International Journal of Sustainable Energy and Environmental Research
2023 Vol. 12, No. 2, pp. 17-30
ISSN(e): 2306-6253
ISSN(p): 2312-5764
DOI: 10.18488/13.v12i2.3422

Investigation of techniques to replace amalgamation in artisanal gold mining operations

Pariya Torkaman[1+]
Marcello Veiga[2]
Leslie Lavkulich[3]
Bern Klein[4]

[1,2,4]*Norman B. Keevil Institute of Mining Engineering, University of British Columbia, Vancouver, Canada.*
[1]*Email:* pariya.tn@gmail.com
[2]*Email:* veigamining@gmail.com
[4]*Email:* bklein@mining.ubc.ca
[3]*Department of Land and Food Systems, University of British Columbia, Vancouver, Canada.*
[3]*Email:* lml@mail.ubc.ca


(+ Corresponding author)

Article History
Received: 5 June 2023
Revised: 21 July 2023
Accepted: 31 July 2023
Published: 11 August 2023

Keywords
Artisanal mining
Eco-friendly
Gold extraction
Gold recovery
Mercury pollution
Sustainability.

ABSTRACT

Artisanal gold mining is the leading source of anthropogenic mercury emissions worldwide. This article explores cost-effective gold leaching methods for skilled miners to address mercury's environmental and health impacts in this sector. A sample from Colombia's La Maria deposit, containing 48.87 ppm gold, ground to 80% below 0.13 mm, served as the basis for comparison. The standard whole ore amalgamation approach, commonly used by miners, resulted in less than 19% gold extraction. However, employing cyanidation with 1g/L of free cyanide extracted 84% of the gold within 24 hours. Among the unconventional processes investigated, using effluent from a local cassava processing plant as a lixiviant demonstrated promise. Two cassava varieties produced liquids with 267 and 600 mg/L of free cyanide, leading to 50.9% and 82.4% gold extraction from the ore in 24 hours, respectively. Another alternative method involved employing Dimethyl sulfoxide, a water-free reagent, as a gold-leaching lixiviant, resulting in a remarkable 96.5% gold extraction in just 2 hours. The researchers also modified the Merrill-Crowe cyanidation process by eliminating filtration and vacuum, instead utilizing bags filled with zinc (or aluminum) in the pulp. With reduced agitation to prevent aeration, over 99% of the gold precipitated on the zinc shavings within 2 hours. Furthermore, testing a hydrochloric solution (50%) with an oxidant demonstrated 83.9% and 100% gold extraction in 8 hours at ambient temperature and 50°C, respectively. It is crucial to note that successful implementation of these alternative strategies necessitates knowledge, investment, and customization to suit specific site conditions.

Contribution/Originality: Our study presents innovative, cost-effective, and sustainable alternatives to amalgamation in artisanal gold mining operations. By introducing cyanidation with effluent from cassava plant, Dimethyl sulfoxide, and modified Merrill-Crowe process, we contribute to the development of safer and more environmentally friendly methods for extracting gold, potentially transforming small-scale mining practices.

1. INTRODUCTION

In more than 70 developing countries, artisanal gold mining (AGM) heavily relies on elemental mercury for gold extraction, resulting in significant environmental and health issues. The release of mercury during gold amalgamation poses severe risks, particularly for operators and nearby communities residing near processing facilities. According to the Global Mercury Assessment (UNEP, 2018), over 2,000 tonnes of mercury are annually released into the environment by over 20 million artisanal miners, making it the largest anthropogenic source of mercury pollution worldwide. These emissions, consisting of approximately 838 tonnes through atmospheric release and 1,206 tonnes through discharges to land and water, contribute to this alarming pollution (Martinez, Restrepo-Baena, & Veiga, 2021).

Moreover, the recent surge in gold prices and the impact of the Coronavirus outbreak have increased unemployment rates in developing countries. As a result, millions of individuals have turned to informal gold mining activities to sustain their livelihoods (Gavin, Van Bockstael, Sauerwein, Hilson, & McQuilken, 2021). This trend further exacerbates the challenges associated with artisanal gold mining and underscores the urgent need for practical solutions to mitigate the environmental and health implications caused by mercury usage.

The focus of researchers and international agencies in the last 40 years regarding the problems of mercury associated with AGM has been to reduce or eliminate mercury by promoting gravity concentration. Nevertheless, most activities by governments, international agencies, and academic researchers have been dedicated to monitoring mercury's environmental and health impacts, as well as suggesting procedures to legalize artisanal miners. These approaches have not resulted in significant reductions in mercury use in this sector. A few projects have been focused on training gold miners to adopt cleaner gold processing techniques (Veiga & Fadina, 2020).

The uses and losses of mercury depend on the type of ore being processed (Figure 1 & 2). When processing secondary ores (alluvial, colluvial, and eluvial), due to their low grades, miners concentrate the gold and amalgamate only the concentrates. Rare cases exist where miners amalgamate secondary ores with copper-amalgamating plates. When mining primary ores, usually with higher grades, the process involves crushing, grinding, and amalgamation of the whole ore in small ball mills or copper-amalgamating plates. Concentration after grinding is not a common practice, particularly in Latin America, but it is used in some cases (Vieira, 2006; Zolnikov & Ortiz, 2018). The leading cause of mercury losses in mining is the amalgamation of the whole ore. Concentration can reduce the mass of material to be amalgamated to much less than 10% of the original ore mass (Veiga, Angeloci-Santos, & Meech, 2014b).

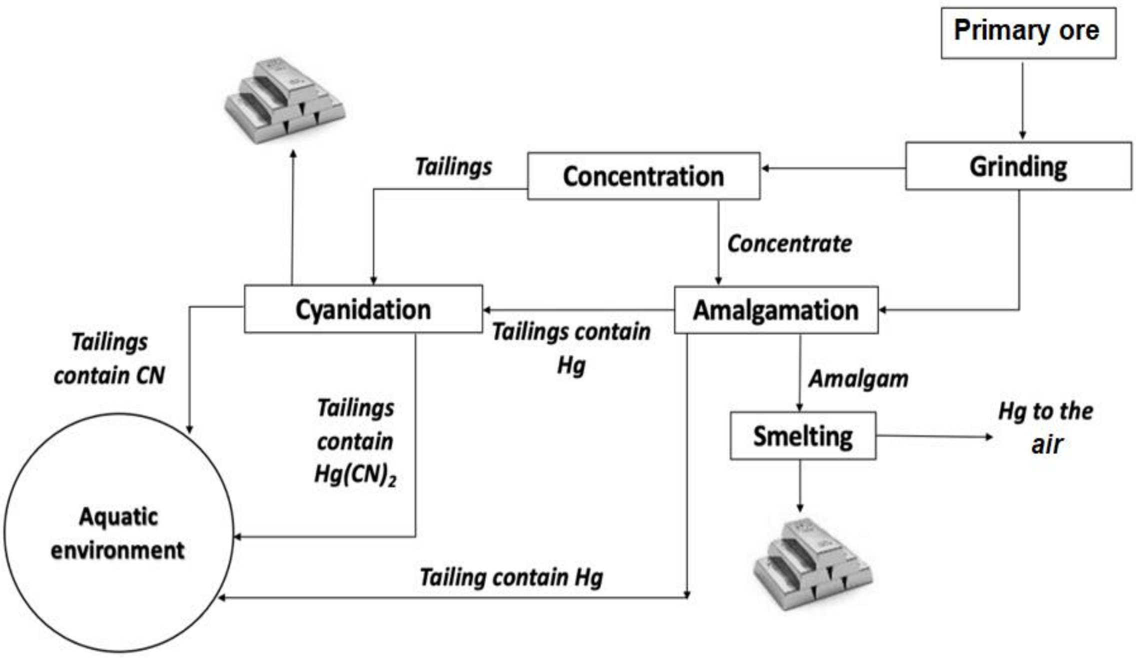

Figure 1. Processing primary ores by artisanal miners.

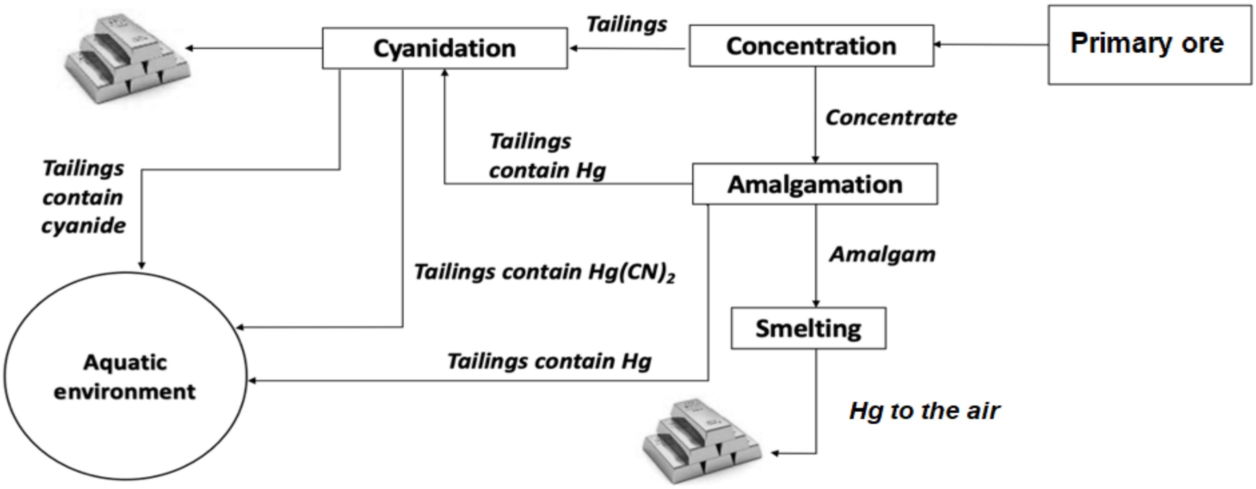

Figure 2. Processing secondary ores by artisanal miners.

Worldwide, most artisanal miners do not have the capital and the skills to process primary gold ores, so they rely on processing centers to extract the gold from their ores. Amalgamation of the whole ore in these centers extracts only the free gold particles (liberated from the gangue minerals), which rarely represent, in these primary ores, more than 30% of the total gold. Miners pay nothing, or a small fee, for the service. The centers' owners retain the tailings and use cyanide to extract the residual gold (unliberated but exposed) from the Hg-contaminated tailings, exacerbating the pollution as mercury-cyanide complexes are discharged into the drainages (Drace, Kiefer, & Veiga, 2016; Marshall, Veiga, da Silva, & Guimarães, 2020; Seney et al., 2020; Veiga, Angeloci, Hitch, & Velasquez-López, 2014a). In a recent experiment with zebra fish and $Hg(CN)_2$, (Da Silva, Kasper, Marshall, Veiga, & Guimaraes, 2023) found as LC_{50} (lethal concentration to kill 50% of the fish in 96 h) the dose of 0.53 mg/L of $Hg(CN)_2$ and 100% mortality happened at 0.64 mg/L.

Gold unliberated from gangue minerals can be concentrated but it is not trapped by mercury. The use of gravity concentration of gold, widely promoted by international organizations as a way to eliminate amalgamation is not effective, as the gold in concentrates must be extracted by a metallurgical process (Martinez et al., 2021). The conventional companies use hydrometallurgical processes leading to cyanidation, while is by far the most popular method. Gold concentration is the keyway to reducing emissions and releases of mercury but rarely eliminates completely the need of other metallurgical process to extract unliberated gold from concentrates. The promoted idea to eliminate mercury by gold concentration followed by smelting, known as the Borax Method, has its drawbacks. If the concentrate does not have a high grade of gold, above 5% (Appel & Na-Oy, 2012), the gold is lost in the slag. The presence of sulfides in a concentrate also hinders acceptable gold recovery in the smelting process. Furthermore, to reach high level of gold in a concentrate, the low gold recovery would result in the concentration process (Veiga et al., 2014b). The direct smelting process is only suitable for miners producing small amounts of gold per day since smelting of large amounts of concentrates require an expensive furnace and technical skill to operate. For alluvial ores, where gold particles are usually liberated from the gangue minerals, this process has been used for centuries. The technical options to replace mercury are not promoted by governments or project-sponsoring institutions. Consultants and companies frequently offer several "new" techniques or proprietary lixiviants to replace gold amalgamation, bonding users to perpetual dependence on reagent supply or royalties to the technology owners.

Cyanide is the usual reagent to replace mercury and is used by all conventional gold mining companies. This raises an additional problem in those organizations of cyanide producers, such as the International Cyanide Management Institute (ICMI), restrict their products' sales to artisanal gold operations, including the rudimentary processing centers. Most of these centers acquire cyanide clandestinely, or from non-ICMI members, such as Korean, Russian, and Chinese cyanide suppliers (Veiga et al., 2014a). 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 mercury and cyanide-contaminated tailings are dumped into local rivers without treatment (Marshall et al., 2020).

A 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).

Any method that replaces amalgamation must be simple and inexpensive to convince processing centers, small companies, or even skilled artisanal miners to adopt. This study recommends the need of introducing alternative techniques for gold leaching that have low costs and higher gold recoveries than amalgamation. The methods studied here are readily performed without special knowledge, but some skills and capital are needed. Using a well-studied and high-grade ore from an artisanal mining operation in Colombia, this study followed a logical sequence of laboratory activities to search for methods to replace amalgamation. This study showed the results of gold extraction using different unconventional techniques to compare with the gold extraction by amalgamating of the whole ore. These methods included: 1) Amalgamation, 2) Bitter Cassava as a Gold Lixiviant, 3) DMSO - Dimethyl sulfoxide, 4) Modified Merrill-Crowe Process, and 5) Chloride Leaching.

Some of the individual processes are described in detail in previous publications (Torkaman & Veiga, 2023; Torkaman et al., 2021). This article discusses and recommends which methods are more suitable for small-scale operations and under which conditions they should be applied.

2. METHODOLOGY

2.1. Sample

A sample of high-grade gold ore from Colombia, mined by artisanal miners and generously donated by the Gramalote Mine Project (50% B2Gold and 50% AngloGold Ashanti Ltd), was utilized for all the leaching tests as a proxy for a concentrate. The sample was obtained from the La Maria site, an operation conducted by 18 artisanal miners within the Gramalote mineral title with permits from the company. Approximately 20 kg of the run-of-mine La Maria head sample was crushed and ground in a disk mill to a grain size below 0.13 mm. The ground ore was homogenized, and eight samples of 100 g were collected and sent to the laboratory for a 30 g fire assay chemical analysis, 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. in Vancouver, BC, Canada. The ore's gold grade was 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.

The La Maria head sample's mineralogy was analyzed using X-ray diffractometry (XRD). To improve mineral detection limit, a gravity concentrate obtained from Knelson laboratory centrifugal concentrator was also analyzed after grinding it below 0.13 mm in a disk mill and finely manually pulverized for the XRD analysis.

2.2. Amalgamation

A series of tests were conducted in the laboratory to assess the efficiency of the whole ore gold amalgamation in small ball mills ("cocos") commonly applied by artisanal miners in Colombia (García et al., 2015) then compared with other methods that were analyzed in this study. Various amounts of mercury were mixed with the ore at different ratios of Hg-to-ore (1:50, 1:100, 1:200, and 1:600) while maintaining a 50% Solid:Liquid (water) ratio, using the same amount of ore (10 g) and at a neutral pH. The amalgam and excess mercury were removed by panning and the residues were dried and analyzed to determine the amount of gold remaining in the ore. For this purpose, 5 grams of each residue were dissolved in 50 mL of hot aqua regia (40 mL HCl and 10 mL of HNO_3) for 3 hours, then filtered using Whatman filter paper Grade 5 with a pore size of 2.5 μm. The aqua regia solutions were analyzed for Au by Atomic Absorption Spectrometry.

2.3. Bitter Cassava as Gold Lixiviant

Bitter cassava contains two types of cyanogenic glycosides: linamarin (95%) and lotaustralin (5%), which generate hydrogen cyanide (HCN) when hydrolyzed (Jaszczak, Polkowska, Narkowicz, & Namieśnik, 2017). When bitter cassava is crushed to make flour, a liquid is produced that makes up 30-40% of the root weight and contains free cyanide (Nitschke & Pastore, 2003). This liquid, with colloidal starch, known as "manipueira" by the Brazilian indigenous people, is often carelessly disposed of on the ground around artisanal flour mills in Latin America. Torkaman et al. (2021) have described the process of gold leaching using a "manipueira" from the State of Bahia, Brazil, which contained 267 ppm (parts per million) of free cyanide. Another "manipueira" from the interior of the Pernambuco State, Brazil, containing 600 ppm of free cyanide was also used to leach gold from La Maria ore.

To conduct each gold leaching test, a La Maria gold ore sample was combined with "manipueira" at pH 10.5 (adjusted with NaOH) in a beaker. All tests were duplicated, with samples being agitated in a shaker for specific durations ranging from 8 to 48 hours. The pH level was regularly monitored during agitation and adjusted to 10.5 using NaOH solution, as needed. Once the leaching process concluded, the solution rich in gold was filtered using Whatman filter paper Grade 5 (2.5 μm), and the solids were rinsed with distilled water to obtain the final solution. Atomic Absorption Spectrometry (AAS) was utilized to analyze the gold content in both the solution and residues. The percentage of gold recovery was calculated by dividing the extracted gold by the initial amount of gold in the sample.

To determine if cassava starch could lead to preg-robbing in the gold leaching process, an experiment was conducted using "manipueira" from a sweet cassava, as a source of starch mixed with pure CN solution. The sweet cassava was acquired from a Vancouver supermarket and processed by peeling, blending, and filtering through a piece of fabric to obtain a cloudy starch solution. The experiment consisted of two series of tests, one using 40 mL of pure NaCN (267 ppm of free cyanide) solution to leach 10 g of ore, and another using a combination of 40 mL NaCN (267 ppm of CN^-) and 40 mL sweet cassava extract at pH 10.5. Once the desired time had elapsed, the samples were filtered using Whatman filter paper Grade 5: 2.5 μm and sent to the chemical laboratory for Au analysis by AAS.

2.4. DMSO - Dimethyl Sulfoxide

Yoshimura, Takai, and Matsuno (2014) have demonstrated the potential of Dimethyl sulfoxide (DMSO) as an effective lixiviant for extracting gold from electronic waste. DMSO is an industrial-grade, water-free reagent that is widely available, low-cost, biodegradable, and FDA-approved for human use. In this process, Cu^{2+} ions added to DMSO to serve as potent oxidizing agents that help to oxidize gold while reducing Cu^{2+} to Cu^{+}. The dissolved gold then forms a complex with halogens. Gold can be selectively precipitated from the loaded DMSO by adding a weak acidic solution which prevents copper precipitation.

The commercial-grade DMSO used in the experiments was provided by Gaylord Chemical, a leading producer of DMSO in North America. For each experiment, $CuCl_2$ and NaCl were dissolved in DMSO, and 10 g of La Maria ore was added, followed by agitation for a designated time. The experiments were conducted at ambient temperature and at 40°C. After the leaching process, the residues were filtered, attacked with aqua regia, and the gold content was measured using AAS. Residues were washed with pure DMSO after each test and analyzed.

2.5. Modified Merrill-Crowe Process (MMCP)

In many artisanal processing centers, gold from Hg-contaminated tailings is extracted using cyanide following precipitation with zinc at atmospheric pressure. The actual Merrill-Crowe process involves leaching the gold with cyanide, filtration and then precipitating it with zinc in vacuum. This process is commonly used in conventional mining operations, especially when the ore has high amounts of silver artisanal processing centers lack filters and vacuum systems, then they allow the pulp to decant for 12 hours followed by siphoning the solution to PVC pipes filled with zinc shavings. This operation is repeated for at least 5 days. As the gold is precipitated on the zinc in contact with air, approximately 6% of the gold remains in solution (Velásquez-López, Veiga, Klein, Shandro, & Hall, 2011).

The gold precipitation process with zinc reduces the gold and silver cyanide complexes to their native states as Au^0 and Ag^0. The idea of modifying the existing rudimentary Merrill-Crowe process used by artisanal processing centers was to avoid the decanting process to clarify the solution. This could be done by filtration systems, but expensive to these processing centers. Another research goal was to avoid the use of vacuum systems when adding zinc to the gold-loaded cyanide solution. To test our Modified Merrill-Crowe Process, a 1 g/L CN concentration solution was prepared by dissolving 1.88 g of NaCN in distilled water. A 10 g sample of the La Maria head sample was leached with this cyanide solution for 24 hours. The resulting solution was divided into ten sub-samples, with one sub-sample being filtered and sent for Au analysis by AAS. The pulp of each remaining sub-sample was agitated with a bag of zinc shavings introduced in the beakers for a specific time, after which the solutions were filtered, and the final solutions were sent to the laboratory for Au determination by AAS.

2.6. Chloride Leaching

Gold leaching experiments were also carried out using diluted hydrochloric acid as the primary lixiviant and various oxidizing agents (5 g) to extract gold from 20 g of La Maria head sample. In the initial tests, sodium persulfate and calcium hypochlorite were employed. Calcium hypochlorite ($Ca(OCl)_2$), commonly used for chlorinating swimming pools, contains 65% active chlorine, and when dissolved in water, it generates nascent chlorine (Askenaizer, 2003) with a redox potential of 1.396 V for nascent chlorine ($Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$) (LibreTexts Chemistry, 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). However, hydrogen peroxide was not tested due to its difficulty in obtaining and transporting (H_2O_2 50% v/v) in developing countries, and it decomposes quickly in hot climates. The desired amount of oxidant was dissolved in a mixture of diluted acid. Each sample was agitated for 8 hours at room temperature. 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. To create gold-chloride complexing conditions, an excess of chloride ions (5 g of NaCl) was added to all samples. Chloride ions act as a ligand to solvate Au(III) in the solution (Baghalha, 2007). The experiments used commercial hydrochloric acid with a concentration of 37%, which was diluted by 50% to make the process more affordable for artisanal miners. Table 1 displays the components and corresponding quantities used in the chloride leaching tests.

Table 1. Conditions of chloride leaching (Always with 20 g of sample and 5 g of oxidant).

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

This method is comparable to the iGoli process developed by MINTEK company in South Africa, which involves dissolving gold from gravity concentrates by using hypochlorite in an acidic medium (Veiga, 2020).

Mahlatsi and Guest (2003) reported high gold recoveries (around 98%), indicating it could be a good replacement for amalgamation processes in artisanal and small-scale gold mining (AGM). However, due to its complexity and technical knowledge requirement, it was challenging to persuade very small artisanal African miners to adopt the iGoli process. The chloride leaching process described here is a simplified version that can be considered a practical option for AGM communities, but some skills are needed to perform this process.

3. RESULTS AND DISCUSSION

3.1. Sample Grade

The La Maria ore was divided into eight sub-samples subjected to fire assay and AAS analysis. The results indicated a gold grade of 48.47 ± 6.52 (2 std) g Au/tonne of ore (ppm). Additionally, the gold content in 14 samples of cassava and NaCN leaching solutions, along with their corresponding residues dissolved with aqua regia, was determined through AAS analysis. The feed gold grade, calculated through a metallurgical balance, was found to be 48.87 ± 6.30 (2 std) g of gold/tonne (ppm) of ore, closely resembling the concentration obtained from the fire assay analysis of the ore samples. The gold grade of 48.87 ppm was utilized for calculations in cases where solution analysis was not feasible. Furthermore, the average copper grade of the head sample was 0.41%, while the average silver grade stood at 95 ppm. These findings validate the assertions made by artisanal miners that the La Maria ore typically contains approximately twice as much silver as gold, despite the gold price being 71 times higher than silver.

The mineralogy of the gravity concentrates and the head sample, obtained by X-ray diffraction, revealed that quartz is the dominant mineral and pyrite, chalcopyrite, and amphibole are present in minor amounts. Based on the copper grade of the ore, it can be inferred the presence of 1.19% of chalcopyrite. The ore contains no coarse gold nuggets but, instead, it has medium-small size gold particles that are easily concentrated by centrifugal process and/or flotation. A previous study of this ore (Gonçalves, Li, Liu, & Shang, 2016) found that 97% of the gold in the La Maria sample could be recovered after five passes in a laboratory Knelson centrifuge when the ore was ground to 80% below 0.13 mm. This process provides good homogenization, and the head sample grades analyzed and calculated based on metallurgical balances of each leaching experiment, show consistent gold grades with minimal variation.

3.2. Amalgamation

Artisanal miners in Colombia typically use a Hg:ore ratio of 1:1400 in their "cocos" for whole ore amalgamation (García et al., 2015). However, even using 28 times more mercury (i.e., a ratio Hg:ore = 1:50) in the laboratory experiments, the highest gold extraction by amalgamation was only 17.4% on average (15.94% and 18.81% in duplicate). When the Hg: ore ratio was lowered to 1:100, gold extraction decreased drastically to approximately 8.7% (Table 2).

It is uncertain whether all gold particles in the La Maria ore were fully liberated and amenable to being captured by mercury, but the grain size of the tests was comparable to that used by Colombian artisanal miners (P80 = 0.13 mm after grain size analysis of their amalgamation tailings) (García et al., 2015). Cyanidation of the same La Maria sample with 1 g/L CN- for 24 hours at ambient temperature resulted in 84% gold. The low efficiency of gold extraction by amalgamation may be attributed to mercury oxidation during the process and/or lack of liberation of gold particles (Rollien, 1936; Veiga & Gunson, 2020). The cyanidation process requires fine gold particles to be dissolved within a reasonable time, in contrast to amalgamation, which is based on surface reactions and the agglutination of gold grains. According to Wenquian 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, while cyanidation works better with fine gold grains (< 0.2mm) (Hylander et al., 2007; Macdonald, 1983; Veiga et al., 2014b). In addition, cyanidation can extract unliberated but exposed gold particles and amalgamation cannot (Torkaman & Veiga, 2023).

Table 2. Gold amalgamation tests results (Some points with duplicates).

Sample #	Hg: Ore	Amalgamated gold (%)
1	1:50	18.81
2	1:50	15.94
3	1:100	9.87
4	1:100	7.54
5	1:200	6.42
6	1:500	4.37
7	1:500	2.47
8	1:1000	1.90

3.3. Bitter Cassava as a Gold Lixiviant

As measured by different methods, the free cyanide content in the "manipueira" sample from Bahia State, Brazil, showed consistent results of 267±80 ppm. In the experiments conducted with La Maria ore leached with this "manipueira," the results of gold extractions showed a maximum of 50.9% gold extraction in 24 hours with 20% solids (Takatori, Kato, Yoshimura, & Matsuno, 2021). For comparison, the ore was also leached with a pure NaCN solution with the same cyanide concentration (267 mg/L of free cyanide) at pH 10.5, and the gold extracted in 24 hours was 85.7% with 20% solids. Table 3 presents the percentage of gold extracted using cassava liquid.

Table 3. Results of gold leaching tests with cassava liquid (267* & 600 ppm).

Sample (No)	Manipueira's free CN (PPM)	S: L (%)	Time (H)	Gold extraction (%) *
1	600	10	24	82.4
2	600	10	18	76.2
3	600	10	8	73.01
4	267	20	24	50.9
5	267	20	18	48.3
6	267	20	8	47.2

Note: * Some data published by Takatori et al. (2021)

Using another variety of cassava that releases 600 ppm free cyanide in the "manipueira," the gold recovery reached 82.4% in 24 hours. In this case, the starch was not removed. The preg-rob effect of the suspended starch was also evaluated, and it was found that the percentage of gold dissolved from the ore by pure NaCN solution was 77% (73.4 and 80.5% in the duplicate) in 24 hours. However, when starch from sweet cassava was introduced, the gold recovery decreased to 59% (48.0 and 69.9% in the duplicate). The preg-robbing effect can be attributed to the starch's reabsorption of the gold-cyanide complex, but the few results are not conclusive, and this may depend on the type of starch of each bitter cassava. To separate these organic compounds, such as starch, from the solution, a centrifuge or flotation of the solution extracted from cassava can be used. Brazilian cassava producing companies extract this starch by industrial centrifuges to sell it for other purposes, such as chemical uses and beer manufacturing. The preg-robbing effect of the starch needs further investigation.

3.4. DMSO - Dimethyl Sulfoxide

The amount of gold dissolved in the DMSO solution was calculated based on the gold grade analyzed by fire assay in all sixteen (16) residues obtained from filtration. The percentage of gold extracted was calculated considering the head sample grade of 48.87 ppm Au, since it was not possible to analyze the DMSO solutions in the Atomic Absorption Spectrometer due to matrix effects. Table 4 provides the experimental conditions for selected DMSO experiments.

After studying different combinations of the reagents, the most effective combination of variables regarding the gold extraction, was 0.6 g NaCl, 1.34 g $CuCl_2$, 10% solids and 2 hours of leaching time at ambient temperature. This resulted in 96.5% gold extraction. When the tests were conducted at 40° C, the gold extraction reached 98.8% in 2 hours.

Table 4. Analytical conditions of some of the DMSO experiments (10 g ore).

Sample (No)	S: L (%)	Time (H)	Temp (C°)	NaCl (G)	CuCl2 (G)	Extracted Au (%)
1	10	2	Ambient	0.6	1.34	96.5
2	10	8	Ambient	0.6	1.34	95.4
3	10	8	Ambient	0.6	2.7	86.31
4	10	8	Ambient	1.16	1.34	78.84
5	30	8	Ambient	0.6	1.34	89.91
6	10	24	Ambient	1.16	2.7	94.86
7	30	24	Ambient	1.16	1.34	79.84
8	10	2	40	0.6	1.34	98.81
9	10	8	40	0.6	1.34	97.91

Table 5 displays the gold precipitation results from gold-loaded DMSO after leaching. Recovering all or most of the dissolved gold was possible by applying 1M H_2SO_4 and lemon juice (containing citric acid, pH 2.0-2.5). This result was similar to 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% chalcopyrite in the ore (Takatori et al., 2021). The results confirm that 1M sulfuric acid (pH = 0) and diluted lemon juice were the best reagents to precipitate the gold.

Table 5. Gold precipitation results from gold loaded DMSO.

Acid used for precipitation	Gold precipitation (%)
Commercial vinegar	25
H_2SO_4 (1.0 M)	100
H_2SO_4 (1.0 M)	89.6
Diluted (half) lemon juice	100
Undiluted lemon juice	100

3.5. Modified Merrill-Crowe Process (MMCP)

The gold extraction in the cyanidation tests using 1 g/L CN^- for 24 hours was 84%, while the use of 2 g/L of CN resulted in 92% gold extraction. However, the focus of this research was not to increase gold extraction during the leaching process but to concentrate efforts on achieving high gold precipitation in the Modified Merrill-Crowe Process (MMCP). As it shows in Table 6 , the zinc cementation process precipitated 99.3% of the gold in just two hours (Torkaman & Veiga, 2023).

Table 6. Gold recovered from by MMCP (some samples in duplicates).

Sample #	Time (Min)	Gold recovery (%)
1	15	50.42
2	30	50.68
3	45	56.38
4	60	76.88
5	60	80.6
6	90	84.61
7	90	89.5
8	120	99.27
9	120	99.41
10	150	99.67
11	180	98.98

Using a permeable fabric, such as thin socks, along with adding zinc shavings inside and inserting it in the cyanidation tank for the purpose of gold precipitation from cyanide solutions, proves to be a simple and effective method for rapid gold production. While the cyanidation process typically requires high aeration, zinc cementation demonstrates greater efficacy in the absence of oxygen. The Modified Merrill-Crowe Process (MMCP) streamlines gold production by eliminating the need for a clear cyanide solution and vacuum. The introduced process allows gold precipitation to occur with minimal agitation in the tank. The gold-laden zinc shavings can be leached using nitric or hydrochloric acid. While sulfuric acid is also an option, its purchase is often restricted in many developing countries due to its potential use in cocaine production. Zinc recovery from the acidic solution can be achieved through precipitation on aluminum foil.

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

The same gold precipitation process was 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.

3.6. Chloride Leaching

The results of the gold leaching experiment with 50% diluted commercial hydrochloric acid (37% v/v) at room temperature showed that sodium persulfate resulted in better gold extraction than calcium hypochlorite in 8 hours Table 7.

Table 7. Gold extraction by HCl with 20 g La Maria ore.

Sample (No)	Oxidant name	Oxidant (G)	Temperature (°C)	HCl concentration (%)	Gold extraction (%)
1	$Ca(OCl)_2$	5	Ambient	50	16.78
2	$Ca(OCl)_2$	5	Ambient	50	23.46
3	$Ca(OCl)_2$	5	Ambient	30	35.45
4	$Ca(OCl)_2$	5	Ambient	30	47.14
5	$Na_2S_2O_8$	5	Ambient	30	41.12
6	$Na_2S_2O_8$	5	Ambient	30	48.62
7	$Na_2S_2O_8$	5	Ambient	50	56.08
8	$Na_2S_2O_8$	5	Ambient	50	68.29
9	$Na_2S_2O_8$	5	Ambient	50	77.76
10	$Na_2S_2O_8$	10	Ambient	50	82.16
11	$Na_2S_2O_8$	10	Ambient	50	83.90
12	$Na_2S_2O_8$	10	50°C	50	89.63
13	$Na_2S_2O_8$	10	50°C	50	100

As a result, in the further tests sodium persulfate was chosen. Using 10 g of sodium persulfate at room temperature, resulted in 83% of gold extraction in 8 hours at ambient temperature. When the temperature was increased to 50°C, this percentage increased to 95%.

Utilizing diluted hydrochloric acid to dissolve gold from gravity or flotation concentrates with high gold grades (e.g., 200 ppm Au, which is worth USD 11,400 per tonne) seems to be an affordable solution to avoid the use of cyanide. The price of commercial hydrochloric acid can vary from approximately USD 75-250/tonne (Alibaba, 2023; ChemAnalyst, 2022) , depending on the supplier and volume requirements, and it is usually available in most developing countries. The acid can be reused or neutralized with $Ca(OH)_2$, which is widely available and inexpensive.

4. CONCLUSION

By using the same sample of ore from the La Maria gold deposit, which has a gold grade of 48.9 ppm and is currently mined by Colombian artisanal miners, we were able to compare the extraction methods suggested in this investigation. The significant results are summarized in Table 8.

Although laboratory experiments have proven the inefficiency of mercury amalgamation, artisanal miners still prefer it due to its simplicity, fast results, and cheap equipment. Any new strategy presented to artisanal miners needs to be inexpensive and more efficient than amalgamation. However, there is no universal solution, and various factors, such as the site location, mineralogical characteristics of the ore, investment span, level of education, and motivation of miners, need to be considered (Veiga et al., 2009).

The increasing dependence of artisanal miners on mercury highlights the need to develop non-mercury technologies (Hilson & Pardie, 2006) or methods that decrease mercury loss (Metcalf & Veiga, 2012).

The processes investigated in this study have the potential to replace mercury (and cyanide in some cases), but their application is site-specific and requires field testing. Approximately 90% of the almost 20 million worldwide artisanal gold miners, process less than two tonnes of ore daily (Veiga et al., 2018). However, they are not the main mercury polluters as they usually amalgamate only concentrates. Artisanal processing centers, frequently amalgamating the whole ores, are the main culprits and they should change their business model 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, Restrepo-Baena, & De Tomi, 2022).

Gold has various uses, such as in jewelry, technology, and by central banks and investors. Its role in the global economy is 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). Accordingly, more small- to medium-sized mines and processing centers are expected to develop and operate over the next decade. However, poverty in rural areas of developing countries, low up-front investment, and a lack of alternative livelihoods draw more people to artisanal mining activities. Therefore, the transformation of artisanal gold miners and 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.

Table 8. Gold extraction results achieved by each method studied in this research.

Gold extraction method	Time (H)	Temperature	Au extracted (%)
Amalgamation Hg:ore =1:50	2	Ambient	19.0
Cyanidation (1g CN/L)	24	Ambient	84.0
Cyanidation (2 g/L)	24	Ambient	92.0
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	100.0

Therefore, practical solutions are needed to address the environmental and economic problems related to artisanal gold mining but always taking into consideration the socio-economic conditions of the artisanal miners and their communities. This research presents unconventional gold leaching processes aimed at reducing the severe impacts of artisanal mining activities on humans and the environment, with particular attention paid to evaluating alternatives to the gold amalgamation process. It is significant because it addresses one of the most challenging global issues of our time, and all the alternative methods described herein would require some level of skill and relatively low investment to be implemented.

Funding: This research is supported by the Natural Sciences and Engineering Research Council, Canada (Grant number: RGPIN-2020-06125).
Institutional Review Board Statement: Not applicable.
Transparency: The authors state that the manuscript is honest, truthful, and transparent, that no key aspects of the investigation have been omitted, and that any differences from the study as planned have been clarified. This study followed all writing ethics.
Competing Interests: The authors declare that they have no competing interests.
Authors' Contributions: Generated ideas in different stages, conceived and coordinated the project, M.V. and P.T.; wrote the manuscript and the experiments, P.T.; supervised the experiments, M.V. and L.L.; reviewed and edited the manuscript, M.V., L.L. and B.K. All authors have read and agreed to the published version of the manuscript.
Acknowledgement: The authors would like to extend a special thanks to the Gramalote Project, consisting of B2Gold and AngloGold Ashanti, for providing the La Maria ore samples and to chemical laboratories, Metsolve and Kemetco for conducting the chemical analysis. The authors are grateful to the Federal University of Pernambuco, CIBUS Company, Federal University of Bahia and EMBRAPA Cassava and Fruit Center in Cruz das Almas, Brazil for their exceptional care and support, which facilitated the completion of this research. Additionally, the authors would like to express their appreciation to Gaylord Chemical Company, L.L.C Newlox Gold Ventures Corp., John Bell Foundation, and Regenx Tech Corp. for their assistance during various stages of this research.

REFERENCES

Alibaba. (2023). *Alibaba*. Retrieved from https://www.alibaba.com/showroom/hcl-acid.html

Appel, P. W., & Na-Oy, L. (2012). The borax method of gold extraction for small-scale miners. *Journal of Health and Pollution, 2*(3), 5-10. https://doi.org/10.5696/jhp.v2i3.30

Askenaizer, D. (2003). Drinking water quality and treatment. In Encyclopedia of physical science and technology, edited by R. A. Meyers. In (pp. 651–671). New York: Academic Press.

Baghalha, M. (2007). Leaching of an oxide gold ore with chloride/hypochlorite solutions. *International Journal of Mineral Processing, 82*(4), 178-186. https://doi.org/10.1016/j.minpro.2006.09.001

ChemAnalyst. (2022). *Hydrochloric acid price trend and forecast*. Retrieved from https://www.chemanalyst.com/Pricing-data/hydrochloric-acid-61

Da 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, 32*, 429–437. https://doi.org/10.1007/s10646-023-02651-w

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*, 443-449. https://doi.org/10.1007/s40572-016-0113-0

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. *Journal of Cleaner Production, 90*, 244-252. https://doi.org/10.1016/j.jclepro.2014.11.032

Gavin, H., 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*, 105315. https://doi.org/10.1016/j.worlddev.2020.105315

Gonçalves, A., Li, H., Liu, S., & Shang, D. (2016). *La Maria project: Metallurgical testwork* (Vol. 2): Report from UBC Dept Mining Engineering to Gramalote Colombian Ltd.

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

Hylander, L. D., Plath, D., Miranda, C. R., Lücke, S., Öhlander, J., & Rivera, A. T. (2007). Comparison of different gold recovery methods with regard to pollution control and efficiency. *CLEAN–Soil, Air, Water, 35*(1), 52-61. https://doi.org/10.1002/clen.200600024

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

LibreTexts Chemistry. (2022). *P2: Standard reduction potentials by value*. Retrieved from https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Electrochemistry_Tables/P2%3A_Standard_Reduction_Potentials_by_Value

Macdonald, E. H. (1983). Alluvial mining: the geology, technology, and economics of placers. In (pp. 508). London: Chapman and Hall.

Mahlatsi, S., & Guest, R. N. (2003). The iGoli mercury-free gold extraction process. *Urban Health Dev. Bull., 6*(4), 62-63.

Marshall, B. G., Veiga, M. M., da 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*(3), 303-310. https://doi.org/10.22215/etd/2016-11464

Martinez, G., Restrepo-Baena, O. J., & Veiga, M. M. (2021). The myth of gravity concentration to eliminate mercury use in artisanal gold mining. *The Extractive Industries and Society, 8*(1), 477-485. https://doi.org/10.1016/j.exis.2021.01.002

Metcalf, S. M., & 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. *Journal of Cleaner Production, 37*, 179-184. https://doi.org/10.1016/j.jclepro.2012.07.004

Nitschke, M., & Pastore, G. M. (2003). Cassava flour wastewater as a substrate for biosurfactant production. In Biotechnology for Fuels and Chemicals. In (pp. 295-301). Totowa, NJ: Humana Press.

RedoxTech. (2023). *Persulfate*. Retrieved from https://www.redox-tech.com/persulfate/

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.

Seney, C. S., Bridges, C. C., Aljic, S., Moore, M. E., Orr, S. E., Barnes, M. C., . . . McKallip, R. J. (2020). Reaction of cyanide with Hg0-contaminated gold mining tailings produces soluble mercuric cyanide complexes. *Chemical Research in Toxicology, 33*(11), 2834-2844. https://doi.org/10.1021/acs.chemrestox.0c00211

Takatori, K., Kato, H., Yoshimura, A., & Matsuno, Y. (2021). Chalcopyrite leaching in a dimethyl sulfoxide solution containing copper chloride. *Mining, Metallurgy & Exploration, 38*(3), 1477-1485. https://doi.org/10.1007/s42461-021-00400-3

Torkaman, P., & Veiga, 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, 13*, 101208. https://doi.org/10.1016/j.exis.2022.101208

Torkaman, P., Veiga, M., de Andrade Lima, L., Oliveira, L., Motta, J., Jesus, J., & Lavkulich, L. (2021). Leaching gold with cassava: An option to eliminate mercury use in artisanal gold mining. *Journal of Cleaner Production, 311*, 127531. https://doi.org/10.1016/j.jclepro.2021.127531

UNEP. (2018). *Global mercury assessment 2018*. Switzerland: UNEP Geneva.

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*. Retrieved from https://www.goldismia.org/sites/default/files/2020-06/VEIGA%20-%20FINAL%20Report.pdf

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

Veiga, M. M., Angeloci, G., Hitch, M., & Velasquez-López, P. C. (2014a). Processing centers in artisanal gold mining. *Journal of Cleaner Production, 64*, 535-544. https://doi.org/10.1016/j.jclepro.2013.08.015

Veiga, M. M., & Fadina, O. (2020). A review of the failed attempts to curb mercury use at artisanal gold mines and a proposed solution. *The Extractive Industries and Society, 7*(3), 1135-1146. https://doi.org/10.1016/j.exis.2020.06.023

Veiga, M. M., & Gunson, A. J. (2020). Gravity concentration in artisanal gold mining. *Minerals, 10*(11), 1026. https://doi.org/10.3390/min10111026

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. *Journal of Cleaner Production, 205*, 995-1005. https://doi.org/10.1016/j.jclepro.2018.09.039

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), 1373-1381. https://doi.org/10.1016/j.jclepro.2009.03.012

Veiga, M. M., Restrepo-Baena, O. J., & De Tomi, G. (2022). Coexistence of artisanal gold mining with companies in Latin America. *The Extractive Industries and Society*, *12*, 101177. https://doi.org/10.1016/j.exis.2022.101177

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. *Journal of Cleaner Production*, *19*(9-10), 1125-1133. https://doi.org/10.1016/j.jclepro.2010.09.008

Vieira, R. (2006). Mercury-free gold mining technologies: Possibilities for adoption in the Guianas. *Journal of Cleaner Production*, *14*(3–4), 448-454.

Wenquian, W., & Poling, G. W. (1983). Methods for recovering fine placer gold. *Canadian Mining and Metallurgical Bulletin*, *76*(860), 47-56.

WGC. (2022). *World gold council publications archive: World Gold Council*. Retrieved from www.gold.org

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*, *149*, 177-182. https://doi.org/10.1016/j.hydromet.2014.08.003

Zolnikov, T. R., & Ortiz, D. R. (2018). A systematic review on the management and treatment of mercury in artisanal gold mining. *Science of the Total Environment*, *633*, 816-824. https://doi.org/10.1016/j.scitotenv.2018.03.241