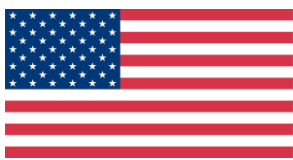


Promoting responsible recovery and handling of mercury from contaminated artisanal gold mining tailings in Colombia

*Technical report
Results from tests to remove mercury in cyanidation processes
September 2022*



Funded by:



Implemented by:



This publication was funded by a grant from the United States Department of State. The opinions, findings and conclusions stated herein are those of the authors and do not necessarily reflect those of the United States Department of State.



Table of Contents

Table of Figures	3
1. Introduction	5
2. Cyanidation process description	7
3. Literature review	10
4. Experiment design for tests to remove Hg after cyanidation	15
4.1. Geometric representation	16
4.2. ANOVA	19
5. Hg removal laboratory tests	21
5.1. Sample preparation	23
5.2. Removal agent preparation	23
5.3. Hg measurement	25
6. Results	30
7. Conclusions	35
8. Recommendations	36
9. Glossary	37
References	39
Annex 1. Statistical analysis method ANOVA	42
Annex 2. Supplementary figures	46
Annex 3. Cyanidation tests	49



Table of Figures

Figure 1. Gold extraction in ASGM activities (provided by Pure Earth).	7
Figure 2. Gold dissolution process. Taken from Restrepo Baena et al. (2017).	9
Figure 3. Solution passed through filters with ZnS. Adapted from (Gabby & Eisele, 2013).	12
Figure 4. Bioadsorption method with banana, orange, and lemon peels. Adapted from (Kelly Vargas et al., 2012).	13
Figure 5. Geometric representation of the 5 x 3 x 3 experimental design. Source: Pure Earth.	17
Figure 6. Variables to evaluate the mercury removal process in watery medium.	18
Figure 7. Proposed diagram per tailings origin for different factors used in the removal of Hg in aqueous media.....	19
Figure 8. Gaussian distribution with the F statistic.	20
Figure 9. Experimental surface. Source: Pure Earth.	20
Figure 10. Sample preparation for Hg measurement.	21
Figure 11. Samples of Hg removal compounds.....	25
Figure 12. Flow diagram for Hg measurement by spectrophotometry.	26
Figure 13. Cyanidation solutions after removal tests.....	27
Figure 14. Sample preparation for atomic absorption spectrophotometry reading.	27
Figure 15. Hg readings through cold vapor atomic absorption.....	27
Figure 16. Representation of the Hg removal experimental procedure.	29
Figure 17. Final Hg concentration after removal process by tailings origin.	31
Figure 18. Hg removal percentages per removal agent (Hg: removal agent).	33
Figure 20. Gaussian curve with test statistic.....	44
Figure 21. Hg removal in samples from Antioquia.	46
Figure 22. Hg removal in samples from Bolívar.....	47
Figure 23. Hg removal in samples from Nariño.	48
Figure 24. Dissolved Hg concentrations during cyanidation tests without removal agents.	49
Figure 25. Test samples.	50



Technical Team

Alfonso Rodríguez Pinilla
Country Director Pure Earth Colombia

Angie Tatiana Ortega-Ramírez
Project Coordinator Pure Earth Colombia

Lina Hernández
Program Director Pure Earth

Diego Fernando Marín Maldonado
Field Investigator Pure Earth

Ferney Londoño
Field Investigator Pure Earth

Acknowledgements

Shun-Ping Chau
United States Environmental Protection Agency (EPA)

Marcello Veiga
Professor Emeritus, University of British Columbia



1. Introduction

The tests for removing mercury in cyanidation processes were developed under the framework of the project “*Promoting responsible recovery and handling of mercury from contaminated artisanal gold mining tailings in Colombia*” (hereinafter, “The Project”), which is being implemented by Pure Earth and financed by the U.S. Department of State. The Project was initiated in October 2018 and will be finalized in June 2023.

The overall goal of the Project is to reduce the amount of mercury present in gold mining tailings in Colombia. Mercury is frequently used in artisanal and small-scale gold mining (ASGM) processes around the world. ASGM in Colombia is regulated under Decree 1666 of 2016 under the category of subsistence and small-scale mining.

The specific objectives of the Project are the following:

- Identify promising responsible mercury recovery techniques and increase understanding of criteria for choosing a technique for use in the Colombian ASGM context. This outcome will be accomplished through the facilitation of an intensive mercury recovery technical workshop with U.S. and Colombian officials and through the drafting of a paper summarizing the discussion.
- Develop a model for the responsible and profitable recovery of mercury and gold from tailings based on experiences with a pilot processing center. The model will include a technical description of the mercury recovery technique and an economic model for commercializing gold recovered from tailings.
- Develop a technical protocol that facilitates responsible tailings management for use by the Colombian government, including the safe handling, transportation, and characterization of tailings as well as the storage and disposal of mercury and mercury wastes from ASGM activities.
- Develop an analysis of the regulatory framework that helps define tailings ownership and identifies legal mechanisms that facilitate tailings treatment and legal commercialization of gold recovered from tailings.
- Develop an analysis of the regulatory framework that identifies institutional and financial mechanisms for installation and maintenance of an interim mercury storage unit.
- Promote responsible mercury handling and storage practices in the Colombian context by establishing a pilot interim storage unit for mercury and ensuring its continued use through operational trainings, chain of custody protocols, and stakeholder buy-in.



The purpose of the current document is to report on an activity designed to partially fulfill the second objective of the Project. This activity involves testing the mercury concentration limit under which it is possible to perform cyanidation to obtain gold from tailings. It is important to note that the practice of cyanidation of mercury-contaminated mining material is not recommended under the Minamata Convention because this practice generates mercury(II) cyanide, a highly contaminating compound. Nevertheless, there is evidence that several ASGM communities in Colombia adhere to this practice to increase the amount of gold extracted from the material. In addition, there is no clear regulation on the practice, and miners often lack knowledge about the risks of combining cyanide and mercury.

Previous activities under the framework of this Project have focused on the capture of mercury from tailings using the copper plate technology. Previous pilot tests of the copper plates have resulted in a reduction of up to 85% of the elemental mercury present in tailings. However, it is important to complement the copper plates with alternative techniques to further reduce the presence of mercury after the tailings have been treated with the plates. Therefore, this report is focused solely on the search for new agents for the removal or precipitation of mercury present in cyanidation solutions.

Finally, it is important to mention that this Project and all documents derived from this Project aim to strengthen the implementation of the Minamata Convention in Colombia as approved on May 11, 2018 by the Colombian Congress through Law 1892¹ as well as provide information to help fulfill the country's responsibilities under the frameworks provided by Article 7 of the Minamata Convention on ASGM, Article 11 on mercury waste, and the National Implementation Plan on mercury.

¹ Law 1892 of 2018 (May 11). By which the government of Colombia approved the Minamata Convention on Mercury, which was created in Kumamoto (Japan) on October 10, 2013.

2. Cyanidation process description

Mercury (Hg) is often used in ASGM due to its capacity to bind with gold, forming an amalgam. A common practice is to add Hg into the *coco* (a rock-crushing machine used to grind mining material), where the Hg will form an amalgam with the gold particles, making it easier to recover gold from the material. This material is then concentrated to recover the greatest amount of Hg and gold in the subsequent amalgamation process (Salinas et al., 2004). The recovered Hg is strained through a piece of cloth to remove the excess Hg and obtain the amalgam that contains the gold particles (see Figure 1).

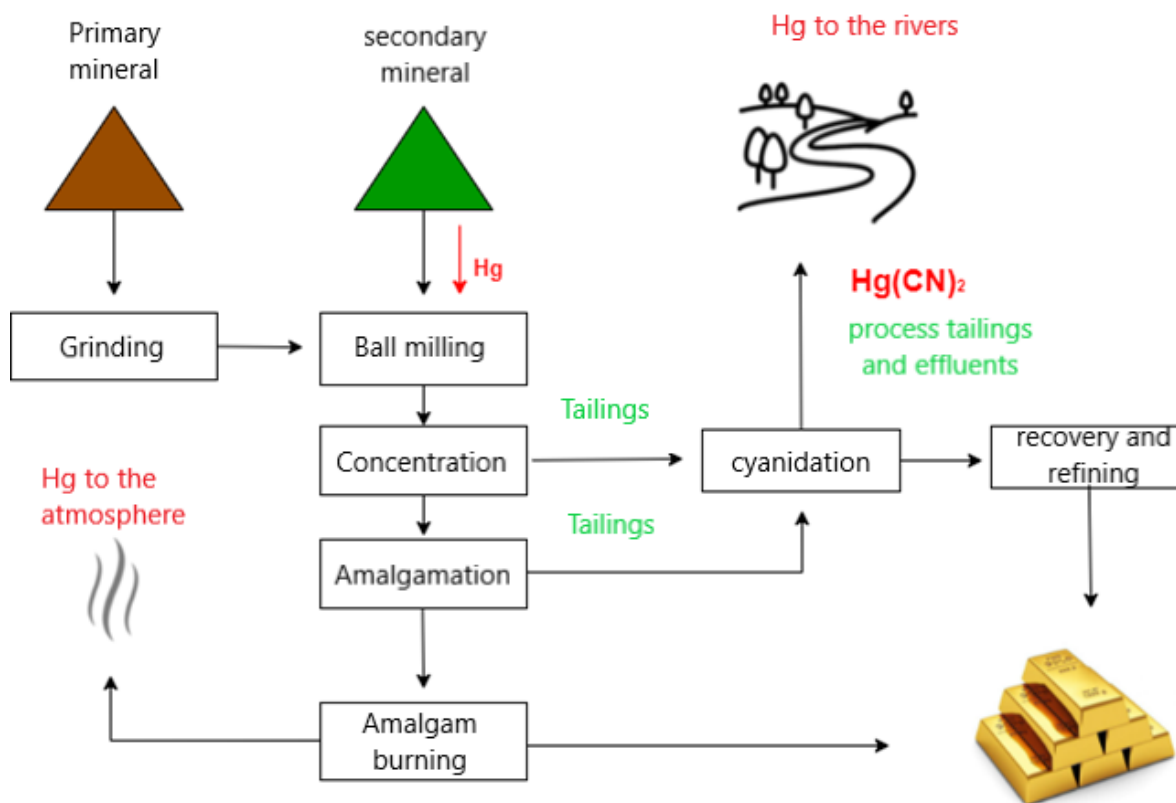


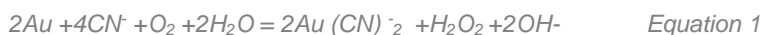
Figure 1. Gold extraction in ASGM activities (provided by Pure Earth).

Cyanidation, which dissolves particles directly from the minerals in which they are contained, is a hydrometallurgical process widely used for extraction. Cyanidation can result in a solution rich with precious metals, which can later be extracted from the solution (see Figure 1). The efficiency of this process depends on various factors that determine the kinetics of the reaction: surface area, pH and temperature of the solution, the degree of agitation, and the concentrations of cyanide and oxygen in the slurry (Stapper et al., 2021). To reduce the amount of cyanide destroyed in this process, lime is usually added to the solution, which helps maintain a protective alkalinity, accelerates the sedimentation of the slurry in the



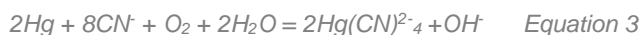
thickened material, and helps precipitate undesirable substances. Similarly, aeration is necessary for cyanidation, wherein air has contact with the gold particles. Because gold particles are distributed throughout the slurry, air bubbles must also be dispersed throughout, thereby guaranteeing contact with the molecules (David, 2017).

The chemical reactions performed during cyanidation are shown in Equation 1 and 2:



Besides mercury, cyanide also creates strong complexes with other metals, such as cobalt and iron. The bonds between cyanide and metal can be so strong that highly acidic environments ($\text{pH} < 2$) along with the presence of heat are required to liberate the cyanide ion from elements such as Co, Au, Fe^{2+} , Fe^{3+} , and Hg (Dzombak, Ghosh, & Wong-Chong, 2005). The total cyanide present in a process of this type corresponds to the sum of all cyanide species that have been converted to hydrogen after the distillation process by reflux of a sample in presence of strong acidic solutions (Marshall et al., 2020).

The parallel reaction with which Hg consumes cyanide is shown in Equation 3 (Kantarci & ALP, 2019):



In cyanidation of mercury-contaminated tailings, the gold-cyanide complex is faster to form than mercury(II) cyanide (Velásquez-López et al., 2011), which can be absorbed by the action of activated charcoal when included in the process (Aliprandini et al., 2020). This mechanism is the main process to eliminate gold from the cyanide solution, avoiding the use of a filtration system. In relation to the complexes, uncharged Hg(CN)_2 is more easily absorbed into the activated charcoal than $[\text{Hg(CN)}_4]^{2-}$, which is the predominant species formed in $\text{pH} > 8.5$ during cyanidation (Adams, 1991; Flynn & McGill, 1995). In contrast, $\text{Hg(CN)}_2(\text{aq})$ forms in $\text{pH} < 7.8$, which makes the mercury(II) cyanide complex discharge more easily in the processed tailings without treating the tailings water (Marshall et al., 2020).

Flynn & McGill (1995) consolidate the states that mercury can adopt in cyanide solutions in relation to the pH of the gold extraction systems. The mercury and cyanide reactions generate the complex $[\text{Hg(CN)}_4]^{2-}$, which is stable at $\text{pH} > 8.5$, and Hg(CN)_2 at $\text{pH} < 7.8$. In addition, other mercury complexes are generated which continue consuming the cyanide due to its affinity. It is therefore important to determine the concentration of cyanide necessary to extract the greatest amount of gold without the cyanide being consumed in parallel reactions with other compounds with which it has affinity.

Stoichiometrically, two moles of cyanide are required to complete one mole of gold (Figure 2). However, if the mineral presents other cyanicidal substances besides gold, this stoichiometric rule will be limited by the consumption of cyanide by other elements such as Cu, Ag, Hg, Zn, and Fe. Therefore, the cyanide concentration needs to be sufficient to be able to complex the greatest percentage of gold cations (Stapper et al., 2021). It is thus important to remove the greatest quantity of sulfides before cyanidation to avoid a high consumption of cyanide in the process.

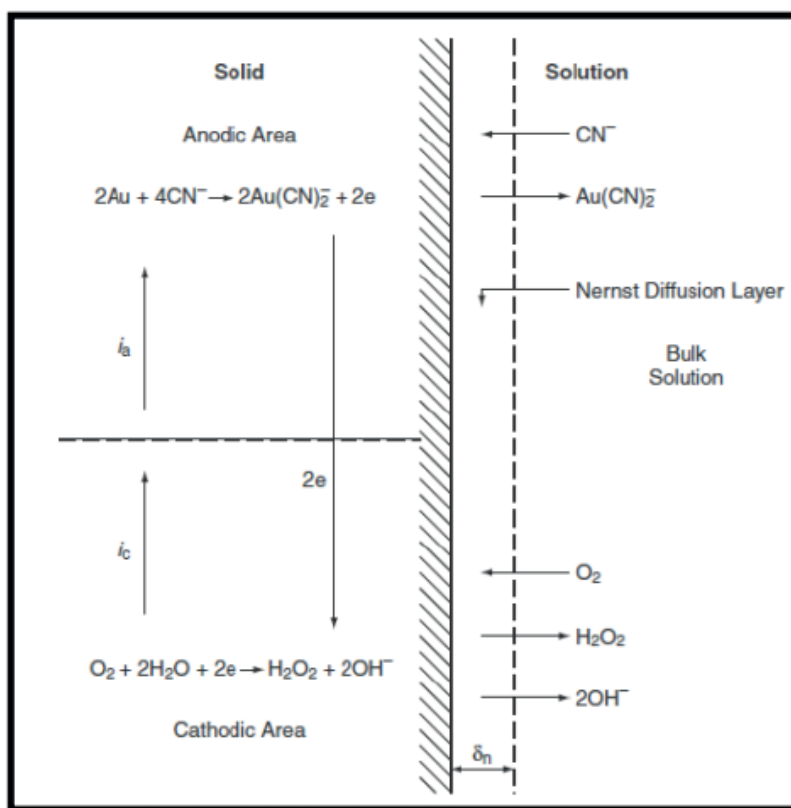


Figure 2. Gold dissolution process. Taken from Restrepo Baena et al. (2017).



3. Literature review

A literature review was conducted in order to understand the current body of knowledge on Hg removal from aqueous media, especially in processes that use cyanide. The review sought to elucidate the different techniques used for this purpose and participating substances. This information can serve as a reference for establishing methods to develop viable models to remove Hg in ASGM processes.

Since the 1980s, international entities such as the Bureau of Mines, a now-defunct agency of the U.S. Department of the Interior, have developed research around problems related to Hg in gold and silver extractive processes. One method that was investigated was the precipitation of Hg by adding sulfides (see Equation 4); this method is possible because Hg has high affinity with sulfur and is found naturally in cinnabar, a mercury sulfide.



Where:

MS: Metallic sulfide

CN: Cyanide

Hg: Mercury

In 1984, the Bureau of Mines conducted research on the effects of adding precipitant compounds such as calcium sulfide (CaS) and sodium sulfide (Na₂S) to cyanidation slurry at concentrations of 0.02 lb of precipitant per ton of mineral, agitating it for 15 minutes. The results showed that a precipitation of Hg solubilized in a solution of 96% and 99.9% of CaS and Na₂S, respectively; however, in the case of Na₂S, the precipitated Hg redissolved in the first 30 minutes after being added to the solution (Sandberg et al., 1984). It should be noted that this technique does not allow for the recovery of metallic Hg, which can only be recovered as an insoluble precipitated product.

In 1998, Misra et al. researched the efficiency of Hg removal from Na₂S and alkyl methylthiocarbamates in solutions with mercury nitrate and mercury cyanide complexes. This study shows that, although sodium sulfide can effectively eliminate Hg from an inorganic mercury nitrate solution, sodium sulfide is not as efficient at eliminating mercury cyanide complexes as alkyl methylthiocarbamates. Potassium dimethylthiocarbamate (KDTC), on the other hand, is very efficient at eliminating Hg from mercury cyanide solutions through forming mercury dithiocarbamate complexes. The study showed that close to 98% of the Hg present in gold mine effluent which contained 6.8 mg/L of mercury could be eliminated through the addition of KDTC with a molar ratio of reactive to mercury of 2:1 (Misra et al., 1998). Another attractive property of KDTC is that, although it precipitates Hg and other heavy metals from cyanide solutions, other compounds present in the solution



such as $\text{Au}(\text{CN})_2^-$ are not affected by its presence; therefore, it does not affect the adsorption of gold in activated charcoal in cyanide solutions (Allen & Misra, 1996).

Atwood (2003) evaluated the precipitation of Hg with 1,3-benzendiamidoethanethiol (BDET) in a solution of 0.998 mg/L of Hg with 0.30% BDET at 0.5 molar. At the end of the precipitation, a solution of 0.001 mg/L of Hg was obtained. The recovery rate of 99.99% is certainly a significant finding; however, BDET costs around \$200/lb, which makes its application for industry purposes unfeasible.

Gabby & Eisele (2013) examined the effect of zinc sulfur (ZnS) or sphalerite on the removal of Hg present in solutions. Initially, the researchers developed a cyanidation process to leach the silver and Hg and obtain their cyanide complexes. Later, they filtered the solution, using it as raw material for the experiments, as shown in Figure 3. In one of the experiments, 1 g of powered ZnS with a particle size of 38 microns was added to a 30 mL of solution with 438 ppb of Hg as $\text{Hg}(\text{CN})_4^{2-}$ and 2240 ppb of silver as $\text{Ag}(\text{CN})_2^-$ and agitated for one hour. At the end of the experiment, a 97% reduction in Hg was achieved.

In another experiment, a solution with 704 ppb of Ag and 921.9 ppb of Hg was passed through a series of three filters with 0.625 gr of ZnS per filter. As the solution passed through each filter, a sample was removed to be measured with atomic absorption. After filtering the solution three times, the Hg removal rate was 100% (Olivares & Guevaras, 2016).

Rocha et al. (2018) examined the bioadsorption of Hg using *gulupa* (*Passiflora edulis f. edulis*) fruit peels in synthetic water, simulating a similar concentration to that of gold extraction effluent. The bioadsorption was tested under different temperatures and biomaterial particle diameters. The researchers concluded that the material adsorbed up to 98.25% of Hg at a temperature of 28 °C and a particle diameter of 0.8 mm. No previous literature had examined the use of *gulupa* peels for Hg adsorption; however, the authors explained that they evaluated its efficiency despite the lack of literature to examine if *gulupa* could be reused in these processes thereby reducing *gulupa* waste. *Gulupa* peels are not typically used for other processes and are thus normally discarded.

Tejada Tovar et al. (2015) reported in “Adsorption of heavy metals in wastewater using materials of biologic origin” that the techniques of bioadsorption implemented through biological waste compounds such as plantain or banana peels, orange peels, lemon rinds, tamarind husks, and *pirul* tree bark, among others. The researchers associated the capacity for adsorption with content of functional groups (ex., sulphate, phosphate, amino, carboxyl, and hydroxyl), which have affinity for metallic cations. Within this research, the authors reference Kelly Vargas et al. (2012), who investigated the bioadsorption of Cd, Pb, and Cu present in effluent, using banana, orange, and lemon peels. These biologic wastes were treated through a process of drying at 40 °C for six days to later be ground and sifted in

order to obtain two particle sizes, 1 mm and 2 mm, which were alkalized with sodium hydroxide (NaOH) at 0.5 N and dried again at 40 °C.

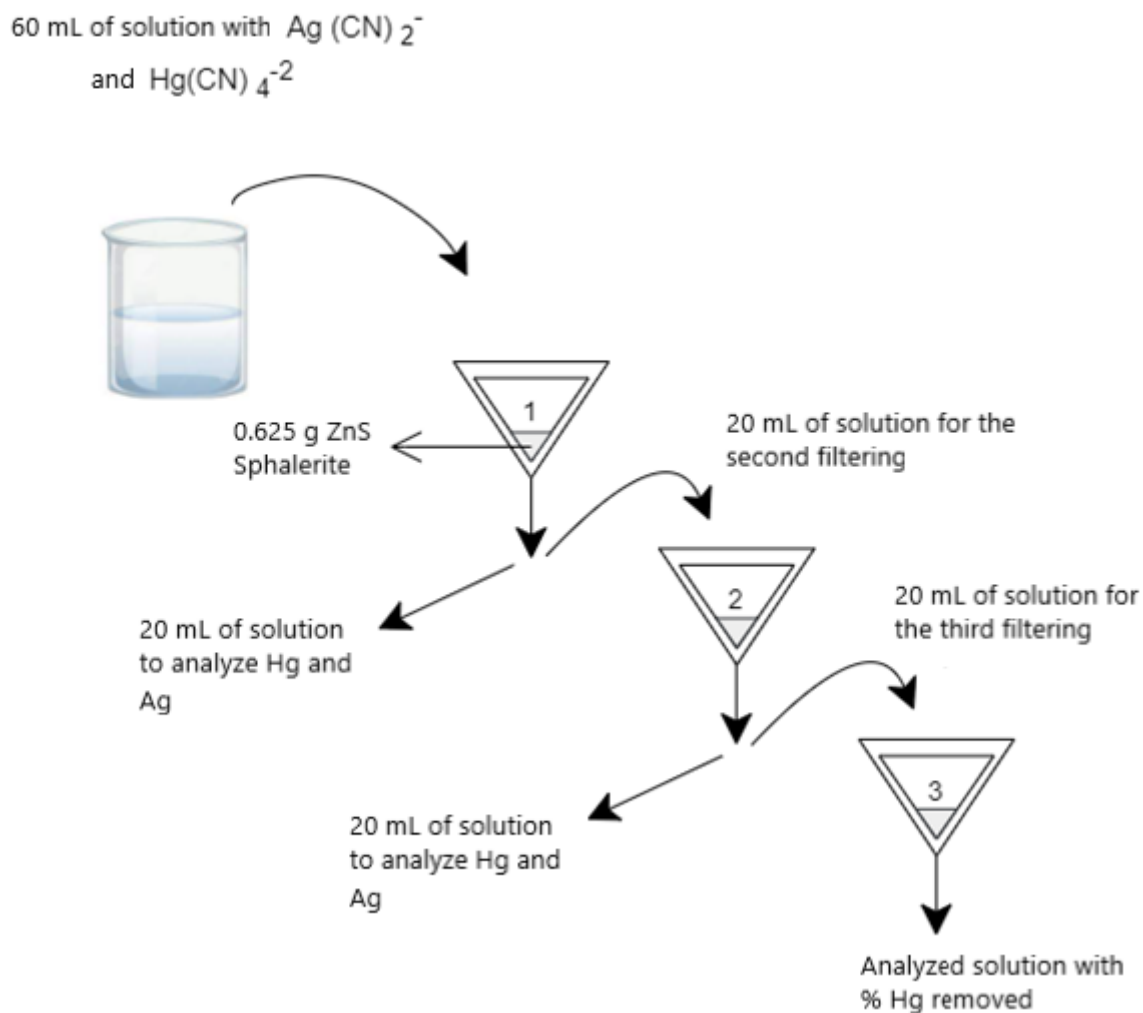


Figure 3. Solution passed through filters with ZnS. Adapted from (Gabby & Eisele, 2013).

Figure 3 shows the experimental process in which 1.5 g of the peels and 25 mL of a synthetic solution with Cd, Cu, and Pb as $\text{Cd}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Pb}(\text{NO}_3)_2$, respectively, are added to a column reactor.

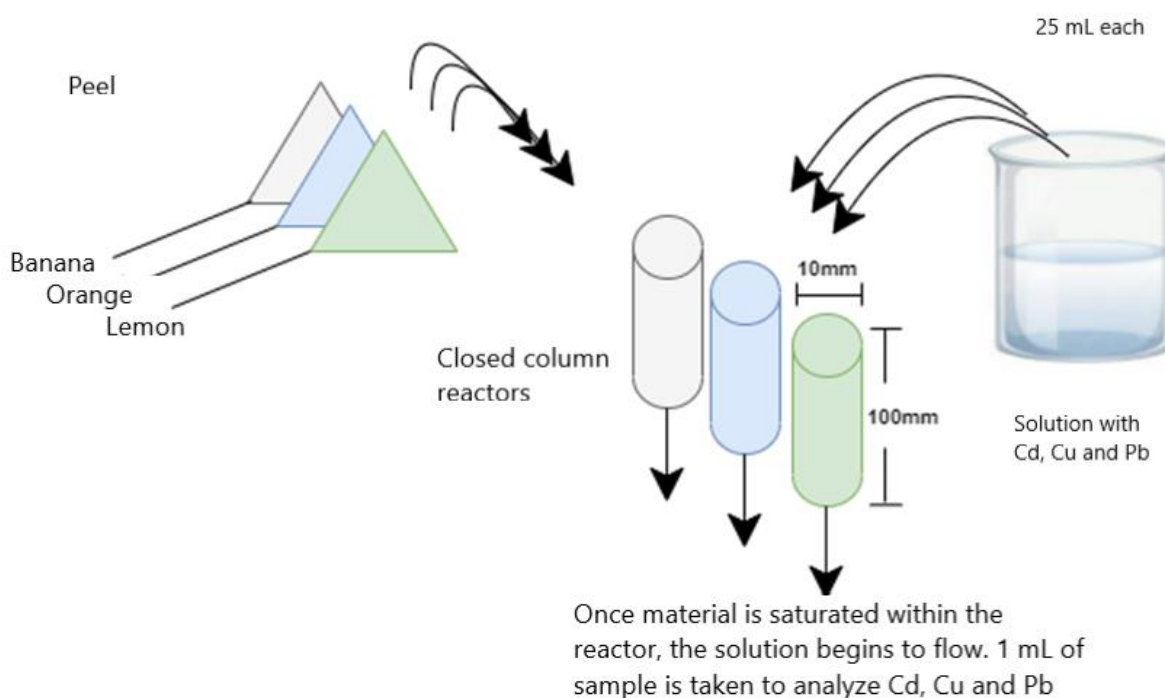


Figure 4. Bioadsorption method with banana, orange, and lemon peels. Adapted from (Kelly Vargas et al., 2012).

Vera Rodríguez (2017) cultured 10 different mushroom strains through the Potato Dextrose Agar culture method. These mushrooms were then subjected to a contaminant load of 3 µg/l of Hg. Of the 10 different strains, 6 displayed Hg absorption rates of 55.5–66.6% (Semana, 2018).

With respect to Hg adsorption, Jorge Tadeo Lozano University, spearheaded by Professor Laura Rosa Conde and considered a hotbed of sustainability research, studied the reuse potential of used tire rubber. 61,000 tons of used tires are discarded per year in Colombia, making tire rubber a waste with high availability. The research described the treatment of the tire rubber which began with pyrolysis to obtain a granular product capable of capturing heavy metal particles like Hg and chrome. Because the research focused on wastewater with pesticides from potato, soy, and fruit crops, its usefulness with regards to mining wastewater is unknown. Other points to be further investigated are the most efficient ratios and whether the material can be reused (UTADEO, 2017).

Sarria-Villa et al. (2020) present a series of technologies for heavy metal removal, including one which highlights adsorption by agricultural waste and modified biologics, such as eucalyptus bark, which is reported to have a Hg adsorption capacity of 33.11 mg/g and pine (*pinus pinaster*) bark which is reported to have an adsorption capacity of 7 mg Hg/g.



As shown by the literature review, numerous techniques exist to remove Hg in solution; some are more viable than others due to application ease and higher efficiency. Nonetheless, the principles by which these methods function could be applied to other materials.



4. Experiment design for tests to remove Hg after cyanidation

Based on the literature review, an experimental design was made to study Hg precipitation by cost-effective alternative agents in the cyanidation of Hg-contaminated tailings.

The selected factors for the experiment design were the following:

1. Tailings type (origin): Mining tailings composition tends to differ by region, potentially affecting Hg precipitation, and was therefore selected as a factor to study under the present experiment design. Pure Earth has previously developed projects associated with mining tailings management and Hg removal treatment in several different regions of Colombia, including the departments of Antioquia, Bolívar, and Nariño. These departments were therefore selected for study to continue analyses and evaluations on the Hg management in these mining tailings.

2. Precipitant/adsorbent type (referred to as removal agents): Based on the literature review, consultation by experts, and information from research centers, the following removal agents were selected: sodium sulfide (Na_2S), shredded rubber, banana peels, *gulupa* peels, and lemon rinds. These materials were selected due to the presence of sulfur compounds that help retain Hg. Additionally, these removal agents are easily accessible to miners due to their high commercial availability and low cost. The fruit peels and rinds are even more accessible because these fruits form an essential part of local nutrition. Finally, the use of the fruit discards and shredded rubber promote the valorization of waste.

The next section describes the physicochemical characteristics of each removal agent.

- Sodium sulfide (Na_2S)

Sodium sulfide promotes Hg removal through its ionic nature and element packing. In Lara (2021), Na_2S concentration and temperature were highlighted as significant contributing influences on the results.

- Shredded rubber

Shredded rubber, which is obtained through the mechanical shredding of used agricultural or industrial tires, contains Fe and textile fiber (Rodríguez Parra, Jiménez Villamarín, & Carvajal Rico, 2017).

- Banana peels

Banana peels, which are generally discarded upon use, could serve as a biosorbent, reducing their environmental impact. They could be potentially recovered locally from where they are generated and then used to treat contaminated bodies of water, as described by Bionolo in “Biosorption of uranium with banana peels”. Carbonyl and hydroxyl functional groups are present in the entire biomass structure of banana peels in forms derived from



cellulose, hemicellulose, and lignin which have a total negative charge, favorable for fixing positively charged metallic ions (Boniolo, 2008)..

- *Gulupa* peels

The *gulupa* is a fruit that originates from the forests of the Amazon. *Gulupa* is round and can be green, yellow, or purple, depending on ripeness. Its flavor is slightly sour, though a bit sweeter than the passionfruit. (Muñoz Echeverri, et al., 2016) states that the *gulupa* and similar citrus fruits have potential as bioadsorbent materials.

- Lemon rinds

Lemon production generates tons of waste, presenting a potential for added value. Espinoza and Marshall (2016) evaluated the bioadsorbent power of lemon and grapefruit peels for the elimination of heavy metals such as Pb and Hg in synthetic wastewater. The lemon rinds proved to be highly effective, with a Hg biosorption of 96.08% and 98.58% when using 1.5 g of biosorbent with a particle size of 630 μm and 3.0 g of biosorbent with a particle size of 315 μm , respectively.

3. Removal agent concentrations: The selected concentrations were informed by the literature and then adjusted so that the ratios were considerably spaced to have a greater evaluation spectrum. Thus, the selected ratios of Hg to removal agent were 1:100, 1:1000, and 1:10000. In other words, for each ppm of mercury, 100, 1000, and 10000 ppm of removal agent were evaluated.

To incorporate the three factors, a test of 5 removal agents at 3 different concentrations was designed to evaluate the behavior in tailings from 3 different sites. Therefore, an experiment design of 3 factors of the form 5 x 3 x 3 was established to investigate the effect of 3 variables on Hg precipitation and to study their interactions through ANOVA. A replicate was added to create a final design of 5 x 3 x 3 x 2.

The next section will elaborate on characteristics associated with the selected experimental design to determine the number of tests needed and the respective combinations to execute in laboratory.

a. Geometric representation

Figure 5 below shows the geometric representation of the selected 5 x 3 x 3 design:

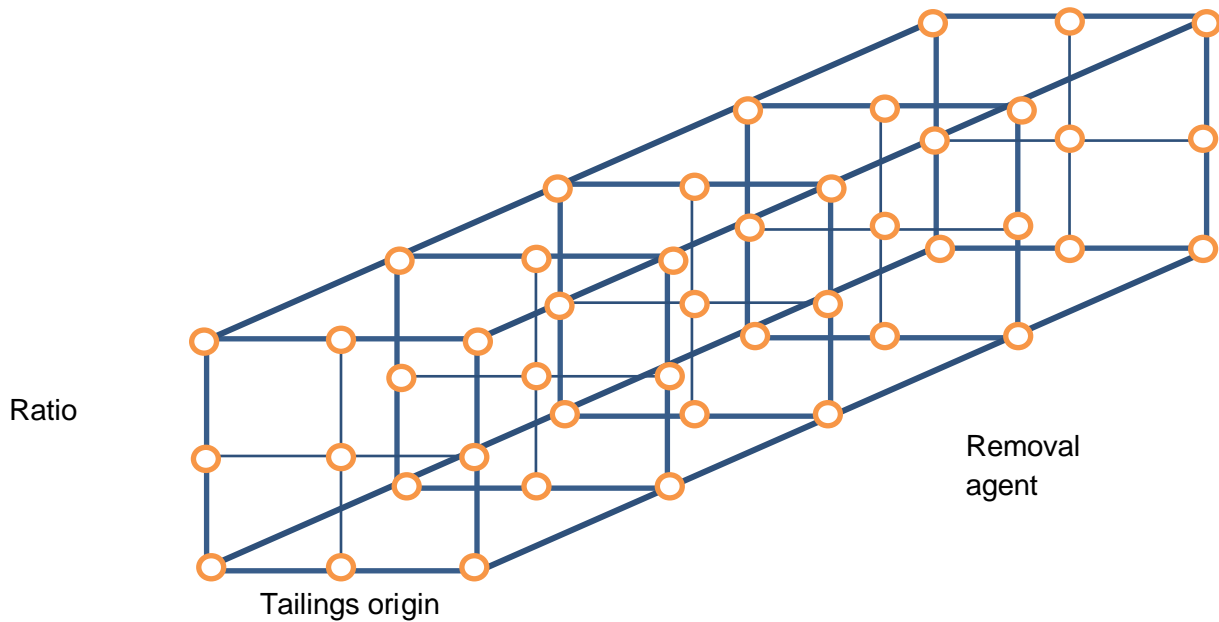


Figure 5. Geometric representation of the 5 x 3 x 3 experimental design. Source: Pure Earth.

The statistical model for the factorial experimental design with three factors (Lara, 2021) is:

$$y_{ijkl} = \mu + \tau_i + \beta_j + \gamma_k + (\tau\beta)_{ij} + (\tau\gamma)_{ik} + (\beta\gamma)_{jk} + (\tau\beta\gamma)_{ijk} + u_{ijkl}$$

$$i = 1, 2, \dots, a ; j = 1, 2, \dots, b ; k = 1, 2, \dots, c ; l = 1, 2, \dots, r,$$

where r is the number of replications, and n=abcr is the number of observations. The number of observations for this model is abcr; that is, 5 x 3 x 3 x 2, which corresponds to 90 observations (45 according to the geometric model but when replicates are considered, the number of datapoints doubles).

Figure 6 below displays the variables and levels for experimental analysis:

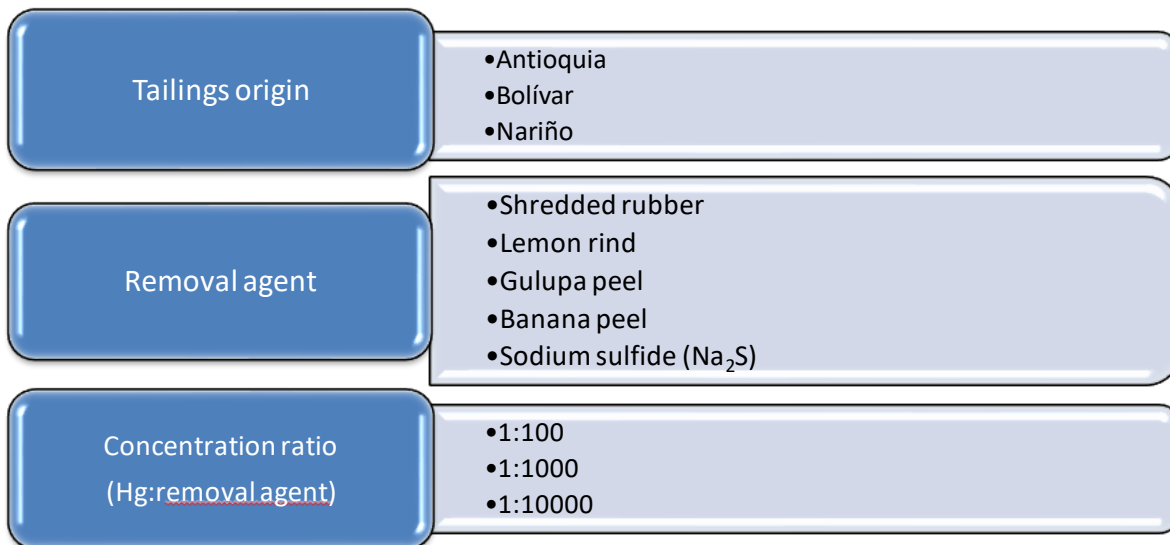


Figure 6. Variables to evaluate the Hg removal process in aqueous media.

Figure 7 below represents the experimental design factors per tailings origin:

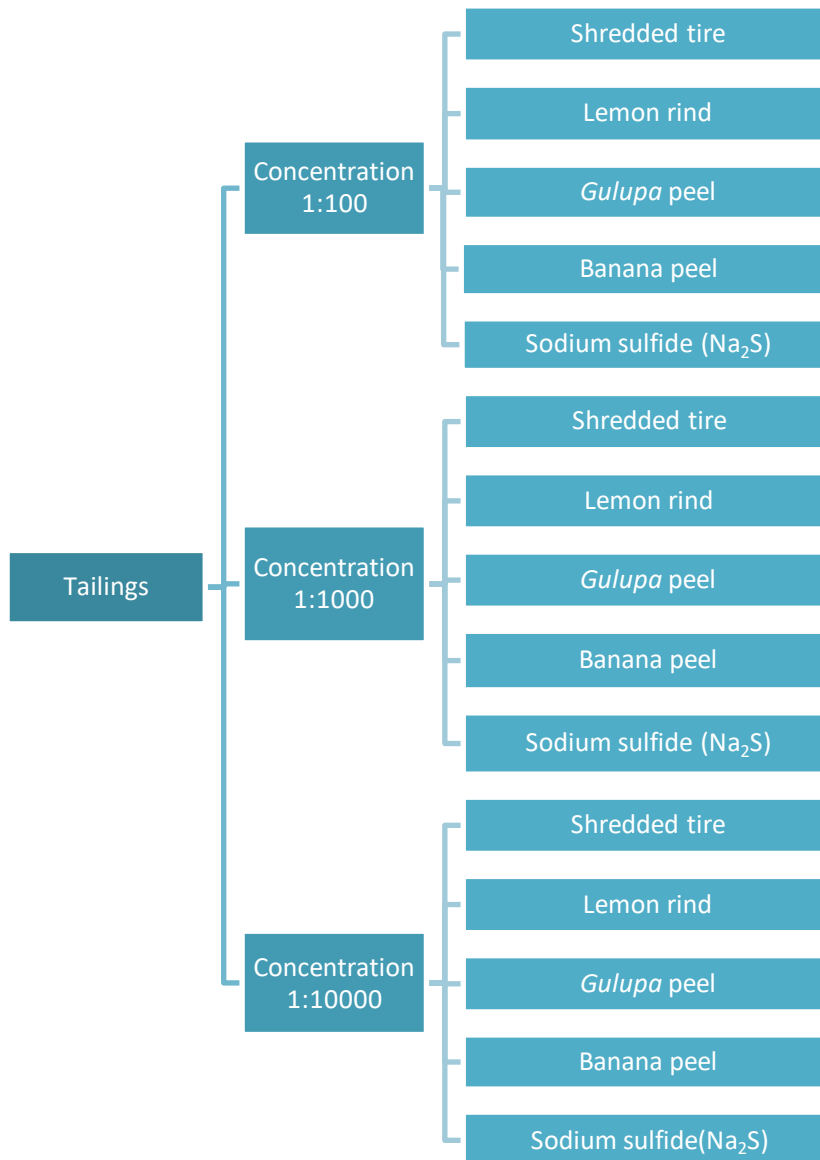


Figure 7. Proposed diagram per tailings origin for different factors used in the removal of Hg in aqueous media.

b. ANOVA

The statistical method selected to validate the significance of the tests was ANOVA. For ANOVA, the following information was needed: the sum of the squares, degrees of freedom, mean squares, F statistic, and F critical value, with a confidence interval of 0.05.

To calculate the F critical value, an Excel function was used with the following inputs: the confidence interval ($\alpha = 0.05$), the degrees of freedom of each effect, and the degrees of freedom of the error. The F statistic and F critical value are necessary for the posterior analysis of the Gaussian distribution, as shown in Figure 8.

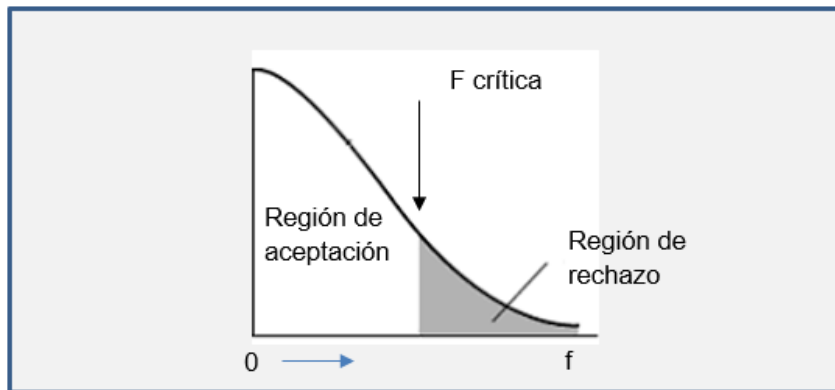


Figure 8. Gaussian distribution with the F statistic.

When the F statistic is greater than the F critical value, the curve is in the reject zone. Therefore, the null hypothesis can be rejected, meaning there is an effect between the factor tested and the results.

Figure 9 shows the three experimental design variables: the removal agent, the concentration ratio between Hg and the removal agent, and the tailings origin (a factor which can affect the chemical, physical, and mineralogical characteristics).

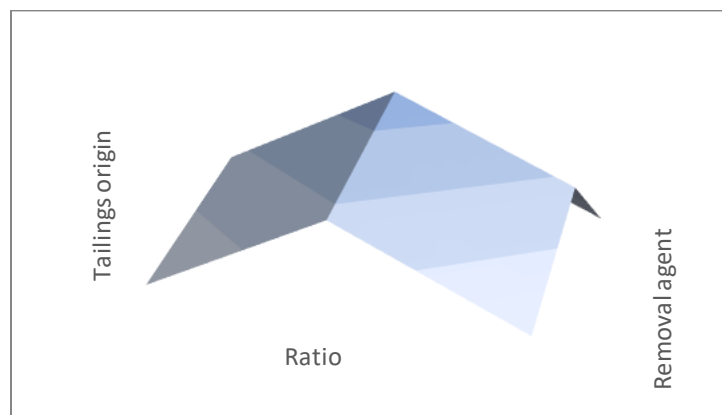


Figure 9. Experimental surface. Source: Pure Earth.

5. Hg removal laboratory tests

This section describes the pilot tests implemented to test Hg removal using the selected removal agents during a typical cyanidation process on solids with a particle diameter less than 5 mm and 22 degrees Celsius. The process begins with the preparation of the tailing's samples used as an initial reference for the Hg concentration and the removal agents used in the experiment. Figure 10 shows the flow diagram for the process leading up to Hg measurement by spectrophotometry:

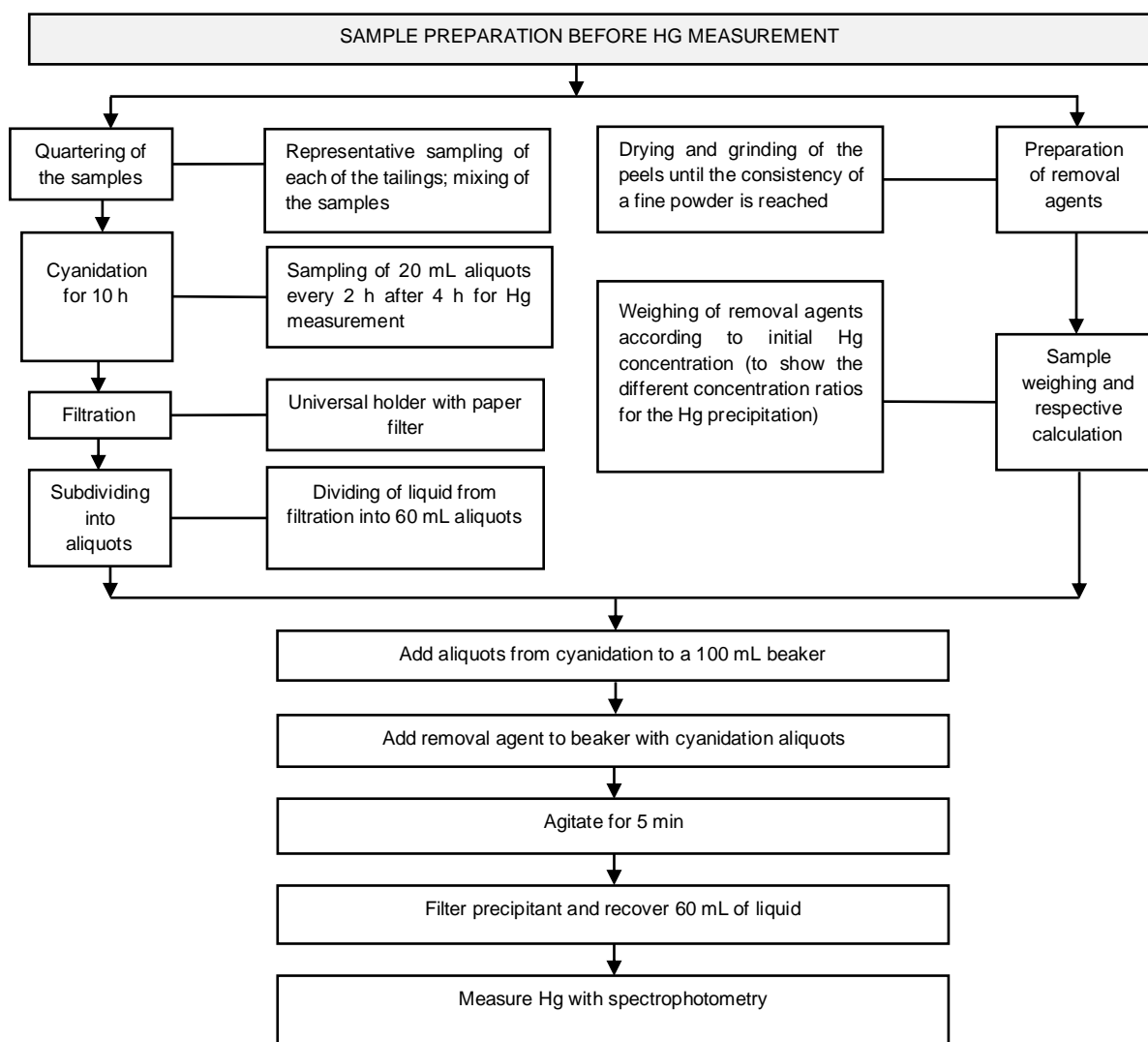


Figure 10. Sample preparation for Hg measurement.

Control parameters should be established for the cyanidation process with sodium cyanide to maintain and control its concentration throughout cyanidation, avoiding its consumption in parallel reactions that are not of interest. Table 1 shows the initial parameters before cyanidation:



Table 1. Initial control parameters for cyanidation with NaCN.

	Antioquia	Bolívar	Nariño
Date	6/4/2022	6/5/2022	6/4/2022
Cyanidation time (hr)	10	10	10
Initial sample weight (g)	603.00	613.70	575.90
Solution volume (mL)	1507.5	1534.25	1439.75
Natural pH	6.00	4.00	5.00
Added lime (g)	0.56	3.94	1.58
Initial NaCN (g)	1.5	1.53	1.44
Salts	No	No	No
G eq AgNO₃ [0.01N]-NaCN	0.000980144	0.00098014	0.00098014
Alkaline pH	10	10	10
Initial time	9:34:00 AM	8:35 AM	8:43:00 AM

These parameters are important to record so that initial conditions can be understood. Note that the natural pH is directly proportional to the lime needed to reach an alkaline pH. A pH of 10 helps maintain the sodium cyanide reaction with the gold atoms present in the solution. Another important parameter is the volume of water available for cyanidation, with an ideal ratio of 1:2.5; that is, 2.5 units of water for every sample unit.

After establishing the initial control parameters, the cyanidation process was performed. Table 2 shows the different measurements taken during cyanidation for each tailings sample:

Table 2. Cyanidation control.

Tailings	Evaluated hour	AgNO ₃ consumed (mL)	NaCN present (g)	NaCN added (g)	Accumulated NaCN consumed (g)
Antioquia	1	0.6	0.887	0.613	0.613
	2	0.7	1.034	0.466	1.079
	3	0.8	1.182	0.318	1.397
	4	1	1.478	0.022	1.420
	6	0.9	1.330	0.170	1.590
	8	0.7	1.034	0.466	2.055
	10	0.7	1.034	0.466	2.521
Bolívar	1	0.8	1.203	0.327	0.327
	2	0.7	1.053	0.477	0.804
	3	1	1.504	0.026	0.831
	4	0.8	1.203	0.327	1.158
	6	1	1.504	0.026	1.184



Tailings	Evaluated hour	AgNO ₃ consumed (mL)	NaCN present (g)	NaCN added (g)	Accumulated NaCN consumed (g)
	8	1	1.504	0.026	1.210
	10	1	1.504	0.026	1.236
Nariño	1	0.7	0.988	0.452	0.452
	2	0.6	0.847	0.593	1.045
	3	0.8	1.129	0.311	1.357
	4	0.9	1.270	0.170	1.527
	6	0.9	1.270	0.170	1.696
	8	0.9	1.270	0.170	1.866
	10	0.8	1.129	0.311	2.177

As shown by Tables 1 and 2, the cyanidation process lasted 10 h for each sample, during which a 1 mL cyanide solution aliquot was taken per h during the first 4 h and then every 2 h until the endpoint of 10 h. These aliquots were taken to conduct titrations with a standard of silver nitrate (AgNO₃) at a concentration of 0.01 N to determine the amount of sodium cyanide present in the solution. From this, the amount of initial cyanide was subtracted to calculate the sodium cyanide to be added to maintain the same concentration as the solution being used for the cyanidation process. Finally, the total consumed sodium cyanide was calculated to understand if cyanidation at scale is viable and to identify potential issues. In the cyanidation of tailings from Antioquia, Nariño, and Bolívar, the amount of sodium cyanide consumed was acceptable and was not related to sample pH but rather to other factors, such as the concentration of metallic elements that present affinity and tend to generate cyanide complexes.

a. Sample preparation

25 kg of samples were taken from each of the Nariño, Antioquia, and Bolívar tailings. Each sample was homogenized, and the cone and quarter method was used to obtain samples weighing 550–650 g. The initial Hg concentration was measured in each sample to serve as a base for later calculations of the removal or retention of Hg at the end of the process. Simultaneously, the removal agents were prepared.

b. Removal agent preparation

To perform the Hg removal tests, the removal agents were added in batches to an agitation system, where each solution obtained from the cyanidation of the tailings of different origins was agitated for 5 minutes with previously defined ratios.

The ratios were defined through findings from the literature review in which some authors such as Gabby and Elisse (2013) used Zinc sulfide (ZnS) to remove Hg present in solution



in ZnS:Hg ratios with ranges of 100, 1000, and 10000 to one. Others such as Worthington et al. (2022) used ratios on the order of thousands, and Sandberg et al. (1984) worked with ratio ranges between 8–50 parts of precipitant or adsorbent substance to dissolved Hg. Therefore, ratios of (Hg:removal agent) of 1:100, 1:1000, and 1:10000 were established to ascertain which would show the highest efficiency of Hg removal.

The initial concentrations of Hg in the tailings were between 4–17 mg/L.

For the precipitation/adsorption process, 60 mL solution samples were needed to test each removal agent. The following is an example of the equation used to calculate precipitant (removal agent) mass needed for an initial tailings concentration of 5 mg/L:

$$Hg\ mass = 5\ ppm * \left(\frac{1\ mg/L}{1\ ppm} \right) * \left(\frac{1\ L}{1000\ mL} \right) * \left(\frac{1\ g}{1000\ mg} \right) * 60\ mL = 0.0003\ g\ Hg$$

$$Precipitant\ mass\ ratio\ 1:100 = 0,0003\ g\ Hg * 100 = 0.03\ g\ precipitant$$

$$Precipitant\ mass\ ratio\ 1:1000 = 0,0003\ g\ Hg * 100 = 0.3\ g\ precipitant$$

$$Precipitant\ mass\ ratio\ 1:10000 = 0,0003\ g\ Hg * 100 = 3\ g\ precipitant$$

Using this equation, the masses for each removal agent were calculated according to the initial solution concentration.

Table 3. Concentration of initial Hg and precipitant mass by concentration ratio.

	Antioquia	Bolívar	Nariño
Initial Hg concentration (mg/L)	2.696	8.865	16.002
Removal agent mass (g) (Ratio 1:100)	0.016176	0.05319	0.096012
Removal agent mass (g) (Ratio 1:1000)	0.161760	0.53190	0.960120
Removal agent mass (g) (Ratio 1:10000)	1.617600	5.31900	9.601200

Given these calculations, the appropriate amount of removal agent was added to the test beaker and agitated for 5 minutes. The solution was then filtered, and the Hg was measured through cold vapor atomic absorption. Figure 11 shows samples of the compounds resulting from this step.



Figure 11. Samples of Hg removal compounds.

c. Hg measurement

After implementing the process of Hg removal for each variable, samples of the resulting solution were prepared to determine the final concentration of Hg by way of spectrophotometer analysis through cold vapor atomic absorption. Figure 12 shows the flow diagram visualizing the process of Hg measurement to compare the initial Hg concentration (after 10 h of cyanidation) and the final concentration (after removal processes). In this way, the best removal agents could be determined.

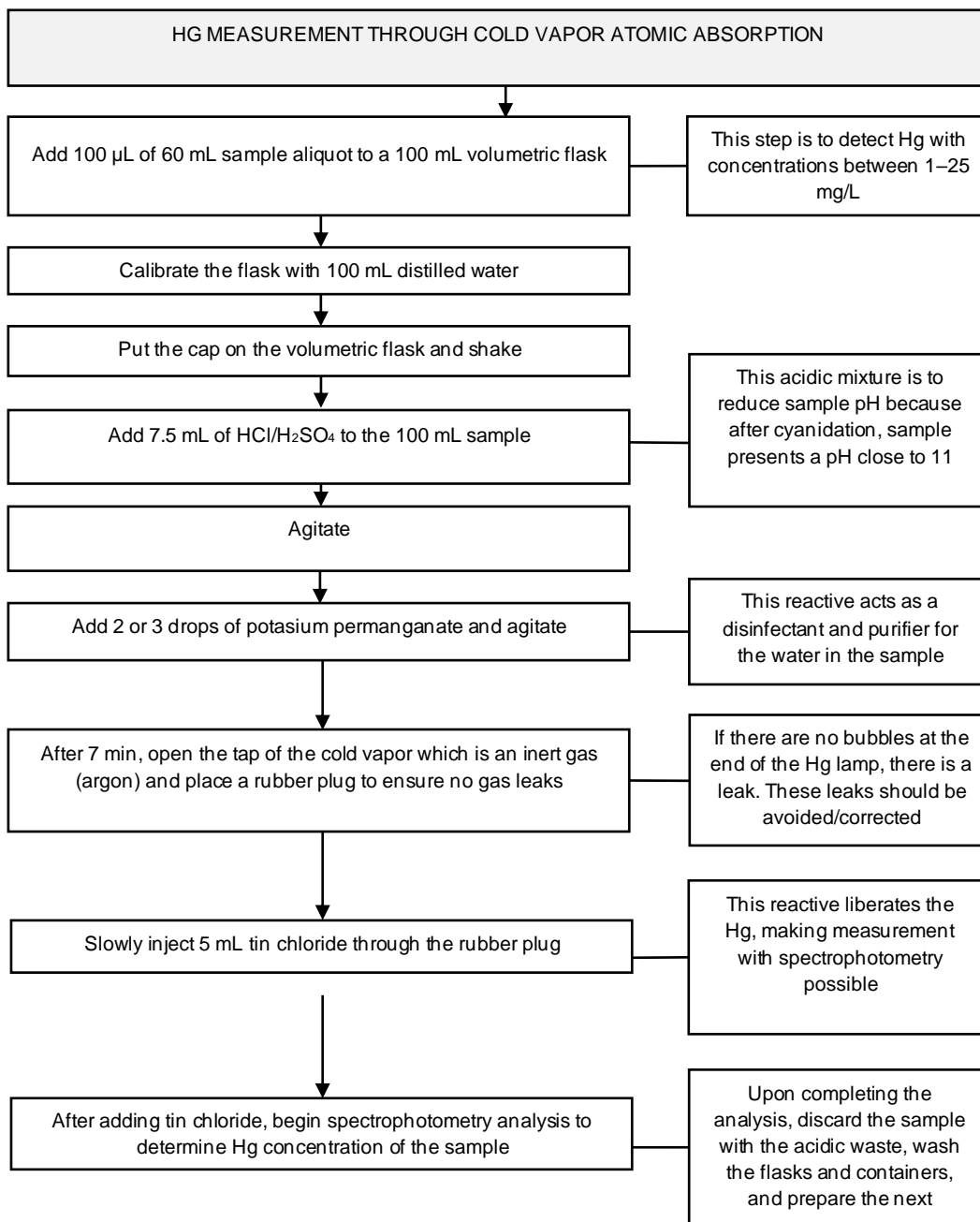


Figure 12. Flow diagram for Hg measurement by spectrophotometry.

Figure 13 shows the precipitated samples ready for the cold vapor atomic absorption analysis. Figure 14 shows the samples to be measured for Hg concentrations.



Figure 13. Cyanidation solutions after removal tests.



Figure 14. Sample preparation for atomic absorption spectrophotometry reading.

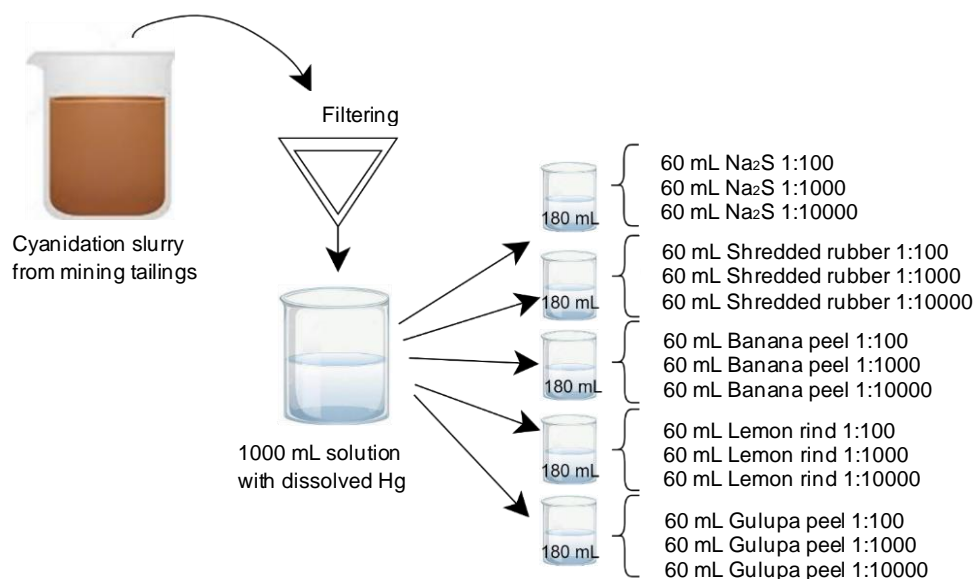
Figure 15 shows the set-up for Hg concentration readings of the precipitated samples through cold vapor atomic absorption spectrophotometry. This consists of a tin chloride injection which liberates the Hg vapor and directs it towards a spectrophotometry Hg lamp with the help of an inert gas, argon in this case. After the reading, the Hg is again diluted in a solution that contains potassium permanganate.



Figure 15. Hg readings through cold vapor atomic absorption.

Figure 16 shows a representation of the experimental phase of the project, beginning with the separation of the liquids from the solids in the cyanidation slurry for the later precipitation and determination of the final Hg concentration in the solution. (The separation of liquids and solids in the slurry is necessary because cold vapor spectrophotometry only allows for liquid samples. The presence of solids during analysis may generate an obstruction of the equipment that would not allow a reading and could even damage the equipment.) 60 mL of solution was taken for each of the 45 samples and divided into 30 mL, with the aim to measure the replicate of each sample, for a total of 90 samples. Each sample was tested with a removal agent during 5 minutes of agitation at 350 rpm and was then measured for Hg with spectrophotometry.

Using the initial Hg concentration measurements and the final Hg concentration measurements after cyanidation, a difference of concentrations was determined which reflects the amount of Hg removed by the applied agent. These results will be reported and analyzed in the following sections of the report.



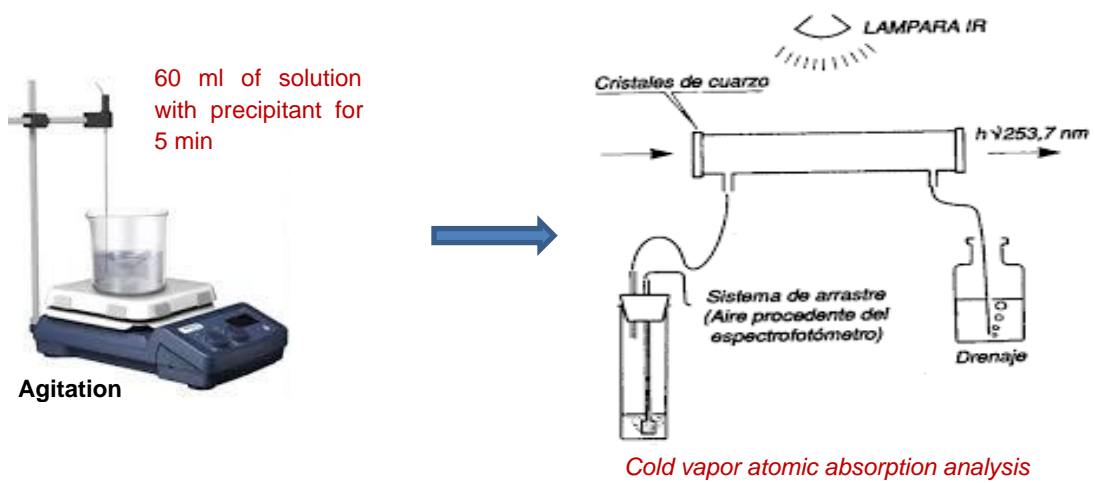


Figure 16. Representation of the Hg removal experimental procedure.



6. Results

To determine the efficiency of Hg removal for each variable, the initial Hg concentration of the samples was measured after 10 hours of cyanidation. Table 4 shows the results:

Table 4. Hg concentration before the precipitations.

	TAILINGS		
	Antioquia	Bolívar	Nariño
Initial Hg concentration (mg/L)	2.696	8.865	16.002

Using the Hg concentrations in Table 4, the removal agent mass was calculated for each ratio (Hg:removal agent of 1:100, 1:1000, and 1:10000). Table 5 shows the results.

Table 5. Removal agent mass required per initial Hg concentration.

Tailings \ Removal agent mass (g)	Antioquia	Bolívar	Nariño
Ratio 1:100	0.016176	0.05319	0.096012
Ratio 1:1000	0.161760	0.53190	0.960120
Ratio 1:10000	1.617600	5.31900	9.601200

Note: The results are shown to 6 decimals due to the use of a precision scale which displayed measurements up to 6 decimals.

Using the data from Tables 4 and 5, the appropriate amount of removal agent was used per ratio and per tailings origin. Table 6 shows the results of the final Hg measurements upon conclusion of the experiment.

Table 6. Final Hg concentrations in the samples.

Removal agent ratio	Concentration # measurement (mg Hg/L)	Tailings								
		Antioquia			Bolívar			Nariño		
		1:100	1:1000	1:10000	1:100	1:1000	1:10000	1:100	1:1000	1:10000
Shredded tire	1	2.5135	2.6724	1.8209	14.1708	7.7717	10.6759	13.8055	16.8685	17.6223
	2	2.4026	3.1681	2.2215	12.2939	10.2363	9.8869	16.3898	16.7231	17.0500
Lemon rind	1	4.0864	5.5770	3.3249	9.7165	7.7028	6.6564	13.4475	14.8800	10.1013
	2	5.6226	4.7217	3.3526	8.4809	6.7367	4.9232	12.6995	14.0303	9.0338
Gulupa peel	1	4.6558	4.4330	3.5820	7.2288	6.5375	16.5972	15.7174	15.5262	13.0818
	2	4.4340	5.3029	3.0913	7.8050	2.4339	4.4582	15.2522	14.2153	14.0707
Banana peel	1	1.9634	2.1638	2.3770	9.2860	10.0630	6.9033	15.2790	16.4156	14.4971
	2	0.6667	2.3539	2.4459	10.2669	4.4511	5.1502	15.7131	17.4006	15.0109
Sodium sulfide	1	1.6544	1.2337	2.2073	12.9052	11.9410	12.7924	3.9056	11.6440	0.7439
	2	1.4655	0.8896	1.2851	12.2559	11.1981	13.4376	3.7801	12.6181	3.1353



Note: The results given by the spectrophotometer have a precision of up to 6 digits. Nevertheless, this report shortens the measurements to 4 digits.

In Table 6, two measurements per box are shown, representing the initial measurement and its respective replicate. In total, there are 90 datapoints, of which 45 correspond to the experimental model 5 x 3 x 3 and the other 45 are the replicate of each measurement. To better visualize the results from Table 6, Figure 17 shows the average of both the initial measurement and its respective replicate.

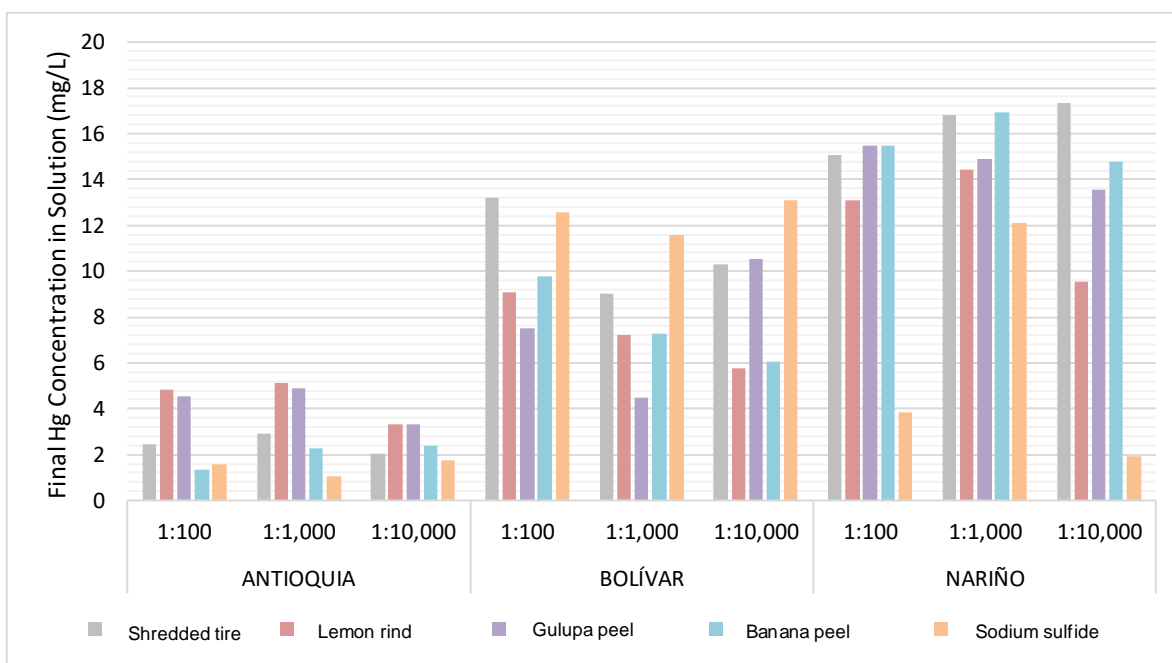


Figure 17. Final Hg concentration after removal process by tailings origin.

Figure 17 shows that, in the case of Antioquia and Nariño, sodium sulfide (Na_2S) is the agent that removed the highest amount of Hg. Within the Na_2S results, in Antioquia, greater Hg removal was achieved with a ratio of 1:1000 (Hg:removal agent) while in Nariño, the greatest effectivity of Na_2S occurred at 1:10000. In Bolívar, the two removal agents removing the highest quantity of Hg were the *gulupa* peel at a ratio of 1:1000 and the banana peel at a ratio of 1:10000. In all three tailings origins, the shredded tire tended to exhibit low Hg removal in any ratio compared to the initial concentrations found in Table 2.

There was not a significant difference between the ratios 1:1000 and 1:10000. These datapoints can be seen in further detail in Annex 1.

The results of the ANOVA analysis showed that each of the three variables studied (tailings origin, type of removal agent, Hg:removal agent ratio) had a direct influence on the results. The only interaction between variables that did not generate an effect on the results is that



between the type of removal agent and the Hg:removal agent ratio, as explained in Annex 1. Annex 2 explains the ANOVA development process from theory to results for this report.

Initial Hg concentrations and final Hg concentrations were used to calculate the percentage of Hg removal per removal agent, ratio, and tailings origin, as show in Table 7.

Table 7. Hg removal percentages.

Tailings	Concentration ratio Removal agent # measurement		Ratio of Hg concentration: removal agent			greatest %	Best performing ratio
			1:100	1:1000	1:10000		
Antioquia	Shredded tire	1	6.77%	0.87%	32.46%	32%	1:10000
		2	10.88%	IR	17.60%		
	Lemon rind	1	IR	IR	IR	IR	1:10000
		2	IR	IR	IR		
	Gulupa peel	1	IR	IR	IR	IR	1:10000 replicate
2		IR	IR	IR			
Banana peel	1	27.18%	19.74%	11.83%	75%	1:100 replicate	
	2	75.27%	12.69%	9.28%			
Sodium sulfide	1	38.63%	54.24%	18.13%	67%	1:1000 replicate	
	2	45.64%	67.00%	52.33%			
Bolívar	Shredded tire	1	IR	12.33%	IR	12%	1:1000
		2	IR	IR	IR		
	Lemon rind	1	IR	13.11%	24.91%	44%	1:10000 replicate
		2	4.33%	24.01%	44.47%		
	Gulupa peel	1	18.46%	26.25%	PN	73%	1:1000 replicate
2		11.96%	72.54%	49.71%			
Banana peel	1	IR	IR	22.13%	50%	1:1000 replicate	
	2	IR	49.79%	41.90%			
Sodium sulfide	1	IR	IR	IR	IR	1:1000 replicate	
	2	IR	IR	IR			
Nariño	Shredded tire	1	13.73%	IR	IR	14%	1:100
		2	IR	IR	IR		
	Lemon rind	1	15.96%	7.01%	36.87%	44%	1:10000 replicate
		2	20.64%	12.32%	43.55%		
	Gulupa peel	1	1.78%	2.97%	18.25%	18%	1:10000
2		4.69%	11.17%	12.07%			
Banana peel	1	4.52%	IR	9.40%	9%	1:10000	
	2	1.81%	-8.74%	6.19%			
Sodium sulfide	1	75.59%	27.23%	95.35%	95%	1:10000	
	2	76.38%	21.15%	80.41%			

Note: IR: Invalid results by error on equipment measure

Table 7 shows that the ratio of Hg:removal agent with the highest percentage of Hg removal was 1:10000. The removal agent that performed the best per tailings origin was the banana peel in Antioquia, the *gulupa* peel in Bolívar, and Na₂S in Nariño. Material differences in chemical and mineralogical composition of the tailings could explain the difference in removal agents results among the tailings. Moreover, in Antioquia, there was a negative



efficiency in the use of the *gulupa* peel and lemon rind and in Bolívar, a negative efficiency in the use of Na_2S . These differences could be explained by the different conditions in which the fruits are cultivated, which could vary in contamination levels due to Hg vapors found in the environment.

Figure 18 below shows the Hg removal percentages per removal agent, tailings origin, and ratio, using the highest percentage of removal among the different measurements.

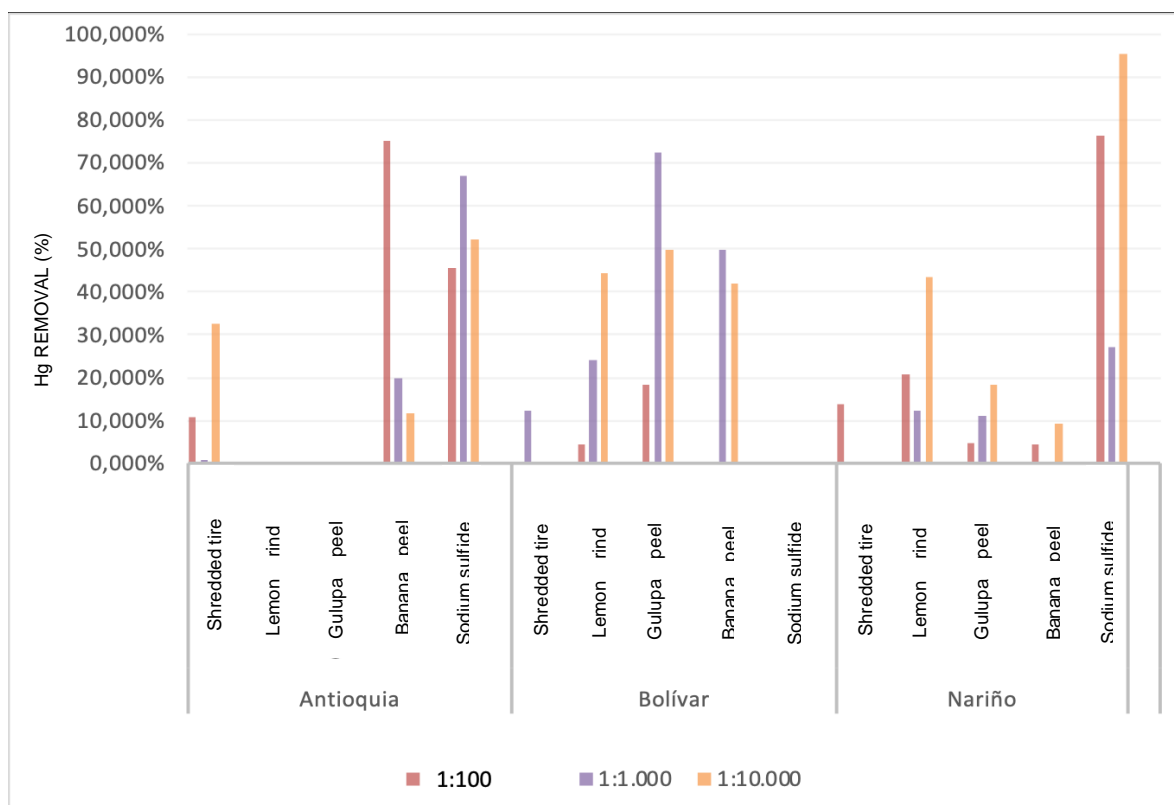


Figure 18. Hg removal percentages per removal agent (Hg: removal agent).

As can be seen in Figure 18, the highest Hg removal was achieved with the removal agent Na_2S using a ratio of 1:10000 in Nariño, which reduced Hg by 88%. Na_2S also displayed a high percentage of Hg removal at 61% when used in the ratio 1:1000 in tailings from Antioquia. For the Antioquia tailings, the removal agent with the best performance was the banana peel which reduced Hg by 51.23% when used at a ratio of 1:100. For the Bolívar tailings, the second-best performance after the *gulupa* peel was the lemon rind, reaching a 35% reduction in Hg at a ratio of 1:10000. Shredded rubber in all tailings origins showed a low performance with a maximum removal average of 25% in the Antioquia tailings with a ratio of 1:10000.

Figure 19 shows the Hg removal percentages by tailings origin and removal agent.

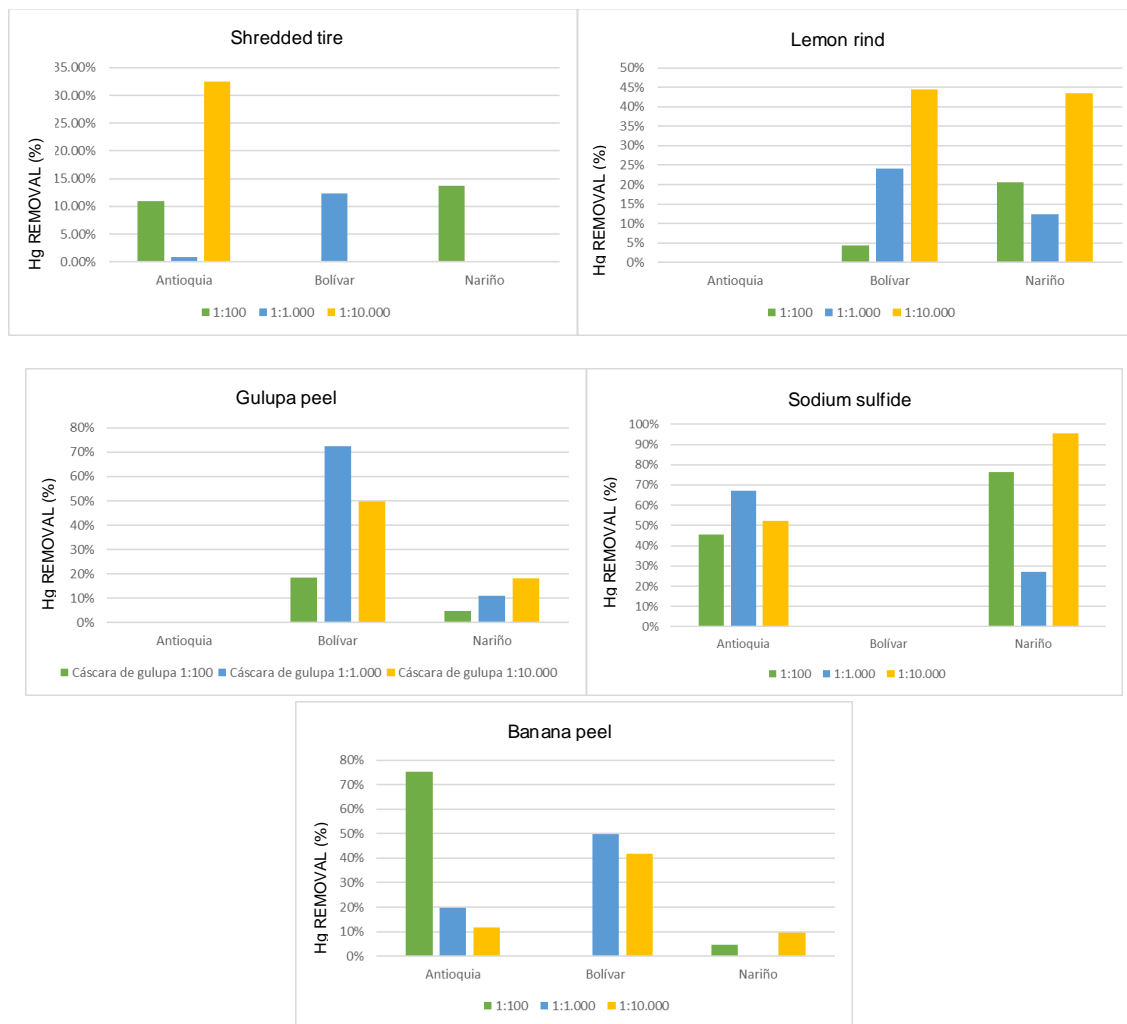


Figure 19. Hg removal percentages vs removal agents.

There is no consistent behavior pattern for each removal agent with the type of tailings used. Perhaps the agitation to which the samples were subjected was not sufficient to surface the mercury oxide, which reduced its chances to react with the cyanide. Oxides tend to reduce the amount of Hg removed. Future studies could investigate increasing agitation to eliminate a greater number of these oxides.



7. Conclusions

The highest percentage of Hg removal in the experiment was 95%, achieved with the use of Na_2S in the Hg:removal agent ratio of 1:10000 in tailings from Nariño. This percentage is consistent with observations by Sandberg et al. (1984) in which 99.9% precipitation was reached with Na_2S . Nevertheless, it is worth mentioning that the results were perhaps influenced by the presence of mercury oxide which, when subject to agitation that is not adequate (either in time or in revolutions), can inhibit the reaction between Hg and cyanide.

Though the shredded tire did not show good performance compared to that of other compounds, it is worth evaluating its performance by a filtration method in which Hg solution is passed through a funnel with the material, as was performed by Gabby and Eisele (2013) with zinc sulfide.

The removal of Hg in whichever form (precipitation, adsorption, and bioadsorption) with the use of absorbent materials (removal agents) proves to be a complementary technique to copper plates to reduce the quantity of Hg released into the environment during ASGM processes. The use of these materials also promotes the reuse of waste materials leading to the development of a circular economy.

Due to high availability and low cost, the research and implementation of the removal agents studied in this experiment for the removal of Hg are an accessible alternative for ASGM miners, mine owners, and people who reprocess tailings.



8. Recommendations

Future studies should seek to perform the experimental phase in a laboratory with greater airtightness and inoculation. In this experiment, performing the tests directly in the processing plant with uncontrolled conditions potentially affected the results.

The method of cold vapor spectrophotometry measures Hg on the order of parts per billion (ppb), which presents a high sensitivity in the results especially in regards to the effects of change in pressure and temperature that affects spectrophotometer absorbancy. Therefore, one recommendation is to implement a ventilation system to maintain constant ambient conditions. Additionally, synthetic samples may permit better control over the initial Hg concentration.

Measurement outcomes can be affected by many variables, including human error, changes in the laboratory environment, and measurement precision. Controlling these variables as much as possible reduces uncertainty, resulting in more precise and true results.

Future studies are recommended to test different treatments of the bioadsorbent materials (lemon rind, banana and *gulupa* peel) through variation in drying times and temperatures, the grinding method, and other variables that could have an effect on the process of Hg removal from cyanide solutions. In addition, future studies are recommended to test other materials mentioned in the literature section, giving a clearer panorama of the efficiency of Hg removal with regards to different materials.

In future experiments, the gold in the tailings could be tested before and after the Hg removal tests to determine whether these materials have a direct effect on the gold particles dissolved in the cyanide solution.

A final recommendation is to conduct an evaluation of the costs associated with implementing these processes in real life to assess financial viability and technical feasibility for the miners. In addition, the costs of the disposal and transportation of the process residues should be considered as an important factor.



9. Glossary

Amalgam

Alloy of mercury with one or more metals such as gold, silver, etc.; generally solid or almost liquid (RAE, 2022).

Amalgamation

Concentration procedure in which native metals separate from non-metallic gangue minerals through selective wetting of metallic surfaces by mercury (Technical Mining Glossary, 2003).

Cyanicides

Metallic minerals (marcasite, pyrrhotite, copper minerals, arsenopyrite) and heavy metals (mercury, arsenic, among others) associated with source minerals of precious metals that can easily dissolve in cyanide solutions, and that consume cyanide, impeding its contact with gold and silver. They are responsible for imparting refractory characteristics to precious metal ores (Technical Mining Glossary, 2003).

Cyanide (CN⁻)

Chemical compound widely used in gold mineral processing plants to dissolve gold and silver (Technical Mining Glossary, 2003).

Cyanidation

Method to extract gold and silver from shredded or ground mineral through dissolution in a sodium cyanide or potassium cyanide solution (Technical Mining Glossary, 2003).

Tailings (*cola/relave*)

Tailings are the material generally containing little valuable metal that remains after leaching and mineral concentration processes. They can be newly treated or discarded (Technical Mining Glossary, 2003).

Mercury compounds

All substances that consist of mercury atoms and one or more atoms of other elements that can be separated into different compounds only by way of chemical reactions: mercury (I) chloride or calomel, mercury (II) oxide, mercury (II) sulfate, mercury (II) nitrate, cinnabar, and mercury sulfide (Minamata Convention) (Technical Mining Glossary, 2003).

Mercury waste

Substances or objects that: a) consist of mercury or mercury compounds; b) contain mercury or mercury compounds; or c) are contaminated with mercury or mercury compounds, in a quantity that exceeds limits as defined by the Conference of the Parties in collaboration with



the pertinent bodies of the Basil Convention to be phased out, proposed to be phased out, or is required to be phased out in a harmonized manner under national law or the Minamata Convention (Technical Mining Glossary, 2003).

Mercury

Metallic element; atomic number 80; liquid; shiny white and silver; very heavy; toxic; bad heat conductor; very good electricity conductor; not common in the earth's core; used in the fabrication of pesticides, technical and scientific instruments, mirrors, and gold and silver alloys used in odontology and medicine (RAE, 2022).

Artisanal and small-scale mining (ASM)

Formal or informal mining exploration, processing, and transportation operations. ASM is generally characterized by the use of low capital but high-intensive labor (EITI, 2022).

Observation

In experimental design, this is a measurement of the conditions determined for one of the treatments.

Tailings dumping site (*relavera*)

Bearing in mind that as of now no legal definition exists for the word "*relavera*", the following definitions were used for this document: 1) Depression used to confine tailings resulting from processing; 2) Area whose lower limit corresponds to a wall or retaining wall where processing effluents circulate, whose primary function is to allow enough time so that the sands and heavy metals settle or for the cyanide to be destroyed before the "clear" water is discharged or reused (Technical Mining Glossary, 2003).

Risk

Probability or possibility that the management of, release to the environment of, and exposure to a material or waste can cause adverse effects on human health and/or the environment (Technical Mining Glossary, 2003).

Sites contaminated by mercury

Contaminated sites, according to Article 12 of the Minamata Convention, are considered those areas that are contaminated with mercury or mercury compounds and could generate harm to human health or the environment (Technical Mining Glossary, 2003).



References

- Rocha, M., Paz, I., & Tejada, C. (2018). Empleo de residuos de Gulupa (*Passiflora edulis* f. *edulis*) para la bioadsorción de mercurio de aguas sintéticas a concentraciones equivalentes a las generadas por la explotación aurífera. *RUMBO* 20.30. CONAMAR, 1-11. Retrieved from <http://www.conama.org/conama/download/files/conama2018/CT%202018/222224321.pdf>
- UTADEO. (2017, 11 02). *Investigación tadeísta sobre reutilización del caucho de las llantas es protagonista en sección de Ciencia de El Tiempo*. Retrieved from <https://www.utadeo.edu.co/es/noticia/utadeo-en-los-medios/home/1/investigacion-tadeista-sobre-reutilizacion-del-caucho-de-las-llantas-es-protagonista-en-seccion-de>
- Semana. (2018, 07 24). *Así se distribuye el mercurio legal en nuestro país*. Retrieved from Legalidad: <https://www.semana.com/contenidos-editoriales/colombia-sin-mercurio/articulo/asi-se-distribuye-el-mercurio-legal-en-nuestro-pais/576622/#:~:text=El%20precio%20por%20kilo%20del,los%20150.000%20y%20600.000%20pesos>.
- González, M., Bodas, A., Rubio, M., Martell, N., Trasobares, E., Ordóñez, J., . . . Torres, M. (2014). Efectos sobre la salud del metilmercurio en niños y adultos; estudios nacionales e internacionales. *Nutrición Hospitalaria*, 989-1007. Retrieved from <https://scielo.isciii.es/pdf/nh/v30n5/03revision02.pdf>
- Lara, A. (2021). *Diseño Estadístico de Experimentos*. España: Universidad de Granada.
- Misra, M., Lorengo, J., Nanor, J., & Bucknam, C. (1998). Removal of mercury cyanide species from solutions using dimethyl dithiocarbamates. *Minerals & Metallurgical Processing*, 60-64.
- Allen, J., & Misra, M. (1996). *The removal of mercury from cyanide leach solutions using potassium dimethyl dithiocarbamate*. Virginia: University of Nevada.
- Espinoza, J., & Marshall, R. (2016). *Evaluación del poder bioabsorbente de las cáscaras de cítricos "limón y toronja" para la eliminación de metales pesados; Plomo (Pb) y Mercurio (Hg) en aguas residuales sintéticas*. Guayaquil, Ecuador: Universidad de Guayaquil, Facultad de Ingeniería Química. Retrieved from <http://repositorio.ug.edu.ec/handle/redug/18100>
- Salinas, E., Rivera, I., Carrillo, R., Patiño, F., Hernández, J., & Hernández, L. (2004). Mejora del proceso de cianuración de oro y plata, mediante la preoxidación de minerales sulfurados con ozono. *Revista de la Sociedad Química de México*.



- Stapper et al, D. (2021). *Best Management Practices for Cyanide Use in the Small- Scale Gold Mining Sector*.
- Kantarci, S., & ALP, I. (2019). Removal of mercury from cyanide solution. *Karadeniz Chemical Science and Technology*(4), XX-XX. Retrieved from <https://dergipark.org.tr/tr/download/article-file/913887>
- Marshall, B., Veiga, M., da Silva, H., & Davée, J. (2020). Cyanide Contamination of the Puyango-Tumbes River Caused by Artisanal Gold Mining in Portovelo-Zaruma, Ecuador. *Current Environmental Health Reports*(7), 303-310. doi:<https://doi.org/10.1007/s40572-020-00276-3>
- David. (2017, 03 18). *911 Metallurgist*. Retrieved from <https://www.911metallurgist.com/metallurgia/cianuracion-oro-plata/>
- Dzombak, D., Ghosh, R., & Wong-Chong, G. (2005). *Cyanide in water and soil: chemistry, risk and management*. Boca Raton: CRC Press: Taylor and Press Group. Retrieved from <https://www.taylorfrancis.com/books/edit/10.1201/9781420032079/cyanide-water-soil-david-dzombak-rajat-ghosh-george-wong-chong>
- Velásquez-López, P., Veiga, M., Klein, B., Shandro, J., & Hall, K. (2011). Cyanidation of mercury-rich tailings iun artisanal and small-scale gold mining: identifying strategies to manage environmental risk in Southern Ecuador. *Cleaner Production*, 19, 1125-1133. doi:<https://doi.org/10.1016/j.jclepro.2010.09.008>
- Aliprandini, P., Veiga, M., Marshall, B., Scarazzato, T., & Espinosa, D. (2020). Investigation of mercury cyanide adsorption from synthetic wastewater aqueous solution on granular activated carbon. *J Water Process Eng*, 34, 1-6. doi:<https://doi.org/10.1016/j.jwpe.2020.101154>
- Adams, M. (1991). The mechanisms of adsorption of Hg(CN)₂ and Hg(Cl)₂ on to activated carbon. *Hydrometallurgy*, 26(2), 201-210. doi:[https://doi.org/10.1016/0304-386X\(91\)90031-G](https://doi.org/10.1016/0304-386X(91)90031-G)
- Flynn, C., & McGill, H. (1995). *Cyanide chemistry - precious metals processing and waste treatment. Information Circular 9429*. United States Department of the Interior, United States Bureau of Mines.
- Aylett, B. (1973). Mercury (II) Pseudohalides: Cyanide, Thiocyanate, Selenocyanate, Azide, Fulminate. *Comprehensive Inorganic Chemistry*(3), 304-306.



Rodríguez Parra, M. X., Jiménez Villamarín, J. E., & Carvajal Rico, K. R. (2017). *Estudios comparativos de mezclas asfálticas aplicando el método Mashall con la adición de ceniza de cascarilla de arroz caucho triturado con los agregados de los ríos Magdalena Cucuana y Saldaña*. Universidad Piloto de Colombia.

Boniolo, M. (2008). *Biossorção de urânio nas cascas de banana*. En : *Disertación de Maestría, Instituto de Pesquisas Energéticas e Nucleares*. Universidad de São Paulo.

Muñoz Echeverri, L., Imbachí Narváez, P., Ospina Arbeláez, L., Quiceno Rico, J., Cardona Bermúdez, L., Gómez, D., . . . Ar. (2016). *Antocianinas a partir de subproductos de gulupa : extractos y usos*. Sena.



Annex 1. Statistical analysis method ANOVA

To use ANOVA, the following calculations were made: sum of the squares, degrees of freedom, mean squares, F statistic, and F critical value; all with a confidence interval of 0.05. The following section describes the theory and application of these variables within the present experimental design.

Sum of squares (SC)

The sum of squares should be calculated for the effects of each variable and the interactions between variables. That is, the effect of A, B, and C should be calculated as well as the interactions AB, AC, BC, and ABC. The error and total sum of squares should also be calculated.

$$SCA = \sum_{i=1}^a \frac{Y_{i...}^2}{bcn} - \frac{Y_{....}^2}{N}; \quad SCB = \sum_{j=1}^b \frac{Y_{.j..}^2}{acn} - \frac{Y_{....}^2}{N}; \quad SCC = \sum_{k=1}^c \frac{Y_{..k.}^2}{abn} - \frac{Y_{....}^2}{N}$$

$$SCAB = \sum_{i=1}^a \sum_{j=1}^b \frac{Y_{ij..}^2}{cn} - \frac{Y_{....}^2}{N} - SCA - SCB$$

$$SCAC = \sum_{i=1}^a \sum_{k=1}^c \frac{Y_{i.k.}^2}{bn} - \frac{Y_{....}^2}{N} - SCA - SCC$$

$$SCBC = \sum_{j=1}^b \sum_{k=1}^c \frac{Y_{.jk.}^2}{an} - \frac{Y_{....}^2}{N} - SCB - SCC$$

$$SCT = \sum_{i=1}^a \sum_{j=1}^b \sum_{k=1}^c \sum_{l=1}^n Y_{ijkl}^2 - \frac{Y_{....}^2}{N}$$

$$SC \text{ ERROR} = SC \text{ TOTAL} - SCA - SCB - SCC - SCAB - SCAC - SCBC$$

Where:

- a: number of levels in a.
- b: number of levels in b.
- c: number of levels in c.
- n: number of replicates.
- N: total number of observations.



Degrees of freedom (GL)

The degrees of freedom should be calculated for each effect and interaction:

$$GL A = a - 1 ; GL B = b - 1 ; GL C = c - 1$$

$$GL AB = (a - 1)(b - 1) ; GL AC = (a - 1)(c - 1) ; GL BC = (b - 1)(c - 1)$$

$$GL ABC = (a - 1)(b - 1)(c - 1) ; GL Error = abc(n - 1) ; GL Total = abc n - 1$$

Mean squares (CM)

To calculate the mean squares, we use the following equations:

$$CMA = \frac{SCA}{GL A} ; CMB = \frac{SCB}{GL B} ; CMC = \frac{SCC}{GL C}$$

$$CMAB = \frac{SCAB}{GL AB} ; CMAC = \frac{SCAC}{GL AC} ; CMBC = \frac{SCBC}{GL BC}$$

$$CMABC = \frac{SCABC}{GL ABC} ; CM ERROR = \frac{SC ERROR}{GL ERROR}$$

To calculate the mean squares in this case, it is not necessary to calculate the total mean squares because this number is not required for posterior calculations.

F statistic (Fo)

To calculate the F statistic, the following equations were used:

$$Fo A = \frac{CMA}{CM ERROR} ; Fo B = \frac{CMB}{CM ERROR} ; Fo C = \frac{CMC}{CM ERROR}$$

$$Fo AB = \frac{CMAB}{CM ERROR} ; Fo AC = \frac{CMAC}{CM ERROR} ; Fo BC = \frac{CMBC}{CM ERROR}$$

$$Fo ABC = \frac{CMABC}{CM ERROR}$$

F critical value (critical F)

The F critical value was calculated using a function in Excel where the entered datapoints were the confidence interval ($\alpha = 0.05$), the degrees of freedom and each effect, and the degrees of freedom of the error. The importance of calculating the F statistic and F critical values is outlined below.

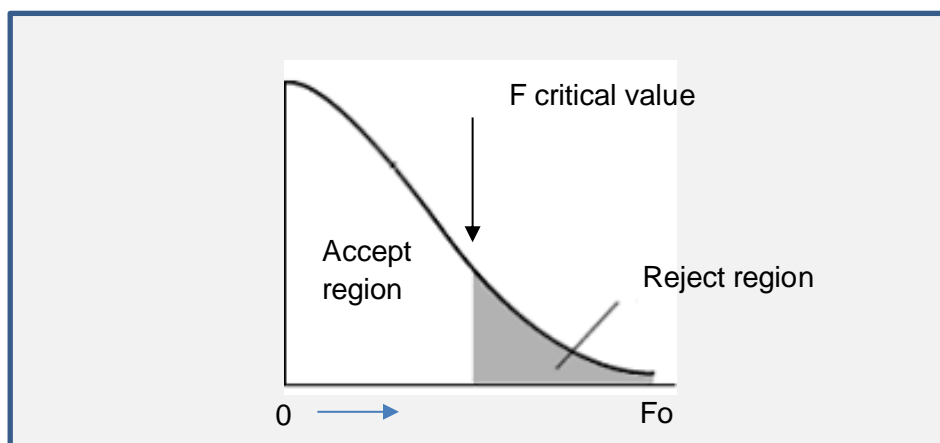


Figure 19. Gaussian curve with test statistic.

When the F statistic is great than the F critical value, this means that the curve is in the reject zone, and the null hypothesis can be rejected, meaning there was an effect between the variable and the results.

ANOVA application for Hg precipitation tests

The results of the experiment are shown in Table 8:

Table 8. Experimental results.

	A1			A2			A3		
	B1	B2	B3	B1	B2	B3	B1	B2	B3
C1	2.513546	2.672447	1.820876	14.1708	7.771679	10.675888	13.805546	16.868484	17.622347
	2.402636	3.168104	2.221522	12.293889	10.236323	9.886889	16.389768	16.723056	17.05
C2	4.086398	5.576971	3.324916	9.716513	7.702789	6.656445	13.447515	14.880041	10.101319
	5.622644	4.721731	3.35258	8.480936	6.736692	4.923173	12.699457	14.030334	9.03379
C3	4.655807	4.433028	3.581972	7.228791	6.537496	16.597205	15.71737	15.526222	13.081843
	4.433986	5.30289	3.091326	7.804977	2.433933	4.458214	15.252156	14.215278	14.070739
C4	1.963353	2.163839	2.376983	9.285952	10.062995	6.903286	15.278986	16.415634	14.497137
	0.666663	2.353903	2.445904	10.266931	4.451145	5.150161	15.713096	17.400586	15.010892
C5	1.65441	1.233667	2.207346	12.905181	11.94103	12.792416	3.905596	11.64398	0.743928
	1.465511	0.889606	1.285074	12.255948	11.198128	13.437577	3.780103	12.618119	3.135294

Table 9 shows the values used for the ANOVA test:



Table 9. ANOVA results.

FV	SC	GL	CM	Fo	Critical F
Effect A	1558.30048	2	779.150239	286.358969	3.20431729
Effect B	19.2128013	2	9.60640063	3.53061431	3.20431729
Effect C	103.022599	4	25.7556498	9.46590396	2.57873918
Effect AB	82.609091	4	20.6522727	7.59027365	2.57873918
Effect AC	499.336425	8	62.4170531	22.9399698	2.15213288
Effect BC	46.5821324	8	5.82276655	2.14002556	2.15213288
Effect ABC	101.002374	16	6.31264837	2.32007049	1.87396762
Error	122.43989	45	2.72088645	-	-
Total	2532.50579	89	-	-	-

According to the previously explained theory, to understand the influence of each variable and interactions between variables, the values of the last two columns of the table corresponding to the F statistic and the F critical value need to be verified. All variables and their interactions exceed the F critical value except for effect BC; that is, there is not a significant influence between the removal agent and the ratios. Nevertheless, that the rest of the null hypotheses are rejected means that the three factors, corresponding to the ratio of Hg:removal agent, tailings origin, and removal agent type, influenced the experiment results.



Annex 2. Supplementary figures

Figures 21–23 show Hg removal per tailings origin, comparing the Hg:removal agent ratio to the removal agent type.

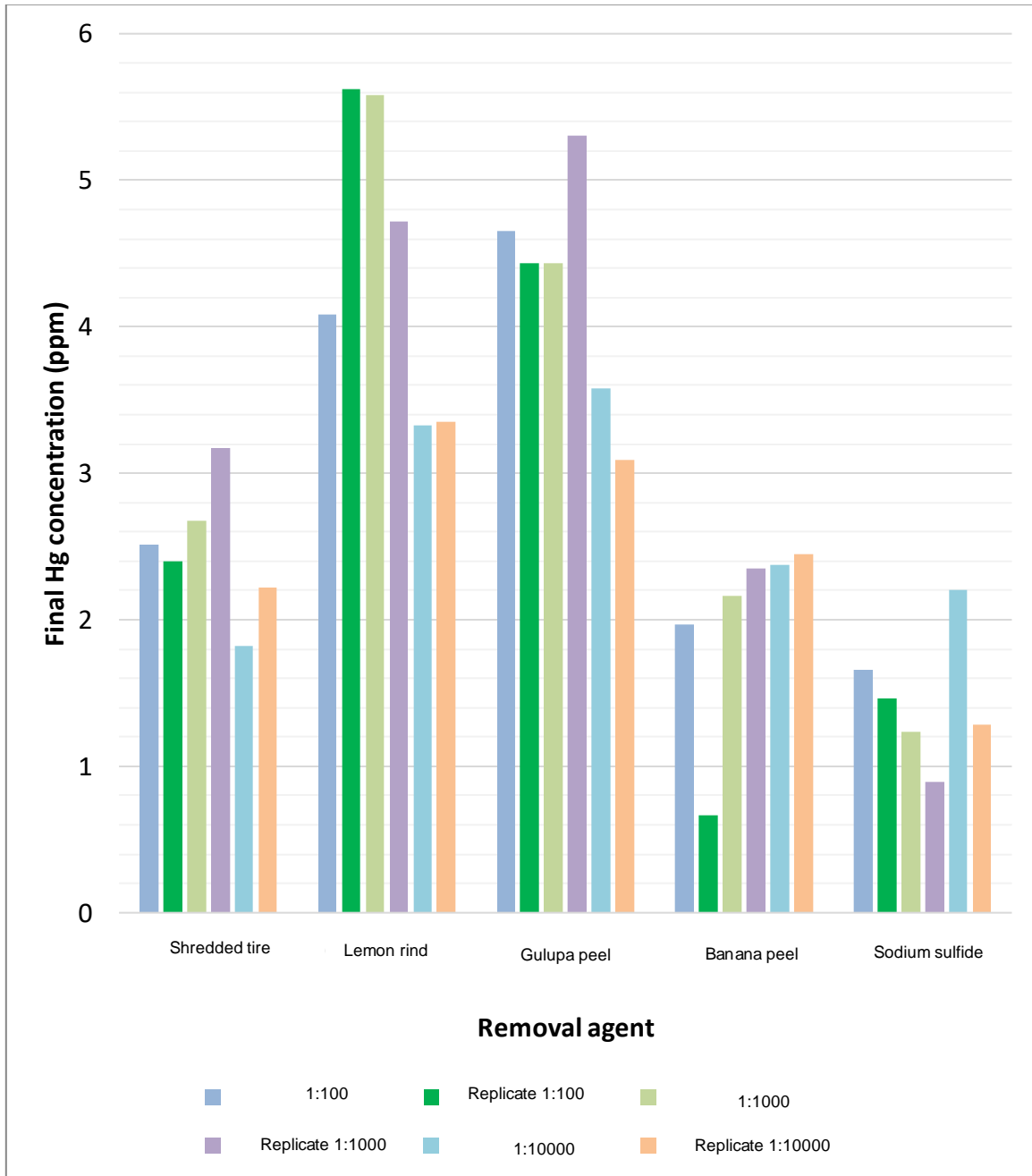


Figure 20. Hg removal in samples from Antioquia.

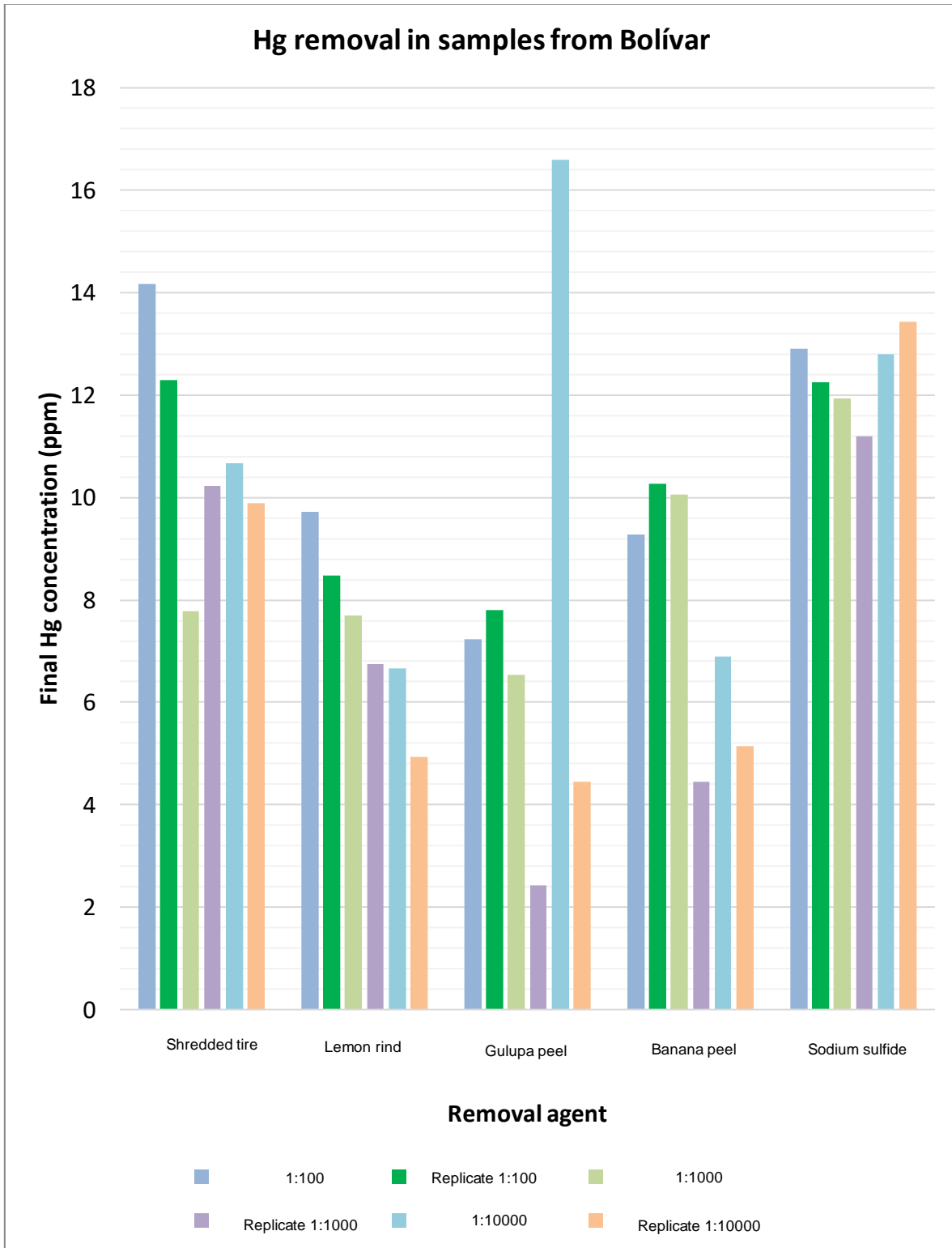


Figure 21. Hg removal in samples from Bolívar.

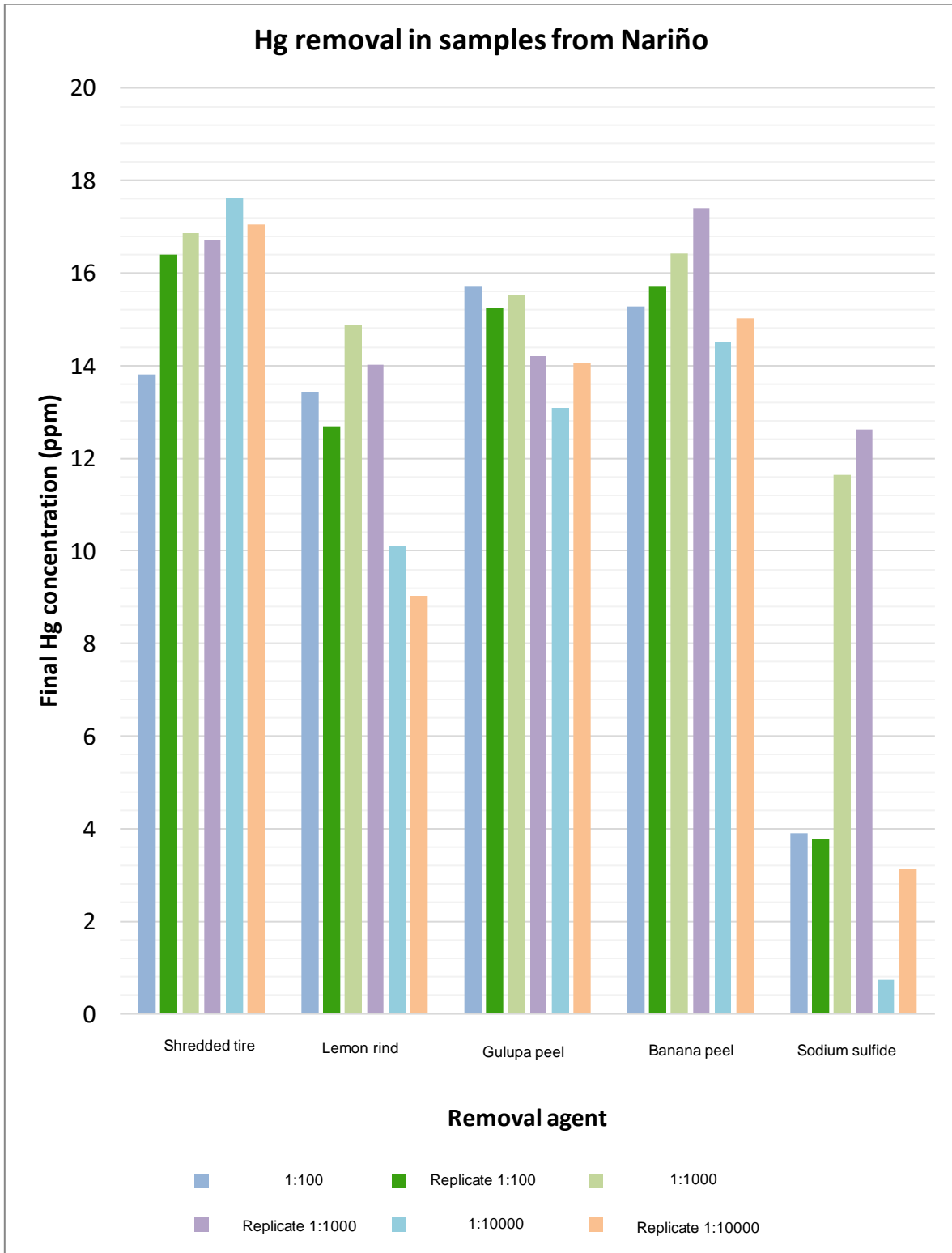


Figure 22. Hg removal in samples from Nariño.



Annex 3. Cyanidation tests

To evaluate the performance of the selected removal agents for the precipitation, adsorption, and bioadsorption of Hg, typical cyanidation tests were performed in laboratory on ASGM tailings with origins from the departments of Antioquia, Bolívar, and Nariño. The characteristics of the cyanidation process are presented in Table 10:

Table 10. Cyanidation process characteristics.

Parameters	Characteristics
Ratio solid:liquid	1:2.5
Alkaline pH	10–11 (Alkalized with lime)
[NaCN]	1 g/L
Agitation	350 rpm
Cyanidation time	10 h

To determine the concentration of dissolved Hg, cyanidation tests with a duration time of 10 hours were performed for each of the three types of tailings and without the addition of any removal agent to evaluate the potential existence of a maximum point of Hg presence. From the cyanidation solution, aliquots were sampled on the fourth, sixth, eighth, and tenth hour. The concentration at hour 10 is the most important measurement because this formed the initial or base concentration with which the results were compared to and a final Hg removal percentage for each variable was calculated. Figure 24 below shows the Hg concentration measured throughout the cyanidation process.

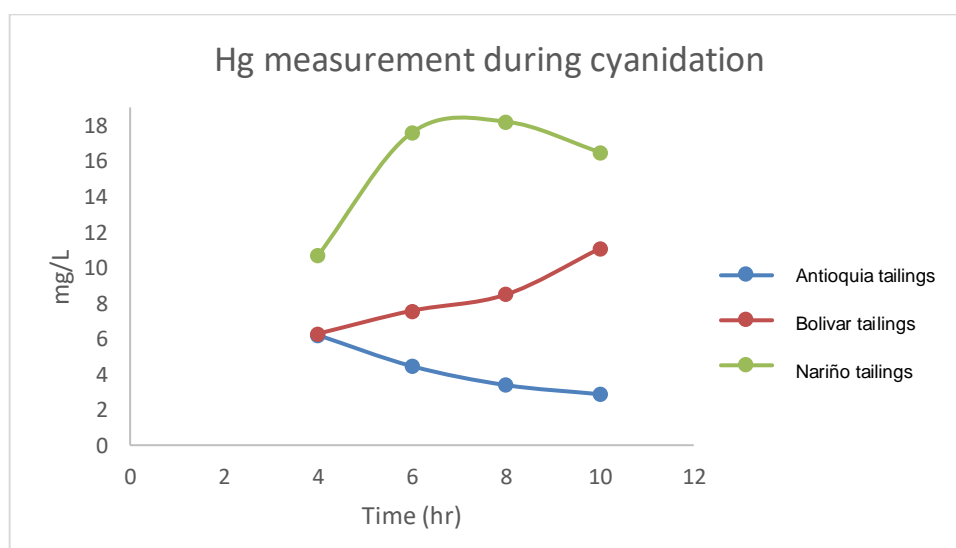


Figure 23. Dissolved Hg concentrations during cyanidation tests without removal agents.



In Figure 24, the different tendencies of each of the tailings origins can be observed; these differences could be due to variables such as chemical, physical, and mineralogical composition and their geological characteristics.

Once the cyanidation of each of the tailings was completed, the cyanidation waste was filtered. From this, 900–1000 mL samples were collected, which were divided into equal volumes to test the Hg removal capacity of the various removal agents in three different concentrations. Because there were five removal agents, the volume of the solution to evaluate each substance was 180 mL, which was divided into three 60 mL solutions to evaluate the proposed ratios per removal agent, as shown in Figure 25.



Figure 24. Test samples.