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Homemade copper-silver plates as an alternative for cleaning mercury-contaminated tailings from artisanal and small-scale gold mining in Colombia

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ABSTRACT

Over 300,000 artisanal and small-scale gold mining operate in almost all Colombia. Despite the poverty alleviation characteristic of the operations in rural regions, these practices have been affecting the environment and health of operators as well as neighboring communities, mainly due to the misuse of mercury and cyanide. The most impacting activity is when processing centers use cyanide to leach Hg-contaminated tailings. This generates toxic mercury-cyanide complexes that are not frequently removed from effluents, and it is very toxic for aquatic life. A study to remove metallic mercury from tailings before cyanidation was conducted with 300 to 500 kg tailings from 15 different mining sites in Colombia using homemade copper plates covered with an electrolytic layer of silver. The experiments resulted in an average of 63% of Hg removed, and a maximum of 85%. The final Hg concentrations in the tailings reached an average of 27 to 47 ppm (depending on the analytical method) from the original grades of 75 to 125 ppm. Mercury droplets from old tailings, with acid generation, were difficult to trap by the plates. The article gives a detailed description on how to make these homemade plates and set up a zigzag cascade configuration for better results. Additional methods to adsorb or precipitate mercury from the cyanide solutions are necessary and they have been discussed.

Contribution/Originality: The introduction of a new low-cost alternative using homemade copper plates covered with an electrolytic layer of silver in artisanal gold mining activities in Colombia will contribute to reduce the current mercury contamination in abandoned tailings. No technologies have been identified that achieve efficiency as referenced in this study.

1. INTRODUCTION

Over 2000 t/a of metallic mercury, to produce almost 600 t/a of gold, has been extensively used and released to the environment by almost 20 million artisanal gold miners worldwide (Martinez, Restrepo-Baena, & Veiga, 2021). Elimination of mercury in artisanal gold processing operations has been pursued for decades but with little success. Instead of education/training projects for miners, an increasing number of useless laws intend to stop the mercury pollution, but legislators do not understand the technical problems and only repeat the scandalous news brought up by the media about mercury pollution. This entangling issue has been opening doors for inadequate techniques

suggested to the miners by pseudo-researchers and equipment suppliers. As a result of this incompetent approach of many governments in developing countries and other stakeholders (frequently with hidden interests in the mercury pollution), the misuse of mercury as well as cyanide to leach amalgamation tailings is growing worldwide exacerbating the pollution (Torkaman, Veiga, Lavkulich, & Klein, 2023).

Colombia is a country with over 300,000 artisanal miners, most of them informally employed, distributed in 44% of the 1122 municipalities (Serrano, Martínez, & Fonseca, 2015; Veiga & Marshall, 2019). The estimated amount of mercury released to the environment by Colombian artisanal gold miners ranged from 150 to 205 tonnes/a (Cordy et al., 2011; De Paula Gutiérrez & Agudelo, 2020). The large majority of the mercury releases to the environment is with tailings (Veiga, Angeloci, Hitch, & Velasquez-Lopez, 2014). Many governments insist that formalization of the artisanal miners is a process to bring order, reduce environmental impacts and introduce best practices to the miners (Marshall & Veiga, 2017; Salo et al., 2016), however this "poorly regulated and sometimes lawless activity, as widely attributed by the public to artisanal miners" (Jonkman & Theije, 2023) in particular in Colombia, is a result of a highly bureaucratic process to provide to the gold deposits' discoverers a legal status. According to a USAID project, a Colombian artisanal miner must follow 280 steps to formalize an operation (Veiga & Marshall, 2019). Güiza Suárez and Aristizabal (2013) mentioned that only 13% of the artisanal gold miners have mineral titles and only 3% have environmental licenses in Colombia. Frequently these titles and licenses are not updated, but miners and ore processors wrongly believe that the permits are forever valid to protect them against any police enforcement. Without training and capital, the governments of developing countries are formalizing only the pollution as even those artisanal miners with legal mineral titles rarely adopt cleaner practices (Veiga & Marshall, 2019). Restrepo and Mendoza (2021) highlighted the cultural aspect of the artisanal miners in Colombia where the bare subsistence and low economic situation are the main difficulties to allow technical improvements to reach cleaner gold production, particularly when dealing with mercury and cyanide usage. Artisanal miners amalgamate free particles of gold from gravity concentrates or, when the ore has high gold grades as in primary ones, they simply mix mercury with the whole ore in grinding systems, or the ground ore goes over copper plates covered with mercury (amalgamating plates) that captures the liberated gold grains (Spiegel, 2009; Zolnikov & Ortiz, 2018). Both methods generate tailings with high grades of mercury. Currently, more than 83 sites with mercury contamination of the soil have been identified in the country, exceeding up to 160 times the national permissible level of mercury (El Nuevo Siglo, 2023). The whole ore amalgamation process in small ball mills ("cocos"), widely used by Colombian artisanal gold miners, is responsible by the largest losses of mercury to the tailings (United Nations Environment Programme (UNEP), 2012). Miners bring their ores to processing centers ("entables") that charge them a low fee to use "cocos" for whole ore amalgamation, but with one condition: the owners of the processing centers must retain the mercury-contaminated tailings to leach them with cyanide to extract residual gold not trapped by the amalgamation process (Veiga et al., 2014) (Figure 1).

Figure 1. "Cocos" used in Colombia for whole ore amalgamation and cyanidation tank to leach residual gold from Hg-contaminated tailings.

Cordy et al. (2011) assessed the mercury losses during the amalgamation of the whole ore in "cocos" in Antioquia, a Colombian Department that produces 47% of the country's gold (Gallego-Cstro, 2020). Conducting a metallurgical balance on 15 operations using "cocos" with approximately 60-70 kg of ore and 80 g of mercury in each small ball mill, the authors estimated that in average 50% of the initial mercury is lost, in which 46.3% is dragged with tailings and 3.7% is evaporated when amalgams are burned without any condensation equipment. "Cocos" grind the ore with steel balls, and, in this process, mercury forms fine droplets that are lost with tailings. After up to four hours of grinding, miners separate the amalgam and excess liquid mercury from the minerals by panning. The excess mercury, not bonded to gold, is recovered after filtering the amalgam with a fabric. Most miners obtain the gold *doré* (unrefined) by burning the amalgam without any method to condense the mercury vapors.

García et al. (2015) estimated that there were 2,600 "cocos" in "entables" in the main five mining municipalities in Antioquia. The authors reduced the speed of 20 "cocos" as well as the amount of mercury being introduced into those small ball mills (45% less). They also introduced retorts to capture the mercury vapors evaporated when amalgams are thermally decomposed. With these strategies, they observed that mercury losses decreased 31.4% on average from the original levels. No impact on the gold recovery was observed. Most mercury lost was with tailings that were leached with cyanide by the "entables' owners".

To demonstrate the inefficiency of the amalgamation of the whole ore in "cocos", a rich (~49 ppm of Au) Colombian artisanal gold ore was recently studied in the lab. The simulation of the whole amalgamation used by Colombian artisanal miners extracted less than 19% of the gold from the ore. When the same ore, not amalgamated, was subjected to cyanidation for 24 h with 1 g/L of CN, 84% of the gold was extracted (Torkaman & Veiga, 2023).

It has been observed in the last 20 years the proliferation of cyanidation plants in processing centers ("entables") (Veiga et al., 2014; Verbrugge, Lanzano, & Libassi, 2021). The mercury-contaminated tailings left by the miners in the centers, as a payment for the grinding and amalgamation services, are frequently leached with cyanide in rudimentary vats or agitated tanks to extract residual gold not trapped by mercury, a practice condemned by the Minamata Convention. In this process, soluble mercury-cyanide complexes are formed. Velásquez-López, Veiga, Klein, Shandro, and Hall (2011) in a metallurgical balance in one small cyanidation plant in Ecuador leaching Hg-contaminated tailings, concluded that less than 4% of the mercury that entered in the leaching tanks with tailings was reported to the activated carbon when this adsorbs the gold-cyanide complexes. At the alkaline pH of the cyanidation process, the activated carbon is not efficient to adsorb mercury-cyanide complexes. According to these authors, approximately 51% of the mercury from the tailings could not be captured by the activated carbon and remained in solution as Hg-cyanide complex. Approximately 45% of the total mercury in the tailings was not dissolved and has been discharged with the tailings as metallic mercury. As a conclusion, the mercury entering the cyanidation with activated carbon (CIP, Carbon-in-Pulp process) goes to the environment either as $Hg(CN)_2$ (aq) or in metallic form.

When the tailings and gold-free cyanide solution are discharged to the local drainages, mercury-cyanide is readily bioaccumulated by the aquatic biota. Aquarium studies have shown total mercury accumulation in the brains, gills, muscles and kidneys in fish exposed to $Hg(CN)_2$ (Silva, Kasper, Marshall, Veiga, & Guimaraes, 2023). This complex is the predominant Hg-cyanide complex in neutral pH. The authors obtained a LC_{50} (lethal concentration to kill 50% of fish) for $Hg(CN)_2$ of 0.16 mg/L, while the LC_{50} for NaCN was 0.53 mg/L. The preferential renal accumulation of $Hg(CN)_2$ in fish generated mortality after 48 h of exposure. The possibility of methylation of mercury-cyanide complexes is still unknown.

The presence of mercury in the cyanidation tanks also increases the cyanide consumption, therefore higher concentrations of NaCN have been used in "entables" to leach residual gold from tailings. In the south of Ecuador, Gonçalves, Marshall, Kaplan, Moreno-Chavez, and Veiga (2017) investigating 65 processing centers, found out that up to 5 kg of NaCN is consumed per tonne of Hg-contaminated tailing leached. Sandberg, Simpson, and Staker (1984) mentioned that 10 to 30% of mercury is dissolved in the usual gold cyanidation conditions whereas 85 to 90% of gold

is extracted. Velásquez-López et al. (2011) observed that 27% of the mercury from a contaminated tailing was dissolved in five days of cyanidation in a small Ecuadorian processing center, when 88% of gold was extracted. Based on the stoichiometry of the reaction of mercury with cyanide and oxygen forming $[Hg(CN)_4]^{2-}$, which is the predominant species at pH (10-11) of gold cyanidation (Flynn & McGill, 1995; Lorengo, 1996) 1 g of Hg consumes almost 1 g of NaCN. If we assume that 30% of the Hg is dissolved in the cyanidation, then roughly, for each tonne of contaminated tailing with 100 ppm of Hg leached with cyanide, about 30 g of NaCN would be consumed by metallic mercury in the tailings. This is a simplification, since the consumption of cyanide by mercury depends on many variables such as size and exposure of the mercury drop, pH, oxidation of the metallic mercury in the tailings, kinetics of the reaction, level of dissolved oxygen, etc. As mentioned above, the mercury-cyanide complexes are more toxic than NaCN (Silva et al., 2023) and it is imperative to remove metallic mercury before or during the cyanidation process of mercury-contaminated tailings (Drace, Kiefer, & Veiga, 2016).

The Colombian government, through its adherence to the Minamata Convention, which was signed in 2013 and ratified in 2019, passed the Law 1658 of 2013, which establishes the prohibition of mercury in mining activities as of June 2018 (Global Environmental Facility (GEF), 2017; Government of Colombia, 2013). Despite police enforcement shutting down in 2019 more than 1400 artisanal gold mines, the use of mercury is still evident in the field (National Police, 2019) openly witnessed by anyone. Whereas the eradication of the mercury use in Colombia is going on in slow pace, the NGO Pure Earth, sponsored by the U.S. Department of State, concentrated efforts in a project for cleaning up mercury-contaminated tailings before these are leached with cyanide. The NGO has identified 86 potentially contaminated sites through the Toxic Sites Identification Program (Pure Earth, 2023a). These sites include residential soil and tailings from artisanal gold mines.

In the search for a solution to remove mercury from contaminated tailings, the project team conducted a review of 17 technologies to identify the most promising, affordable, and feasible technique for the Colombian context (Pure Earth, 2023b). The gravity concentration methods are not so useful to extract mercury from contaminated tailings. Tests with centrifuges usually do not reach mercury extractions above 15%, as shown in lab test with an amalgamation tailing from Peru (Curo & Valdivia, 2016). Also, in a lab test at the University of British Colombia using a Colombian amalgamation tailing with 246 ppm Hg, the Knelson centrifuge extracted 12% of mercury in the first pass and a total of 28% in three passes (Correa, Liu, & Veiga, 2018).

An expedite and simple procedure to remove metallic mercury from tailings has been employed for more than 30 years (Ignea, 2022) and commercialized by two Brazilian companies. The procedure involves the use of copper plates covered with a thin electrolytic layer of silver and other metals to retain metallic mercury drops from the tailings. The plates produced by one of these companies, Goldtech, are sophisticated and expensive, but they perform very well as observed in successful tests in Brazil and Venezuela to decontaminate tailings (Veiga et al., 2005).
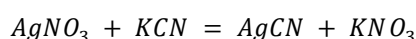
The idea of this research project was to develop simple and affordable plates to be disseminated to artisanal miners in Colombia and processing centers to remove mercury from tailings before cyanidation process. This article describes the development and results of the performance, under the Colombia´s context, of homemade Cu-Ag plates in removing mercury from 300 to 500 kg of 15 different tailings from Colombian artisanal gold mining sites.
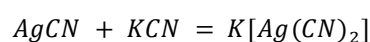
2. METHODOLOGY

This study was developed with mercury-contaminated tailings obtained from the artisanal gold mining operations in different sites of Colombia. Mercury of any kind was never added to the tailings. The recovered mercury, accumulated on copper plates, was disposed using a hazardous waste service according to the current regulation of Colombia.
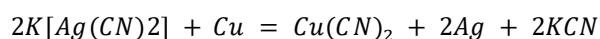
2.1. Preparation of Copper-Silver Plates

Copper is only a support medium for a smooth deposit of electrolytic silver which is the metal in contact with the mercury-contaminated tailings. The copper plate must be previously sanded to create a rough surface to anchor the silver layer and subsequently to capture the mercury drops. The silver deposit on the copper plate must be homogeneous and thick enough to avoid the oxidation of the copper surface below the silver layer. The project team tried to use ordinary steel plates, cheaper than copper ones, but the adherence of silver was not as good as on copper. Silver is a metal that can be displaced from the solution by virtually all metals (Bard & Faulkner, 2001) and it is deposited with great speed in the form of a black powder without any adhesion. The only way to avoid this drawback is to decrease the concentration of silver in solution. In addition, the use of complex salts, such as silver cyanide, favors a smooth deposition of silver. In this case, for the formation of silver cyanide, silver nitrate ($AgNO_3$) and potassium or sodium cyanide (KCN, or NaCN) were mixed in solution following this reaction:

$$AgNO_3 + KCN = AgCN + KNO_3$$

With the silver cyanide formed, the desired product, which is a silve-cyanide complex, was achieved according to the reaction shown below:

$$AgCN + KCN = K[Ag(CN)_2]$$

The silver complex compound can be characterized by its Formation Constant of $K_f = 10^{21}$ which shows high strength of the interaction between cyanide and silver to form the complex. This complex should produce a homogeneous and bright silver deposit (Bard & Faulkner, 2001). Then the solutions with silver-cyanide complexes, after tests, have shown as the best candidate for the plates' manufacture. Once the silver-cyanide complex is formed, silver is deposited on the copper plates by electroplating. A possible reaction can also occur on the plate surface:

$$2K[Ag(CN)2] + Cu = Cu(CN)_2 + 2Ag + 2KCN$$

The thickness of the silver layer to be on the plate must be enough to promote a homogeneous and non-porous surface to avoid oxidation of the copper surface. This oxidation forms yellow stains on the surface of the plate and reduces the ability of the plate to collect mercury drops. The detailed manufacturing process to produce a set of four Cu-Ag plates, each one with dimensions of W=30 cm x L=30 cm x T=2 mm, is shown in the list below:

1. Sand the copper surface with a coarse sandpaper (10 Mesh, 2 mm).
2. It is needed stainless steel 5 plates to produce 4 Cu-Ag plates.
3. Make horizontal lines on the surface of the copper plate to decrease the flow of the trapped mercury drops on the surface creating a retention area (Figure 2).

Figure 2. Surface of the Cu-Ag plate and operating in cascade mode.

4. Remove oxidation and impurities from copper plate surface with diluted nitric acid (HNO_3 25%v/v)
5. Make solution #1: Dissolve 30 g of silver nitrate ($AgNO_3$) in 300 mL of distilled.
6. Make solution #2: Dissolve 11.5 g of potassium cyanide (KCN) in 300 mL of distilled water.

7. Mix gently solution #1 and #2 until a white precipitate is observed.

8. Filter the solution on filter paper to get rid of the white precipitate.

9. Make solution #3 by dissolving 18 g of potassium cyanide (KCN) in 300 mL of distilled water.

10. Use solution #3 to dissolve the white precipitate and <u>mix all solutions</u>. This can produce four copper-silver plates.

11. Fill a 35 x 10 x 35 cm Plexiglas tank (20 L), until 2 cm below the maximum height with distilled water only.

12. Hang four copper(cathode) and five stainless-steel (to be used as anode) plates on the electrolytic cell in an alternate way: S-Cu-S-Cu-S-Cu-S-Cu-S (Cu = copper plate, S = Stainless steel plate).

13. Connect the power supply wires as follows: the red (+) clamp on the stainless-steel plate (anode), and the black (-) (cathode) clamp on the copper plate.

14. Add the prepared solution into the cell and connect the plates to a power source ensuring to generate current of 4 Amperes.

15. Turn on the power supply. Leave work for 14 minutes. For a total time of 14 minutes the thickness of silver might be approximately 0.3-0.4 mm. The time for plating may vary depending on the direct current (DC) system.

16. Remove the plates from the electrolytic cell and dry the Cu-Ag plate with a hair dryer.

17. Wrap the dried plates with plastic films, and store in a dark place at room temperature.

18. When in use to remove mercury from the tailings, in the case of some silver or mercury oxide is formed on the surface of the plate, to reactivate the plate before using it, rub the surface with a cloth with vinegar.

19. Mercury drops can be removed from the plates with a plastic card.

2.2. Assembling the Plates

Two different arrangements of copper-silver plates have been developed: sluicing and cascade. The sluicing arrangement (Figure 3a) consists of rows of plates assembled on a flat surface, inclined 15 degrees, which is an angle to allow the tailing slurry to flow and to have adequate contact with the plate surface. The cascade arrangement (Figure 3b) works with the inclined plates arranged in zigzag that forms a cascade effect of the slurry allowing collisions between the mercury-contaminated tailing and the plate. The devised set had six cascades with 12 plates (Ortega-Ramírez et al., 2020).
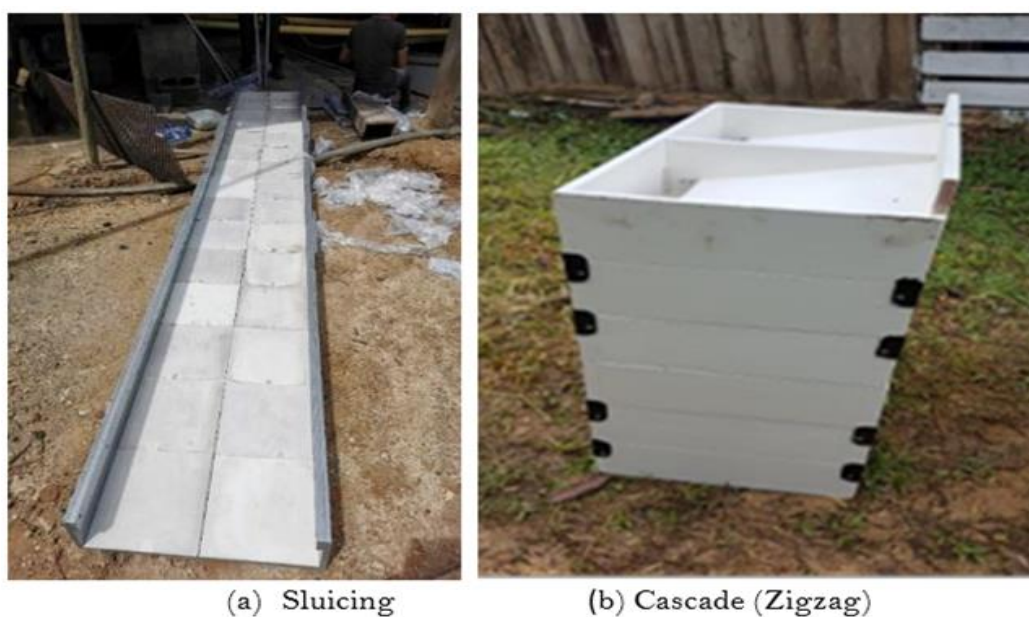

(a) Sluicing   (b) Cascade (Zigzag)

Figure 3. Arrangements of the plates.

The cascade arrangement (Figure 4) performed better than the sluicing one, visually removing more mercury drops from tailings. The sluicing arrangement, although it does retain some mercury, requires a greater number of plates and the slurry velocity increases with the length, making it more difficult to trap mercury droplets. This was also previously observed in Venezuela when the zigzag cascade arrangement extracted more mercury from tailings than the sluicing set (Veiga et al., 2005).
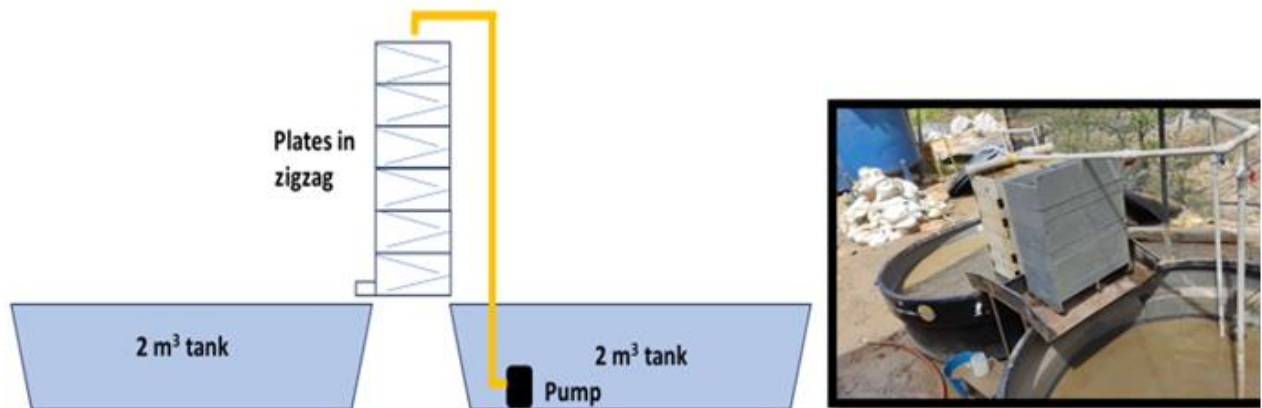

Figure 4. Final configuration of the tests using the zigzag cascade system.

The most convenient configuration for the plates was set up with two tanks, where 2,000 L of pulp (with 17% solids) was agitated by a submerged 1 Horse Power (HP) pump. The pump also pushed the slurry to the top of the cascade arrangement with 12 plates (six modules of two plates) in zigzag. No mercury drop was observed to be settled down at the bottom of the tank (Figure 4). Each test involved processing between 300 and 500 kg of contaminated tailing.

2.3. Initial Mercury Grades

The initial chemical analyses of the tailings to be treated by the Cu-Ag plates were conducted by two techniques: portable X-ray Fluorescence device (XRF) and flameless Atomic Absorption Spectrometry in a lab. Analyzing the tailings before and after the Cu-Ag plate treatment it was possible to estimate the efficiency of mercury extraction from tailings. The XRF technique seems to be handy for immediate results, but it is very sensitive to adequate XRF standards and grain size of the samples. Therefore, it is advisable to use these results with care, understanding the semi-quantitative nature of the XRF results.

3. RESULTS AND DISCUSSION

The initial mercury concentration, as an average of the analyses of 15 different tailing samples, was approximately 75 ppm (STD = 28 ppm) based on the semi-quantitative portable XRF and 125 ppm (STD = 35 ppm) based on Atomic Absorption Spectroscopy (AAS) analysis. Table 1 shows the analytical results and, due to the uncertainties inherent to the analytical procedures, no decimals were considered when expressing the results. Tailings from whole ore amalgamation in "cocos" can reach initial grades as high as 155 ppm of Hg, as observed in Table 1. The difference between the initial mercury grades analyzed by semi-quantitative XRF and flameless AAS reached a maximum of 60% but with average of 39% and the difference between final grades analyzed by the two methods was also in average 39% with a max of 49%. Despite the analytical differences from a semi-quantitative and a quantitative analytical method, the difference between the two methods to obtain mercury removal was only 0.12%, but a maximum of 98% of difference was observed in sample 6. Based on the AAS analyses, it was observed that the tailings stored for less than one year had an average mercury removal of 70% and those tailings older than 1 year, 59% of mercury extraction.

Table 1. Results of Hg removal with 12 Cu-Ag plates in zigzag.

Sample	XRF			AAS			Age of tailings (Years)
	Initial mercury concentration (ppm)	Final mercury concentration (ppm)	% Mercury removal	Initial mercury concentration (ppm)	Final mercury concentration (ppm)	% Mercury removal	
1	62	10	84	75	20	74	<1
2	84	27	68	141	42	71	<1
3	68	21	69	137	20	85	<1
4	89	21	76	90	20	78	<1
5	113	48	57	150	58	62	<1
6	92	4	96	100	52	49	<1
7	88	29	67	155	48	69	1-3
8	119	65	45	179	109	39	1-3
9	60	17	72	147	37	75	2-4
10	60	14	76	147	31	79	2-4
11	29	15	48	72	23	68	3-5
12	59	36	38	148	65	56	3-5
13	29	15	49	72	25	65	3-5
14	59	29	50	148	99	33	3-5
15	109	53	51	110	60	45	4
Average	75	27	63	125	47	63	NA
Standard deviation	28	17	16	35	28	16	NA

The initial mercury concentrations in tailings found in this research are compatible with what were observed in similar operations in Ecuador, using a similar whole ore amalgamation process in ball mills. Velásquez-López et al. (2011) analyzing six operations of whole ore amalgamation obtained a concentration of mercury of 74 ± 29 ppm in tailings. In Indonesia, where miners add approximately ten times more mercury into similar small ball mills, Krisnayanti et al. (2012) found an average of 3000 ppm Hg in the tailings.

The ages of the tailings were not easily established as most artisanal miners do not have accurate information about this, but it seems to be a characteristic that affects the recovery of mercury from the tailings. For example, tailings stored for up to 5 years have shown an acidic pH, less than 5, as a result of ARD – Acid Rock Drainage. When tested on Cu-Ag plates, these tailings quickly deteriorated the plates, oxidizing the silver layer, and sometimes the copper plate surface, decreasing their useful life and reducing the mercury retention capacity to negligible values. The grain size of the tailings also has an influence on the plate's performance. Materials with fine sand form a smooth pulp easily flowing over the plates. On the other hand, clayey tailing makes it difficult to disaggregate the crusts of mud to obtain a homogeneous pulp. This hinders the full contact of the material with the plate surfaces and keeps the mercury droplets trapped in a ball of clay (Ortega-Ramírez et al., 2020). The good mercury removal of up to 95%, as reported by Veiga et al. (2005) used an efficient commercial GoldTech plate to process mercury-contaminated tailings from primary ores with low clay, and recently produced by Venezuelan processing centers. Therefore, with less mercury oxidation than older tailings.

The configuration in zigzag cascade is simple to set up and plates are easily removed. The excess mercury trapped on the plate surfaces is simply recovered by scratching the plates with a plastic card.

It was also observed that no gold was collected along with the mercury deposited on the plates, basically because the tailings no longer have free gold particles. It is expected that most of the liberated gold particles in the ores were already extracted by the artisanal miners when they used the "cocos".

Additional steps to increase mercury removal from old acidic tailings can improve the mercury extraction, such as addition of lime to reach neutral pH and strong agitation in a tank to scrub the tailings removing the mercury oxide film on the metallic mercury drops. The main drawback of strong agitation of tailings with lime before treating

them with the plates is the fact that this increases aeration, disperses more mercury in minuscule droplets, making it more difficult to capture them, and increases mercury solubilization as $Hg(OH)_2$ (aq). The Eh-pH diagram shown by Tromans, Meech, and Veiga (1996) indicates that the soluble mercury hydroxide can be formed even in pH 7 with high aeration. At higher pH (e.g., around 11), the soluble mercury hydroxide can be present even with low oxidation potential (0.1 V), common in natural freshwater environments (Meech, Veiga, & Tromans, 1997; Randall & Chattopadhyay, 2004). These additional procedures to improve mercury removal also increase the cost of the operation, but they will be tested and evaluated soon.

Despite the significant mercury removal by the Cu-Ag plates, additional extraction of mercury from the cyanidation tanks is necessary to avoid the presence of mercury-cyanidation complexes in effluents. Based on literature, removal of mercury from cyanide solutions is applied in two ways:

1) Removal of mercury-cyanide complexes with sorbents, and

2) Selective precipitation of Hg from the cyanide solution.

In the first case, bio-sorbents have been used to remove metals in solution, including mercury, from effluents. Materials such as chicken feather, fruit passion, banana peels, orange peels, eggshell, have been tested and reached interesting results (De Angelis, Medeghini, Conte, & Mignardi, 2017; Jacques, Lima, Dias, Mazzocato, & Pavan, 2007; Kamsonlian, Suresh, Majumder, & Chand, 2011; Shar et al., 2016; Tesfaye, Sithole, Ramjugernath, & Chunilall, 2017).

Despite the simplicity and low price of the application of bio-sorbents to remove mercury from cyanide solutions, the most used process in the industry is the selective precipitation of mercury in the gold cyanidation tanks (Atwood, 2003; Coles & Cochrane, 2006; Matlock, Howerton, Van Aelstyn, Nordstrom, & Atwood, 2002; Misra, Lorengo, Nanor, & Bucknam, 1998; Simpson, Staker, & Sandberg, 1986). In some Nevada gold mines, where mercury occurs as an impurity in the gold ore, many studies have been conducting using sulfides (Na_2S, CaS, ZnS), thiol surfactants or sulfur-based organic substances, such as potassium or sodium dimethyl dithiocarbamate (DDC), to selectively precipitate the mercury-cyanide complexes from gold cyanide solutions (Miller, Alfarol, Misra, & Lorengo2, 1996). The high effectiveness of the DDCs has been demonstrated (Kantarcı & İbrahim, 2019; Lorengo, 1996) as well as their selectivity towards mercury, not interfering with the gold leaching process or the activated carbon adsorption (Tassel, Rubio, Misra, & Jena, 1997). Lorengo (1996) mentioned that CaS precipitates mercury sulfide and the pollutant is less prone to be re-dissolved in cyanide solution than when the precipitation is conducted with Na_2S. The main problem is that silver is also precipitated as AgS, when sulfides are used.

The most affordable method and most accessible reagents for the artisanal and small-scale cyanidation plants must be investigated to remove mercury from the cyanidation tanks. Aliprandini, Veiga, Marshall, Scarazzato, and Espinosa (2020) reached 81% of mercury removal with activated carbon at neutral pH from a synthetic solution with $Hg(CN)_2$. The mercury-cyanide complex $[Hg(CN)_4]^{2-}$ is stable at pHs above 8.5 and $Hg(CN)_2$ (aq) is stable at pH below 7.8 (Flynn & McGill, 1995). This latter species is easily absorbed on activated carbon but $[Hg(CN)_4]^{2-}$ is not (Adams, 1991). Then, activated carbon in the cyanidation process, usually at pH 10.5-11, does not adsorb too much mercury as shown by Velásquez-López et al. (2011) in Ecuadorian processing centers. These authors also showed that when zinc cementation process (Merrill-Crowe) is used to extract gold from cyanide solution, more mercury is extracted than when activated carbon is used. In small-scale cyanidation plants in Colombia the use of activated carbon is more familiar to the owners of the cyanidation plants, therefore a mercury precipitation agent must be studied to complement the mercury removal process using the Cu-Ag plates.

4. CONCLUSION

The homemade Cu-Ag plates are affordable and easy to be fabricated and employed by artisanal gold miners and processing centers. The mercury removal tests using 300 to 500 kg of 15 contaminated tailings from Colombia reached a maximum of 85% of extraction but with average of 63% (STD = 16%). The final concentrations of 27 ppm Hg (STD = 17 ppm) to 47 ppm Hg (STD = 28 ppm) from 75 ppm Hg (STD = 28 ppm) to 125 ppm Hg (STD = 35

ppm), depending on the analytical method, are still high and further treatment of the cyanide solution is needed either by removing mercury with sorbents or precipitating it in the cyanidation tanks. The possible reasons for this high mercury content in the final treated tailings would be the oxidation films on the mercury drops, especially in old tailings, as well as the low pH of these tailings. The availability of the mercury droplets to be collected by the silver surface is not a simple problem since many droplets can be strongly attached to hydrous ferric oxides or clay minerals of the tailings and not free enough to be captured. Another challenge of this homemade Cu-Ag plates is to estimate the useful life of the plates, in which operation projections can be made depending on the type of tailing will be processed.

The plates in zigzag cascade-configuration are an efficient system for a primary removal of a good portion of the mercury in the tailings but the concentration of mercury going to the cyanidation circuit is still high and further chemical process must be used to adsorb or precipitate the mercury-cyanide complexes avoiding discharges of these pollutants to the environment.

This research is just the tip of an iceberg of a complex problem of eliminating mercury use in artisanal gold processing, but it is an important step to make the processing centers aware of the need to remove mercury from tailings in their cyanidation plants.

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