 8.2 mg/L dissolved oxygen. In agitated reactor leaching, the NaCN concentration may vary between 0.05 to 0.5 g/L, while in the presence of cyanide-consuming minerals, the concentration of NaCN is kept between 2 and 10 g/L. Most of the time leaching is operated at room temperature. The dissolved oxygen concentration is typically maintained between 5-10 mg/L with air sparging, while the particle size distribution (d80) of the material is from 150 um to 45 um (Altinkaya et al., 2020).The pH of the solution can be adjusted with calcium hydroxide (Ca(OH)2) or sodium hydroxide (NaOH) to between 10 and 11. At lower pH values, hydrogen cyanide (HCN) is formed by the hydrolysis of cyanide ion in water. Due to the toxicity and environmental concerns about cyanide spills as well as the inability of cyanidation to leach refractory ores, many alternative leaching methods have been investigated and developed. However, alternative reagents should be inexpensive, efficient in metal extraction, recyclable, nontoxic, safe to transport and handle, well-suited for downstream recovery procedures, in order to replace the use of cyanide in industrial gold production (Altinkaya et al., 2020 and Azizi et al., 2021).

2.5 Optimizing gold recovery yield

As an attempt to optimize the yield of the α·K·Br co-precipitate research was carried out with respect to temperature, Ph and the molar ratio of α-CD to KAuBr4. Observations made by Lui and his colleagues indicates that the lower the temperature, the more efficient the co-precipitation process. All together higher initial concentrations of KAuBr4 and lower crystallization temperatures lead to the higher yields of the co-precipitated α·K·Br adduct. This study states that 0 °C is a practically operable temperature for the co-precipitation of α·K·Br on account of the accessibility of ice water baths **(**Lui et al., 2016**).** In addition the co-precipitation of a-CD with [AuBr4] is dependent on Ph of which the pH range 2.5–5.9 is the suitable one to initiate this co-precipitation process **(**Lui et al., 2013). One would easily suggest that increasing the amount of α-CD would increase the KAuBr4 yield. In contrast to that studies indicate that, upon increasing the amount of α-CD after reaching a 1:2 molar ratio of KAuBr4 to α-CD, the yield of the co-precipitated adduct remains constant. It can be concluded that the co-precipitated adduct α·K·Br has the constant composition of 1:2 for KAuBr4 to α-CD **(**Lui et al., 2016**).**

2.6 Gold recovery method using Alpha cyclodextrin

The method includes several steps. The first step includes adding a hydrogen halide and an acid to the gold-bearing material to form a first dissolved gold solution. Second to that includes adding a base to the first dissolved gold solution to form a second dissolved gold Solution. This is followed by adding a cyclodextrin to the second dissolved gold solution to form a precipitate in the second dissolved gold solution. Finally the precipitate from the second dissolved gold solution is isolated in the form of a gold-cyclodextrin complex (Lui et al., 2013).

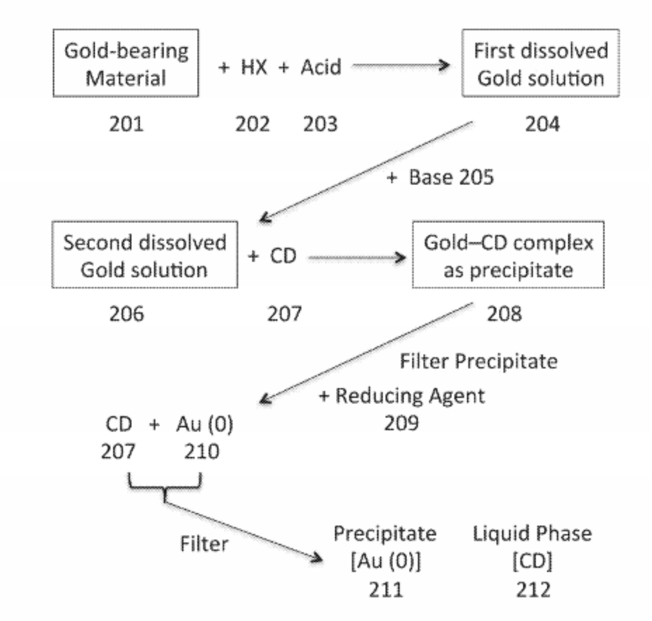


Figure 2.7 gold recovery using alpha-cyclodextra

The results of previous studies show that α-CD gold recovery process has exhibited high recovery of gold from a simple bimetal alloy (red gold alloy scrap: 89% yield and 97% purity and yellow gold alloy scrap: 92% yield and 95% purity) utilizing mild reaction conditions (Lui et al., 2013). Lui and colleagues also state high selectivity of α-CD in extracting gold even in the presence of other noble metals like platinum (Pt) and palladium (Pd) (Lui et al., 2016). Complementary to these results a study was carried out in Nigeria using α-CD to recover gold from gold ores instead of gold scraps. In this study the researchers collected (4 kg) from Shanono gold deposit site Kano State, Nigeria. The 4kg ore was crushed with a sledge hammer to a size acceptable by the laboratory jaw crusher. Then, 1 kg was sent for fire assay, and the remaining gold ore sample (3 kg) was crushed in the laboratory jaw crusher and further ball milled for 6 h and sieved to 80% passing 75 μm . Next this sample was subjected to gravity concentration using a Denver shaking table serial no. 79107, resulting in the collection of 500 g of the gold ore concentrate. The 500-g gold ore concentrate was further super concentrated to 250g gold ore by the froth flotation using a Denver Equipment BJAE 19282 with methyl isobutyl carbinol (MIBC) as frothers and xanthate as collector. This super concentrate was then used for gold recovery see figure 2.7. The fire assaying (FA), showed the average concentration of gold present in the ore to be 4.71 ppm of gold. In order to understand the effect of pH on the selective precipitation of gold, five monsters of [HAuBr4] solutions (40 ml) with pH values of 2.0, 3.6, 4.0, 5.4, and 6.0 were prepared. The recovered gold from each pH was characterized using AAS (PG AA500) with the concentration of pH value of 2.0 recorded as 1.258 ppm, pH of 3.6 is 1.824 ppm, pH value of 4.0 is 2.138 ppm, pH of 5.4 is 1.509 ppm, and pH value of 6.0 is 1.321 ppm (Anthony etal,2020).

3.0 Materials and Methods

This chapter provides detailed information on how the experimental work was carried out to achieve the thesis objectives. It also provides information on the materials and reagents used, experimental setup and methods. When conducting a soil survey, it is important that you know which soil type occurs there for example whether it is transported or residual, whether it is ripened or juvenile. So, the soil profile is important. Normally, the so-called B-horizon is sampled during a geochemical soil survey (Leo Stephan,2004). Suriname's gold mineralization is produced by primary as well as secondary deposits. The primary deposits are commonly linked to quartz- and quartz carbonate veins while the secondary or placer gold occur as colluvial and alluvial deposits from weathered material in terraces of rivers and streams. The Rosebel deposits, located in the Brokopondo District, has many characteristics that enable classification of the ores as an orogenic gold deposit. These deposits are hosted in the Armina and Rosebel Formations (Daoust et al., 2011). The main gold mineralization consists of a quartz, carbonate, tourmaline, pyrite cluster. Except for primary deposits, secondary gold is also being mined at Rosebel. This secondary gold occurs as free coarse grains or is attached to iron (hydro)oxides. With that being said, a laboratory scale gold ore from the deposist of the Rosebel formations will be made.

3.1 Materials

The gold mining site in Brokopondo near Nieuw-koffie Kamp was visited to gain information on the Artisanal and Small-Scale Mining proprietors (ASM) involved in the mining process. The gold ore samples were collected from pits already dug by artisans using stratified sampling method under supervision of Dhr Finkie. The first approach was to look for Quartz veins in the bedrock wall and then collected those veins in a bag for further preparation in the laboratory. The geographic coordinates of the two sampling points were determined with a Garmin global positioning system (GPS) and are respectively 712395Mn 555660 and 712462Mn 555654mE. A total of 4 kg of gold ore samples was collected. The picture below holds the sight of the mining pit.

Photo 1 Mining site near nieuw koffie kamp

The pit where the samples were taken from, was already excavated by the artisans at the time the samples were collected. The samples were taken at two points with a distance of 80 meters from each other. This was done under technical supervision of Dhr Finkie and Bsc Soesman. Since gold is most often found in quartz rock, the samples were taken from quartz veins in the stretched wall. Photo 2 gives an overview of the bedrock wall and photo 3 of quartz veins.

Photo 2 excavated bedrock wall in the pit where samples were taken from

Photo 3 Spotted quartz vein which most likely contains gold in bedrock wall

The collection of the samples was done with a Geologist's hammer. The hammers were used to break small chips off quartz rocks. These small chips were first collected in a pan. At last they were placed in a used rice bag. See the pictures below for an overview of the collection.

Photo 4 breaking down large rocks into small chips

photo 5 quartz rocks collected in a rice bag

Photo 6 overview of a collected quartz vein

3.2 Sample Preparation

The preparation of sample usually involves crushing, grinding, sieving, and working down or reducing volume. The most dependable way to obtain a laboratory sample is to crush the initial sample very finely to mix the mass and work it down to the required final weight. All geological samples must be dry, prior to sample preparation. It is important that all the moisture content of samples are removed to ensure that particles do not adhere to the preparation equipment.

3.2.1 Crushing and grinding

Once in the lab the collected samples (4kg) were categorized. Then the samples were poured onto aluminum baking sheets intended for microwave ovens, placed in a microwave oven and dried with heating for 15 minutes, while the sample was heated to t = 98 ° C. The dried sample was cooled in air for 5-6 minutes and sent for crushing. The larger ore were separated and crushed with a sledge hammer to a size acceptable by the laboratory jaw crusher as seen in photo 7 and 8.

Photo 7 Manually crushed ore

photo 8 Pulverizing of ore

3.2.2 Sieving

Particle or grain size determinations of the soil samples is necessary to ensure that they perform as intended for their specified use. The distribution of particles or by size within a given sample, can quantitatively be determined by a sieve analysis or gradation test (Precision Eforming, 2018). In compliance with the design and production requirements for the large scale goldmining, a size of 75 μm was chosen. The crushed ore sample were wet sieved to 80% passing 75 μm see photo 9. As there was a lot of material, the ore was first sieved through a 125μm in order to separate the larger and grover material. Next the sieved ore was set aside to air dry for about five days before going into the oven see photo 10. The reason it had to dry beforehand is because the oven cannot dry ore with a high water content. After the samples were air dried, they were placed in the oven for proper drying for 48 hours. This left the sample to form a soft plate like pattern as shown in photo 11.

Photo 9 Wet sieving

photo 10 Air drying material

photo 11 plate like dried material

photo 12 stamping of the dried material

3.2.3 Mass reduction by splitting and Conning

One of the recommended method for mass reduction is riffle splitting. The general principle is that the sample to be divided is introduced to a rectangular area, divided by parallel chutes leading to two separate receptacles (Petersen, Dahl, and Esbensen, 2004). After the sample was oven dried, it was crushed until it had a powder like substation as viewed on photo 12. This was followed by placing the sample into the splitter. The split mass was obtained in two rectangular containers which was placed under the splitter. Photo 13 gives an overview of the splitter used.

Photo 13 splitter

In order to achieve high efficiency and to yield one composite sample, an alternative mass reducing technique was used namely the coning–quartering method see figure 3. This is the process of reducing a representative sample to a convenient size, or to divide a sample into two or more smaller samples for further testing. The quartering was done on the hard surface of a table. First a cone was formed with the material and then it was flatten. Second to that the material was divided into half with a roller and then divided into four quarters. Thirdly two opposite quarters of the material were removed and the two remaining ones were mixed together. This process was repeated until a sample of the required size was obtained which was about 2 kg see photo 14.

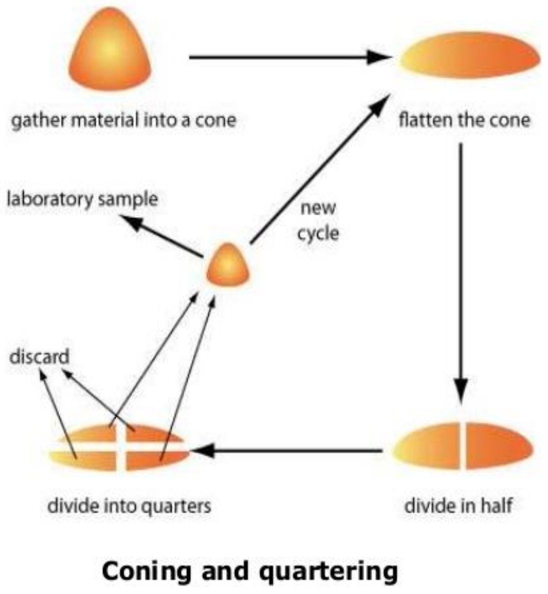


Figure 3 coning and quartering (Abhishek Kumar,n.d.)   photo 14 laboratory scale coning

3.3 Laboratory scale Gold recovery

The laboratory scale gold recovery was conducted by adopting the method described by Liu and his colleagues see figure 3.1. For the gold ore recovery three monsters were prepared respectively the positive control consisting of 250 mg concentrated gold, the blank analysis consisting of 250 mg non gold ore and the lab control containing 1g (2.685 ppm) gold ore obtained from the site near New Koffie Kamp. The blank analysis and positive control (250 mg) were both individually digested in the mixture of concentrated HBr and HNO3 (3/1, 4ml, v/v) while cooking under reflux with a constant temperature T = 100°C for about one to two hours before total dissolution. The positive control was then split into two aliquots of which one was send to Enza Analytical lab to analyze the amount of gold digested in the AR mixture and the other aliquot was used for further treatment.

The dissolved solutions were then neutralized to pH of 5 using KOH (25.0 M) as base and filtered to remove insoluble silver base metal present. Then, α-CD (1.44 g) was added followed by decanting of the solution. This was then dispersed into water and reduced with Na2S2O5 (300 mg) to give the recovered gold metal as a precipitate. The recovered gold metal was collected by decanting off the aqueous solution and sent to FILAB for the determination of the gold content . The lab control containing 1g of (2.685 ppm) gold ore was dissolved in the mixture of concentrated HBr and HNO3 (12/4, 16ml, v/v) while cooking under reflux with a constant temperature T = 100°C for about one to two hours before total dissolution. The dissolved gold solution was split into 4 aliquots and neutralized to pH of 5 using KOH (25.0 M). Then, α-CD (1.44 g) was added followed by decanting of the solution. This was then dispersed into water and reduced with Na2S2O5 (300 mg) to give the recovered gold metal as a precipitate. The recovered gold metal was collected by decanting off the aqueous solution and sent to FILAB for the determination of the gold content.

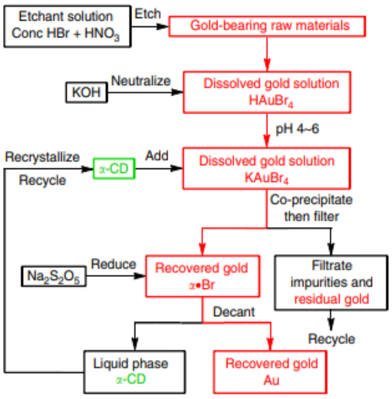


Figure 3.1 Laboratory scale gold recovery (Zhichang Liu et al., 2013).

3.3.1 Chemicals and materials used for the laboratory scale gold recovery

All chemical reagents used in this work were of analytical grade and all stock solutions were prepared using distilled water

- 20 g Alpha-CD (1.48M)
- 50 ml 18M HBR (reagent grade, 48%)
- 20 ml 23M HNO3 reagent grade
- 20 ml 25M KOH
- 1 L aquadest
- 1 g Na2S2O5

Appliances / glassware:

- 50 ml measuring glass 3X
- 5 ml Pipette
- Whatman filter paper
- Hanna checker Ph meter
- Erlenmeyers
- Hour glass
- Funnel
- Glass stirring rod
- Analytical balance
- Rotary shaker
- Hot plate

4.0 RESULTS and DISCOSSION

The purpose of this thesis is to verify the proposed method by Postdoc Zhichang Liu for gold recovery using alpha cyclodextrin and to test its potential on the recovery of gold from Surinamese ore, with an attempt to reduce the use of cyanide and mercury in Suriname through a green gold mining process in order to protect existing water resources. In this chapter the results from the experiment and α-CD comparative studies are presented and discussed.

4.1 Characterization of the gold ore

In order to determine the concentration of gold present in the gold ore obtained from the site near Nieuw-Koffie kamp a fire assay (FA), which is the standard process for determining gold platinum group elements (PGE), was conducted. The fire assay (FA) analysis was performed with 1 kg of the pulverized gold ore sample by ENZA analytical lab. This showed the average concentration of gold present in the ore to be 2.685 ppm of gold.

4.2 The blank analysis

The blank analysis was done to verify the reliability of the method. Therefore (250 mg) of non-gold bearing ore was digested in the mixture of concentrated HBr and HNO3 (3/1, 4ml, v/v). The dissolved solution was then neutralized to pH of 5 using KOH (25.0 M) as base and filtered to remove base metal present. Then, α-CD (1.44 g) was added to the solution. As expected there was no sign of precipitation. The sample was sent to ENZA analytical lab for the determination of the gold content by fire assay (FA). The amount of gold found in this sample was 0.012 ppm see table 4.

4.3 The lab control

The lab control was carried out to find out if the method containing alpha-CD works for extracting gold out of Surinamese gold-ore. The lab control containing 1g of (2.685 ppm) gold ore was dissolved in the mixture of concentrated HBr and HNO3 (12/4, 16ml, v/v). As expected the solution self-heated and emitted brown gasses for fifteen minutes at room temperature. The yellow-brown fumes contain NOBr, Br2, NO, and NO2, gasses which must not be inhaled (Mayoral etal., 2014; Heini etal.,2017; Baharun and Pek

Ling, 2014; Ming Chen and Lena Q. Ma, 2001; Baghalha, 2009; Chmielewski, Urbtiski and Migdal,1997; Potgieter, Mbaya and Teodorovic, 2004). After the solution cooled down and the formation of the gasses halted it was subjected to cooking under reflux on a cooking plate at a temperature of T= 100°C. At this stage the formation of the brown gasses started all over again. After one and a half hour all particles were dissolved, the emission of the gasses had stopped even after adding excess HBr to the solution, and the solution turned yellow see photo 15. The dissolved gold solution was neutralized to pH of 5 using KOH (25.0 M) and further treated with Alpha-CD. The gold concentration after FA analysis by ENZA analytical lab was found to be 0.137ppm which is 5 % gold concentration from the beginning stage see table 4.

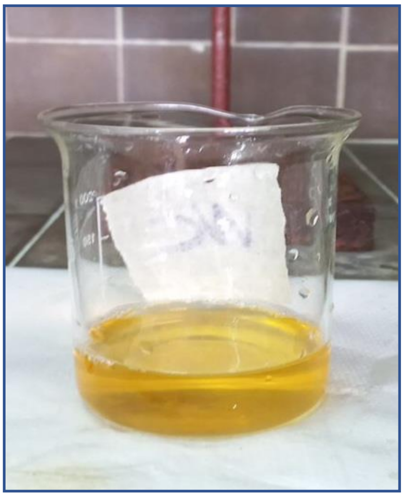


Photo 15 full dissolved particles of the lab control

4.3 The positive control

In order to verify if the method used and described by Liu works and to verify the recovery rate, the positive control was carried out. The positive control consisted of 250 mg concentrated gold from Surinamese gold ore.The positive control (250 mg concentrated gold ore) was digested in the mixture of concentrated HBr and HNO3 (3/1, 4ml, v/v)). As expected the solution self-heated and emitted brown gasses for fifteen minutes at room temperature. After the solution cooled down and the formation of the gasses halted it was subjected to cooking under reflux on a cooking plate at a temperature of T= 100°C. At this stage the formation of the brown gasses started all over again. After one hour all particles were dissolved and the emission of the gasses had stopped and the solution turned reddish see photo 16. The yellow-brown fumes contain NOBr, Br2, NO, and NO2, gasses which must not be inhaled (Mayoral etal., 2014; Heini etal.,2017; Baharun and Pek Ling, 2014; Ming Chen and Lena Q. Ma, 2001; Baghalha, 2009; Chmielewski, Urbtiski and Migdal,1997; Potgieter, Mbaya and Teodorovic, 2004).

Photo 16 dissolved gold in the positive control

The dissolved solution was then split into two aliquots of which one was analyzed for the concentration of dissolved gold and the other was neutralized to pH of 5 using KOH (25.0 M) as base and filtered to remove insoluble base metal present. Unlike earlier studies, this experiment found that the concentration of 1M KOH could not give a significant change in PH, but a higher concentration was needed (Anthony et al.,2020). Then, α-CD (1.44 g) was added to the solution, the rapid co-precipitation occurred in the positive control with the formation of potassium tetrabromoaurate alpha-cyclodextrin complex (KAuBr4·α-CD) immediately after adding Alpha-CD, which is in line with the findings of Liu and his colleagues. At this point the solution turned orange as shown in photo 17. The co-precipitated KAuBr4·αCD namely, recovered gold was separated by decanting. The KAuBr4·α-CD was dispersed into water and then reduced with Na2S2O5 (300 mg) to give the recovered gold metal as a precipitate. The recovered gold metal was collected by decanting off the aqueous solution and sent to ENZA analytical lab for the determination of the gold content which was 408.540 ppm. The aliquot which was analyzed directly after being digested in AR showed a total gold concentration of 1012.500 ppm see table 4. This gives a recovery rate of 40% at a PH of 5.

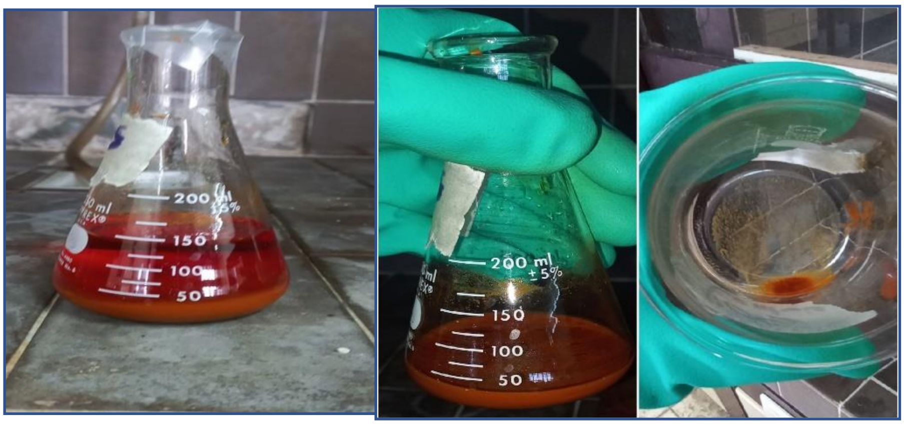


Photo 17 Rapid co-precipitation of Alpha-CD within the positive control

Table 4 Overview of the FA-AAS results

Sample ID	Sample Ref	1st cut au ppm	Method
GB-AU00	Au content in lab control before gold recovery.	2.685	FA-AAS
GB-AU001	Dissolved au in positive control before gold recovery.	1012.500	FA-AAS
GB-AU002	Au content in Positive control after gold recovery.	408.540	FA-AAS
GB-AU003	Au content in Lab control after gold recovery.	0.137	FA-AAS
GB-AU004	Au content in the blank analysis	0.012	FA-AAS

4.4.1 The alpha-CD method in previous studies

The results of previous studies show that α-CD gold recovery process has exhibited high recovery of gold from a simple bimetal alloy (red gold alloy scrap: 89% yield and 97% purity and yellow gold alloy scrap: 92% yield and 95% purity) (Zhichang Liu et al., 2013). Complementary to these results a study was carried out in Nigeria using α-CD to recover gold from gold ores instead of gold scraps. The fire assaying (FA), showed the average concentration of gold present in the ore to be 4.71 ppm of gold. In order to understand the effect of pH on the selective precipitation of gold, five monsters of [HAuBr4] solutions (40 ml) with pH values of 2.0, 3.6, 4.0, 5.4, and 6.0 were prepared. The recovered gold from each pH was characterized using AAS (PG AA500) with the concentration of pH value of 2.0 recorded as 1.258 ppm, pH of 3.6 is 1.824 ppm, pH value of 4.0 is 2.138 ppm, pH of 5.4 is 1.509 ppm, and pH value of 6.0 is 1.321 ppm (Anthony etal,2020). Figure 4.0 gives an overview of the gold recovery rate at varying PH.

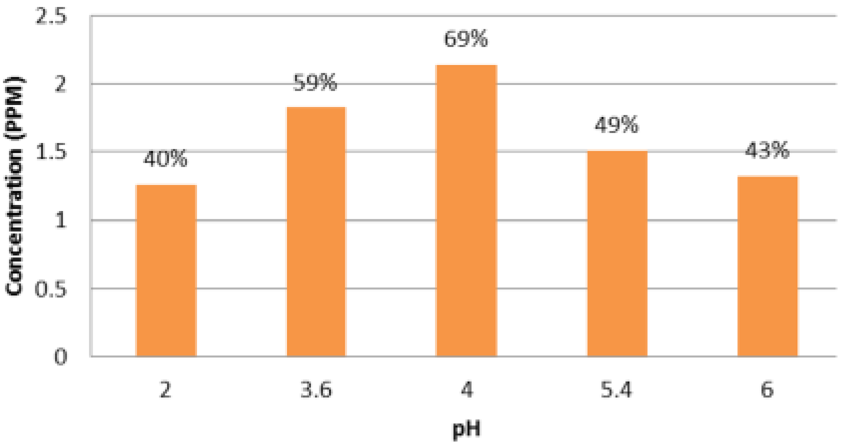


Figure 4.0 overview of the gold recovery rate at varying Ph (Anthony etal, 2020)

5.0 CONCLUSION and RECOMMENDATIONS

There is a growing demand for environmental friendly and techno-economically efficient gold extraction methods. This study investigated to what extent the proposed method by Postdoc Zhichang Liu for gold recovery using cornstarch, containing the fragment alpha cyclodextrin, can serve as an potential alternative in the gold recovery process in Suriname. Thus the following conclusions can be made:

- In Suriname gold mining is divided into the small scale gold mining sector and the industrial scale gold mining sector. The most familiar mining methods used by miners in Suriname are based on gravity concentration. Most of the small-scale mining activities are informal and they usually make use of the amalgamation method, involving mercury (Hg) for the extraction of gold from gold ore. The industrial gold mining on the other hand is frequently referred to as being more contained, controlled, and less destructive to the environment than small-scale mining. In contrast to ASGM these Multinational Companies make use of for the extraction of gold from ore.

- Both the formal and informal sections of the gold sector pose great threat to the environment which are classified into two broad categories: the physical effects (vegetation destruction, wastage of resources, and river siltation) and chemical effects (mainly pollution from mercury and cyanide) (Maponga and Ngorima, 2003). Mercury is recognized as a substance producing significant adverse neurological and other health effects, with concerns expressed about its harmful effects on infants and unborn children.The small scale gold mining sector gained attention in context to mercury contamination and the pollution of freshwater. When mercury enters the aquatic environment the methylation process of elemental mercury by bacteria into methylmercury starts. Methylmercury is an inorganic compound which is the most poisonous form of mercury being able to e (Ouboter, 2015). Cyanides are very poisonous compounds and can be lethal if exposed in high concentrations. Despite this given it is extensively used in many industries such as the large-scale gold mining industry (Gupta et al., 2010; Dash et al., 2009; Ebbs, 2004). It has been used as a leach agent at gold mines for over one century, because of its high efficiency and relatively low cost. If exposed to in large quantities, cyanide can cause immediate dead to animals and humans. It binds to the iron-carrying enzymes required for cells to use oxygen, thus inhibiting bodily tissues from extracting oxygen from the blood. In return the body exhibits symptoms of oxygen starvation and suffocation. Having this said, caution must be taken in the significant risk of eventual dam break of the tailing ponds as such events took place worldwide. In most of these cases, cyanide from processing operations has entered the environment either by leakage through tears or punctures in protective heap leach liners, or by spillage from overflowing solution ponds or tailings storage areas. (ACT,n.d; Hilson and Monhemius, n.d).

- The blank analysis was done to verify the reliability of the method. Therefore (250 mg) of non-gold bearing ore was digested in the mixture of concentrated HBr and HNO3 (3/1, 4ml, v/v). The dissolved solution was then neutralized to pH of 5 using KOH (25.0 M) followed by the addition of α-CD (1.44 g). As expected there was no sign of precipitation. The sample was sent to ENZA analytical lab for the determination of the gold content by fire assay (FA). The amount of gold found in this sample was 0.012 ppm. With this results it can be concluded that the method is reliable.

- In order to verify if the method used and described by Liu works and to verify the recovery rate, the positive control was carried out. This gave a recovery rate of 40% at a PH of 5 which is in line with the earlier study where the recovery rate of concentrated gold ore at PH 5.4 is 49% (Anthony et al.,2020). Even though this method is proven to work, it still exhibits a low recovery rate for application in the gold mining sector.

- The lab control was carried out to find out if the method containing alpha-CD works for extracting gold out of Surinamese gold-ore.The lab control containing 1g of (2.685 ppm) gold ore was dissolved in the mixture of concentrated HBr and HNO3 (12/4, 16ml, v/v), neutralized to pH of 5 using KOH (25.0 M) and further treated with Alpha-CD. Unlike what was stated by Liu, the solution did not precipitate after adding the Alpha-CD (Zhichang Liu et al., 2013). This observation may indicate that the gold present in the feed material was insufficient to have a noticeable precipitation with Alpha-CD. The gold concentration after FA analysis by ENZA analytical lab was found to be 0.137ppm which is 5 % gold concentration from the beginning concentration of 2.685 ppm. Given this result it can be concluded that this method has the potential to extract gold from Surinamese ore. However the percentage in which it does so is too low for application in the gold mining sector.

- Based on the findings above, it can overall be concluded that the optimal conditions for the extraction of gold from gold ore are 18M HBR, 23M HNO3, 25M KOH concentration, pH = 4 with a recovery rate of 69% (Anthony etal,2020) and T = 100 °C. Despite being a proven technology, this method is associated with high chemical consumption, high chemical and energy cost and features process parameters that are difficult to control. Due to this the method is not as environmentally benign as described by Zhichan liu. The acidic condition under which the leaching has to be done pose considerable threat to the environment in case of a spill. While leaching gold ore into HNO3 and HBr toxic gasses are emitted posing serious threats for health and the environment. This method is under researched with considerable obstacles to be overcome before it could be used as an alternative method in the gold mining Industry.

Recommendations for further study

- Further study aimed at the process scaling up should be done with a larger amount of gold bearing ore for more accurate results.
- Lab analysis must be carried out of the applied method for the extraction of gold from gold ore, which has first been subjected to gravity concentration or other concentration methods resulting in super concentrated gold ore, leading to a high gold recovery.
- Comparative study of the environmental and economical of the researched gold extraction processes to cyanidation has to be done.
- An in-depth study focusing on dissolution mechanisms and leaching kinetics of gold in HBR-HNO3 media should be carried out.
- With regard to the leaching of gold in HBR-HNO3 media, the level of free HBR concentration should be investigated to determine its effect on the recovery of gold and the effectiveness of Alpha-CD.

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APPENDIX 1: Conventional Aqua Regia vs New Aqua Regia

Aqua Regia is a very corrosive and strong oxidizing solution known for its ability to dissolve gold and platinum. Aqua Regia is usually prepared by slowly adding one volume of concentrated HNO_3 to three equivalent volumes of concentrated HCl in a suitable glass vessel. Upon mixing, the colorless solution quickly becomes hot and turns yellow in color, which successively darkens to an orange or red fuming solution over several minutes. The yellow-brown fumes contain NOCl, Cl_2, NO, and NO_2, which must not be inhaled. The Aqua Regia solution is now ready for use, which must only occur in open or vented glass vessels. Once the solution returns to a yellow color and gas evolution ceases, Aqua Regia has lost its potency (though it remains strongly acidic and oxidizing).

The nitric acid is a good oxidizing agent. Chloride ions from the hydrochloric acid from coordination complexes with the gold ions, removing them from solution. Reducing the concentration of the Au^{3+} ions shifts the equilibrium towards the oxidized form. Reaction equation:

$Au(s) + 3NO_3^-(aq) + 6H^+(aq)$ $Au^{3+}(aq) + 3NO_2(g) + 3H_2O(l)$ $Au^{3+}(aq) + 4Cl^-(aq)$ $AuCl_4^-(aq$

$Au(s) + HNO(aq) + 4\ HCl(aq) \longrightarrow HAuCl(aq) + 2\ NO(g) + 2\ HO(aq)$

The solution may turn brown from dissolved oxides of Nitrogen.When brown fumes are no longer evolved and the bubbling of the solution is quiet a little hydrochloric acid is usually added. Sometimes a further spurt of activity is seen, the original hydrochloric acid having been depleted leaving some unused nitric acid available, excess hydrochloric acid is not harmful. More aqua-regia may be added as before and the cycle repeated until the addition of fresh aqua-regia produces no reaction, i.e. brown fumes and bubbling. Enough aqua-regia must be added to dissolve all of the gold, however the excess aqua-regia that is required to accomplish this will later have to be removed so large excesses should be avoided. Toward the last the reaction is much slower and it is desirable to warm the solution and to agitate it regularly, but the aqua-regia should not be heated to boiling. If heated too much it will produce brown fumes merely because it is too hot, this wastes acid and obscures the end of the solvent action. When the gold is dissolved, the mixture can be filtered through Whatman no. 42 paper.The filtered liquid is usually a clear green color, due to nickel and copper. If only gold chloride were present it would be yellowish. The excess aqua-regia that was added to insure complete solution of all gold is, of course, still in the solution at this stage and must be eliminated to allow the gold to be precipitated. The classic procedure for nitric acid elimination is repeated boiling to near dryness with the addition of hydrochloric acid with some sulphuric acid near the end. This is a lengthy and patience-trying process. Factors stimulating the rapid dissolution of gold by aqua regia are, particle size smaller than 100 µm, agitation speeds 700 rpm eliminated, HNO3-to-HCl volume ratio, liquid-to-solid mass ratio which is usually 5:1, and the reaction temperature varying from 20 to 100 degrees. (Mayoral etal., 2014; Heini etal.,2017; Baharun and Pek Ling, 2014; Ming Chen and Lena Q. Ma, 2001; Baghalha, 2009; Chmielewski, Urbtiski and Migdal,1997; Potgieter, Mbaya and Teodorovic, 2004).

Earlier investigators suggested that hydrobromic acid might be a suitable AR component as the new HNO3/HBr mixture. Research showed that changes in the HCl/HNO3 (AR) mixture minimize the formation of volatile gold chloride species, form a new acid mixture that retains strong oxidizing ability, and stabilize new Au-containing species that do not volatilize at relatively high temperatures. A mixture of HNO3/HBr oxidizes elemental Au in a similar manner as the conventional aqua regia HNO3/HCl (Yong Wang and Brindle Ian,D. n.d.).

HNO3 + 3HBr → NOBr + Br2 + 2H2O

2Au + 2Br- + 3Br2 ↔ 2AuBr4

Full conversion and stabilization of gold, in the form of AuBr4 - in acidic solutions, is a delicate process. Therefore elemental bromine which can easily be lost via vaporization should be present in the solution. The presence of a slight excess of free Br2 is the key to complete extraction of Au into solution. Data suggest that gold recoveries could drop 10-20% where there is no dissolved bromine in solution (Yong Wang and Brindle Ian,D. n.d.).

APPENDIX 2: Laboratory scale gold recovery method

All practices should be done in the in the draft chamber.

1) Wash all glassware with aquadest and make sure they are clean from organics.
2) Weigh 250 mg gold, 1 g artificial gold ore (2.685 ppm) and 250 mg non gold bearing ore separately in a Erlenmeyer on an analytical balance.
3) Pour 30 ml HBr (18M) into a 100 ml measuring glass and cover it with a glass plate.
4) Pour 10 ml HN03 (23 M) into a 100 ml measuring glass and cover it with a glass plate.
5) Slowly pour 12ml Hbr solution into the Erlenmeyer containing 1 g artificial gold ore, 3ml Hbr soloution into the Erlenmeyer containing 250 mg gold and the 3ml in the one containing 250 mg non gold bearing ore.
6) Add 4 ml HN03 (23 M) into the Erlenmeyer containing 1 g artificial gold ore, 1ml HNO3 solution into the Erlenmeyer containing 250 mg gold and the 1ml in the one containing 250 mg non gold bearing ore.
7) Cover the mixtures with an hour glass and place them on a rotary shaker at a rotating speed of 1000 rpm at room temperature and let the solution cool for 15 minutes until there are no more brown gasses produced.
8) Place the solutions on a cooking plate and heat up to T= 100°C by cooking under reflux until all particles dissolve.
9) Measure the PH with a Hanna Checker Ph meter or PH strip and neutralize with KOH (**25M)** to a PH of 5. Stir the solution until the Ph stabilizes.
10) Filter the mixtures with a 0.45 um pore size Whatman filter into separate Erlenmeyer's to remove the insoluble base metals from the solution and wash the solution with aquadest.
11) Weigh out 1.44 g of alpha-CD **(1,48 mmol, 1,44 g**) and add to the filtrate. Stir the solution with a clean glass swab until Co-precipitation occurs. Keep an eye on the time here.
12) Filter the solution again and let the residue air dry for 10 minutes.
13) Dissolve the residue in distilled water.
14) The "werkelijke monster" and "negatieve controle" are capped to send to filab or Enza for fire assay. The following steps are for the "positieve controle" monster.
15) Weigh out 300 mg of Na2S2O5 (1.58 mmol) and add this to the gold solution and allow to precipitate.
16) Decant the solution and add Aquadest to send to filab or enza for fire assay.