UNIVERSIDAD DE INGENIERÍA Y TECNOLOGÍA

CHEMICAL ENGINEERING CAREER

DESIGN OF HYDROMETALLURGICAL STAGES FOR REPROCESSING ARTISANAL MINE TAILINGS FROM MADRE DE DIOS

THESIS

Submitted for the Professional Engineering Degree in Chemical Engineering

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Dedication:

To my parents, sister, and grandparents, for guiding me in the
quest to become a good professional and person.
I owe you everything and I hope one day to become as human
as you have always shown me that one should be.

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To my advisor Juan Carlos Rodríguez, for discovering and fostering in me the seed of research for several years.
To my colleagues and friends, for continually seeking my personal and professional growth.

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ABSTRACT

The objective of this work was to design hydrometallurgical stages to reprocess artisanal gravimetric table concentration tailings from Madre de Dios. These tailings are currently considered waste, even though they still contain gold and rare earths. The scope is limited to the design and technical-economic assessment of leaching stages of gold and rare earths, as well as their subsequent recovery and the neutralization of effluents. Leaching stages were experimentally evaluated in a laboratory scale through a three-step experimental design. Each stage evaluated one independent variable on two levels and its effect on reagent consumption and gold or rare earths extraction. The first step considered gold extraction through thiourea leaching with ferric sulfate as oxidizing agent in an equivalent molar proportion to thiourea. The second step evaluated the inclusion of a hydrochloric acid leaching stage at 80°C before gold leaching. Finally, the third experimental step included a pretreatment at 80°C with potassium hydroxide before the other two stages. According to experimental results, rare earth extraction was too low to consider it further, while thiourea leaching achieved 86.8% of gold extraction after 1 hour, using a thiourea concentration of 8 g/L on a 40% solids slurry. Based on these results, the designed batch process included the following stages: thiourea leaching, sedimentation of solids, cementation of gold using zinc powder, effluent neutralization, and zinc dissolution with sulfuric acid to recover zinc-free, high purity solid gold. Reagent and energy requirements were estimated for 40 kg batches of tailings. Approximately 0.5 g of gold are obtained per batch. An economic assessment indicated that for a five-year projection on which 500 batches are processed yearly, the net present value of the project is $2555.37, and the internal rate of return is 27.2%. A sensitivity analysis revealed that the project can remain profitable if the capital expenditure and the cost of reagents are modified within a ±20% range, while the price of gold and the number of yearly batches can only be reduced by 7.5% and 11.4%, respectively.

KEYWORDS:

Tailings reprocessing; thiourea gold leaching; rare earth leaching.

INTRODUCTION

Metallurgical processes to extract valuable metals from minerals and concentrates constitute a key aspect of the metals and mining sector and contribute significantly to the Peruvian economy [1] However, the sustainability and effectiveness of these processes is often questioned: despite the consumed resources, it is not always possible to extract all species of interest from the minerals or concentrates due to the complex nature of the samples to be treated [2], [3]. As a result, tailings in this industry still contain small concentrations or traces of valuable metals such as gold or others, which could be utilized for greater economic benefit.

The department of Madre de Dios in the Peruvian jungle is home to artisanal gold concentration tailings that, in addition to low gold concentrations, contain metals that belong to the rare earth elements [4]. Despite the high demand for both gold and rare earths [5], these tailings are currently considered waste and are not exploited, since no technique capable of extracting both the gold and the rare earths from the tailings has been developed yet. In this regard, there are numerous techniques designed to extract gold [6], [7] or rare earths [8] as isolated purposes. However, these have not been integrated yet in such a way that it is possible to extract sequentially the valuable elements that make up the tailings. Additionally, techniques for obtaining gold often employ toxic reagents, such as mercury in small alluvial mining and cyanide in large-scale mining [9]. While large-scale mining is formal and has special strategies and procedures for the handling, transport and disposal of cyanide, artisanal mining is informal and discharges over 40 tons of mercury into the environment per year in Peru alone [4]. Thus, it is advisable to use alternative reaction routes, which allow gold to be extracted without this reagent, such as through the use of thiourea in acidic medium [10] or sodium thiosulfate in alkaline medium [11].

As a result, the following research question defines the present work: Is it possible to design an economically and environmentally sustainable hydrometallurgical process to reprocess gravimetric concentration tailings from Madre de Dios, tentatively by extracting and recovering rare earths and gold sequentially?

The identification of a technique to sequentially integrate the extraction and recovery of rare earths and gold from concentration tailings is justified from different perspectives. Firstly, the concatenation of processes could save resources if both stages of extraction are interrelated, either in terms of reagent consumption or in the beneficial effects that one stage may directly or indirectly have on the other. In addition, using alternative reagents to cyanide as gold leaching agents justifies the research project from an environmental and social perspective, since the handling and disposal of cyanide solutions is very harmful to both human health [12] and the environment [9]. Moreover, this technique would imply an additional economic benefit for metallurgical companies, since they will be taking advantage of a material that was previously considered a waste [13]. However, the economic benefit that could be obtained is also subject to the evaluation of the additional costs associated with the implementation of the new strategy. If profitable, the implementation of the reprocessing scheme could contribute to the establishment of greener artisanal mining techniques in the Peruvian jungle, which are not dependent on cyanide or mercury. An additional benefit would be that adhering to these strategies could be the first step towards responsible mine site closure, although this evaluation is beyond the scope of this study.

The scope of the project includes the design and technical-economic assessment of the leaching stages of gold and rare earths, as well as gold recovery through cementation and neutralization of the generated effluents. Thus, all previous instances, such as extraction and gravimetric concentration are excluded from the study. The leaching of gold will be performed with thiourea in acidic medium [10], while the extraction of rare earths will be based on acid leaching preceded by an alkaline treatment [8]. The environmental impact assessment of the project will not be detailed herein.

OBJECTIVES

General objective

To design hydrometallurgical stages to reprocess artisanal mine tailings from Madre de Dios.

Specific objectives

- To determine experimentally the extraction performance and reagent consumption when employing thiourea as a leaching agent to extract gold from concentration tailings.
- To establish the rare earths extraction performance during acid leaching of concentration tailings on an experimental basis.
- To develop downstream processing stages to recover the valuable metals extracted during leaching.
- To evaluate the implementation of the reprocessing scheme of gravimetric table tailings through an economic analysis.

CHAPTER I

THEORETICAL FRAMEWORK

This chapter details the main theoretical concepts required for the development of the thesis, including the definition of the leaching process, as well as its technical, kinetic, and thermodynamic characteristics. Likewise, the modalities of leaching of minerals at an industrial level are described. Finally, hydrometallurgical processing of both gold with thiourea in acid medium and of rare earths are presented.

1.1. Leaching

Leaching is a solid-liquid extraction to selectively dissolve a species of interest that is contained in a solid matrix. To do this, a leaching agent that is capable of dissolving only or preferably the desired element or compound is used. This agent will react poorly or not at all with the species that are desired to remain in the solid phase. After the process has occurred, a leaching liquor rich in the species of interest is obtained. The objective of obtaining this solution is to be able to recover, following different reaction routes, the substances extracted from the original matrix [14].

Leaching thermodynamics evaluates the redox potential and pH requirements to dissolve a given species, based on chemical equilibrium information. Some species require acidic, basic, oxidizing, reducing or combinations of these conditions to dissolve. The thermodynamic requirements for the development of leaching reactions of a given system in aqueous phase can be obtained from their respective Pourbaix diagrams (Eh-pH) [15]. Referentially, one of these diagrams is presented in **Figure 1.1** for the gold-thiourea system. In this diagram, the small area of thermodynamic stability of the thiourea-gold complex can be appreciated:

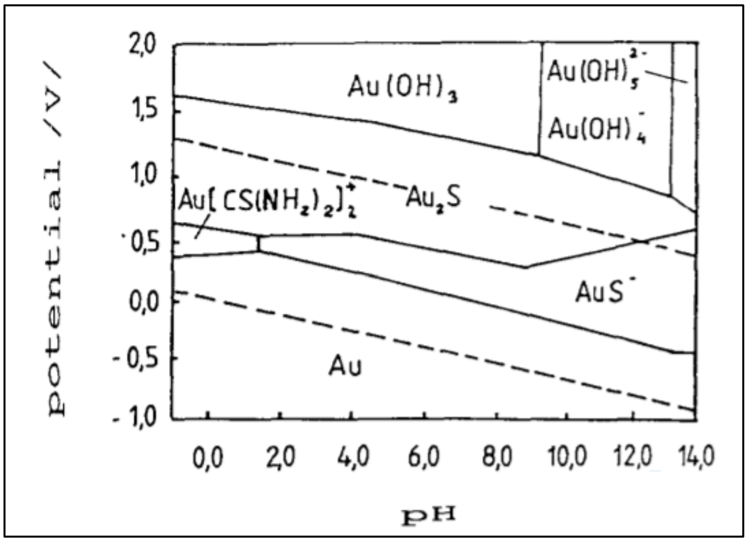

Figure 1.1. Pourbaix diagram (Eh-pH) for the gold-thiourea system considering a thiourea activity of 10^{-1} and a dissolved gold activity of 10^{-2} [16].

Leaching kinetics can be described by the following stages: transport of the leaching agent from the bulk of the fluid to the solid-liquid interface, diffusion of the agent to the desired solid surface to be extracted, dissolution reaction of the solid, diffusion of the product from the solid surface to the solid-liquid interface, and transport of the leached product to the bulk of the fluid. Out of these stages, transport to or from the bulk of the fluid is usually rapid, so the kinetics of leaching are usually controlled chemically or by internal diffusion in the mineral matrix [14], [15].

The temperature and concentration of the leaching agent are two operational parameters that have an important effect on both the thermodynamics and kinetics of leaching. Thermodynamically, temperature impacts the Eh-pH diagram of aqueous systems, while a concentration increase of the leaching agent causes a displacement of the equilibrium, promoting the formation of leached products. On the other hand, the kinetics of leaching are favored by increasing either reaction temperature or leaching agent concentration [15].

The kinetics or thermodynamics of leaching can be impaired due to refractoriness phenomena: presence of species that consume the leaching agent in an excessive manner, formation of passivating surfaces that reduce or prevent the diffusion of the leaching agent or existence of adsorbents in the matrix that retain the products on the surface of interest [7].

1.1.1. Leaching processes at an industrial scale

Industrially, there are three main methods of leaching minerals: leaching in piles, vat leaching, and leaching in stirring tanks. Leaching in piles consists of sprinkling the leaching agent over low-grade ore stacked on a waterproof surface, and then recovering the pregnant leach solution from the bottom of the pile. Vat leaching involves flooding medium-grade ore placed in waterproof tanks with the leaching agent. Finally, leaching under stirring is used for pulps of high-grade minerals, which are introduced into stirring tanks to enhance the kinetics of the leaching reaction [15].

1.1.2. Thiourea leaching of gold in acid medium

Gold is a noble metal capable of remaining in its metallic state in the presence of numerous reagents, so it is necessary to use very specific leaching agents to dissolve gold. Cyanide is the most common leaching agent of gold, due to its ability to form stable complexes with this metal; however, it has serious environmental considerations. Therefore, there is a need to evaluate alternative leaching agents for gold, such as thiourea (NH_2CSNH_2), whose leaching reaction is presented below, alongside its equilibrium constant at 25°C (calculated from $\Delta G° = -8994$ cal/mol) [17]:

$$\mathrm{Au_{(s)}} + 2\mathrm{NH_2CSNH_{2(ac)}} + \mathrm{Fe^{3+}_{(ac)}} = [\mathrm{Au(NH_2CSNH_2)_2}]^{+}_{(ac)} + \mathrm{Fe^{2+}_{(ac)}}\ (\mathrm{K} = 3.99 \times 10^{6}) \quad (1)$$

The leaching of gold with thiourea is carried out under acidic conditions (pH between 1 and 3), since thiourea is unstable in alkaline medium. Likewise, to carry out the process, the presence of an oxidizing agent such as the ferric ion is required [18], preferably in sulfuric acid [19] at a redox potential of between 0.42 V and 0.45 V (with respect to the standard hydrogen electrode) to avoid the decomposition of thiourea due to unwanted side reactions [18].

The kinetics of gold leaching with thiourea depend on both the concentration of thiourea and of the oxidizing agent, as well as on the temperature and pH of the medium. It is also known that the presence of ferric ion reduces the rate of decomposition of thiourea by oxidation. However, from a thermodynamic perspective, the ferric ion promotes the formation of Fe(III)-thiourea complexes [19] such as the following three [20]:

$$\mathrm{Fe^{3+}}_{\mathrm{(ac)}} + \mathrm{SO_4^{2-}} + \mathrm{NH_2CSNH_{2(ac)}} = [\mathrm{FeSO_4NH_2CSNH_2}]^{+}\ (\mathrm{K} = 4.26 \times 10^{6}) \tag{2}$$

$$\mathrm{Fe^{3+}}_{\mathrm{(ac)}} + \mathrm{NH_2CSNH_{2(ac)}} = [\mathrm{FeNH_2CSNH_2}]^{3+}\ (\mathrm{K} = 1.58 \times 10^{2}) \tag{3}$$

$$\mathrm{Fe^{3+}}_{\mathrm{(ac)}} + 2\mathrm{NH_2CSNH_{2(ac)}} = [\mathrm{Fe(NH_2CSNH_2)_2}]^{3+}\ (\mathrm{K} = 2.75 \times 10^{8}) \tag{4}$$

It is noteworthy that **Equation (2)** has an equilibrium constant that is comparable to that of **Equation (1)** for the formation of the gold-thiourea complex, while the equilibrium constant of **Equation (4)** is approximately 69 times greater than that of gold complexation with thiourea.

Also, both thiourea and cyanide are leaching agents of low selectivity, since they can also dissolve other metals present in the matrix, which causes a high consumption of the leaching agent. Because of this, acid pretreatments are commonly performed to eliminate substances that degrade or consume thiourea [19].

After leaching, gold can be recovered from the pregnant solution through cementation. This process relies on redox interactions between the gold-containing complex and a less noble metal that is added to the solution, such as zinc [21].

1.1.3. Leaching of rare earths

Rare earths are a set of 17 metals of similar properties that are useful for various industries. These elements include scandium, yttrium, and lanthanides. Currently, the most abundant rare earth minerals worldwide are monazite ($CePO_4$), bastnasite ($Ce(CO)_3F$), and xenotime (YPO_4), where cerium and yttrium atoms are usually replaced by other rare earths [22].

In general, rare earths dissolve moderately in sulfuric or hydrochloric acid, so there are several verified processes that employ these substances under different operating conditions. Some processes, such as the *Indian Rare Earths Ltd. Process* (IRE) for monazite, include a concentrated alkaline medium (50-70% NaOH by weight) pretreatment at temperatures of around 140°C to form rare earth hydroxides that are more amenable to hydrochloric acid leaching [22]–[24]. In this sense, the chemical reaction for the alkaline treatment of monazite (represented in its generic form) is presented below, which allows to obtain insoluble hydroxides of rare earths (R) in alkaline medium [24]:

$$\mathrm{RPO_{4(s)} + 3NaOH_{(ac)} = R(OH)_{3(s)} + Na_3PO_{4(ac)}} \tag{5}$$

Subsequently, the solid hydroxides of rare earths must be washed to remove the soluble species, among which is sodium phosphate, a species that has commercial value [22]. The hydroxides will then be exposed to hydrochloric acid to dissolve them and obtain leaching liquors rich in rare earth chlorides, which can then be processed to obtain solid products of rare earth chlorides, carbonates and hydroxides [23]. The acid leaching reaction of rare earth hydroxides is presented below [8]:

$$\mathrm{R(OH)_{3(s)} + 3HCl_{(ac)} = RCl_{3(ac)} + 3H_2O_{(l)}} \tag{6}$$

The IRE process scheme for rare earth leaching is shown in **Figure 1.2**, which also indicates the stages before and after alkaline attack and acid leaching, which are beyond the focus of the present study. Unit operations or processes marked in red constitute the stages that are included within the scope. As seen in the scheme, the alkaline attack at 140°C followed by acid leaching is not selective to extract only rare earths, as it will also remove other species that could have commercial value, such as uranium or thorium [23].

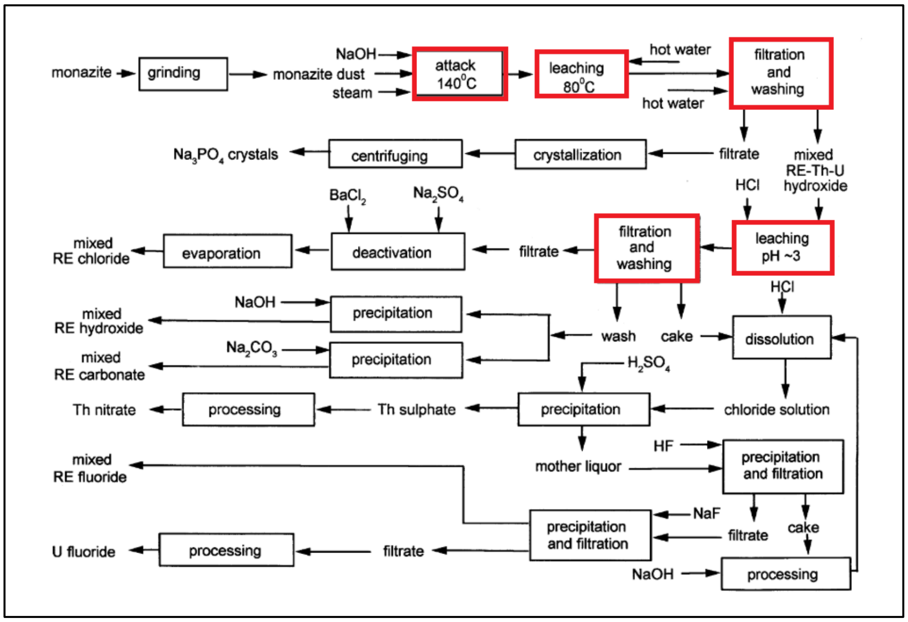

Figure 1.2. Block flow diagram for the IRE process for monazite acid leaching after performing an alkaline pretreatment. Red boxes limit the stages that are within the scope of the present study. Adapted from [23].

CHAPTER II

STATE OF THE ART

This chapter reviews the state of the art of the topics and technologies of interest related to the leaching of gold with thiourea in acid medium and its subsequent recovery through cementation. Additionally, studies on pretreatments to enhance gold extraction are presented, as well as current research on rare earth leaching.

2.1. Thiourea leaching of gold in acid medium

In 2017, a study by Guo et al. compared 2 gold leaching processes from a sulfide-based refractory concentrate. A one-step process considered a biological oxidation treatment followed by washing, filtering, and leaching with thiourea in acid medium. The alternative two-step process performs a second stage of biological oxidation, whose residue is not washed and filtered before leaching with thiourea, to take advantage of the ferric ion generated by the bacteria, which is required as an oxidant for the thiourea leaching stage. The main characteristics and results of both processes are compared in **Table 2.1.** The study concluded that the main advantage of the two-step method is to omit any external oxidizing agents, since the necessary ferric ion will be provided by the bacteria from the first step. Likewise, the two-step process offers a slight increase in total gold extraction, although at the cost of a longer total processing time and the need to operate at a higher temperature. Thus, a detailed evaluation of the process is required to determine the advisability of employing one or two stages [25].

Parameter	One-step leaching	Two-step leaching
pH	1.5	1.5
Initial thiourea concentration	2.75 g/L	2.75 g/L
Slurry density	33.3%	20% in first step 33% in second step
Reaction time	6 hours	6 hours of biological oxidation 6 hours of thiourea leaching
Temperature	25°C	35°C
Thiourea consumption	4.44±0.15 kg/t	4.47±0.06 kg/t
Consumption of other reagents	3 g/L $Fe_2(SO_4)_3$ 1 g/L Na_2SO_3	*9K* culture medium
Gold extraction	92.2%±1.54%	95.0%±0.73%

Table 2.1. Comparison of parameters and results for a thiourea leaching process involving one or two steps. Adapted from [25].

In 2019, an experimental and statistical study by Olyaei et al. was conducted to identify the optimal conditions of thiourea leaching and cyanidation to extract gold from a sample of oxides with a high silica, alumina, and arsenic content. An analysis of variance (ANOVA) identified the effect of parameters such as ore granulometry, leaching time, consumption of reagents, solid percentage, and pH on the extraction of gold in each of the processes. Likewise, the study determined the optimum operating conditions for each of the processes for the mineral in question, which are shown in **Table 2.2** [26]:

Parameter	Thiourea leaching	Cyanide leaching
pH	1.7	10.6
Particle size (d_{80})	63 µm	63 µm
Solid percentage	40%	40%
Reaction time	5 hours	12 hours
Temperature	Room temperature, not controlled	Room temperature, not controlled
Consumption of reagents	13.32 kg/t thiourea 47.34 kg/t $Fe_2(SO_4)_3$ 1.1 kg/t H_2SO_4	1.23 kg/t NaCN 2 kg/t quicklime
Gold extraction	90.47%	95.21%

Table 2.2. Comparison of optimum parameters and results for thiourea leaching of gold and cyanidation. Adapted from [26].

The results reported by the authors indicate that cyanidation is economically more convenient, as it requires a lower consumption of reagents and extracts a greater amount of gold. However, thiourea leaching offers as advantages faster processing and the generation of less dangerous effluents [26].

Additionally, a 2019 study by Bernaola-Flores et al. compared the thermodynamics and kinetics of silver leaching of a synthetic acanthite ore with thiourea with respect to the cyanidation of that mineral. The study identified that for a similar molar concentration of leaching agent (65.7 mM of thiourea and 61.2 mM of sodium cyanide) and considering the same temperature, stirring rate and solid percentage, the kinetics of leaching with thiourea is faster: the reaction reaches equilibrium in less than 2 hours. On the other hand, the end of the cyanidation reaction in the 4 hours of experimentation was not observed, as shown in **Figure 2.1.** Although the extraction of silver by the action of thiourea was greater than that due to sodium cyanide at that time, the authors clarify that there is no certainty of the behavior of the extraction trend after the first 4 hours [27]:

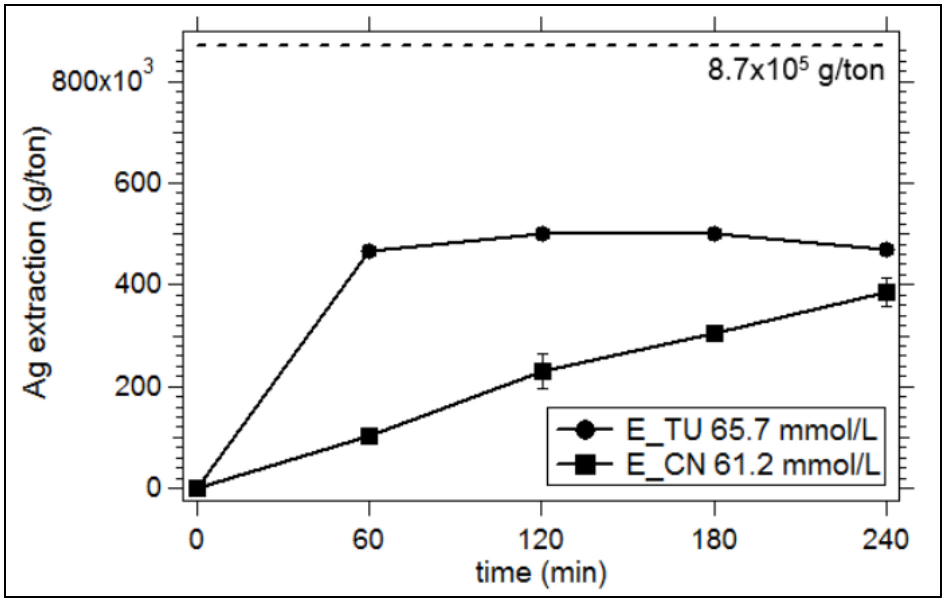

Figure 2.1. Silver extraction as a function of time for a synthetic acanthite sample subject to thiourea leaching (circular markers) or to cyanidation (square markers). The dashed line in the upper section of the figure indicates the total silver content per ton of mineral [27].

The study by Bernaola-Flores et al. concludes that the more spontaneous a leaching reaction is, the higher the percentage of silver extracted. However, it specifies that other factors may have an influence on this result. Thus, the research conclusions should not be immediately generalized to other minerals or to other leaching systems [27]. However, the study on the synthetic silver mineral can be taken as a basis for the behavior of gold leaching, since both are noble metals encapsulated in a refractory matrix, in which case thiourea has a better kinetics than cyanide.

On the other hand, a 2020 study by Xu et al. experimentally evaluated the effect of 6 parameters on the leaching of gold with thiourea in acid medium from a refractory mineral with high sulfur and arsenic content, which was pretreated through biological oxidation. The independent variables considered were leaching time, initial pH, temperature, thiourea concentration, stirring speed and ferric ion concentration, while the dependent variables were gold extraction and total thiourea consumption. From the statistical treatment of the data, neural networks were used to identify and validate a predictive model for the two response variables. This model predicts that the initial pH and stirring speed are parameters that have little impact on the response variables, while the concentration of reagents, leaching time and temperature have a greater impact on them. Likewise, the study specifies that, for the used mineral, the optimum conditions identified were 4 hours of leaching at 35°C, considering an initial pH of 1.5, a concentration of thiourea of 6 g/L and of ferric ion of 9.33 g/L, all subject to a stirring speed of 400 rev/min. These operating conditions allowed the extraction of 77.6% gold and consumed 8.1 kg of thiourea per ton of processed ore. Finally, the study recognizes that the concentration of solids and the granulometry of the particles are two parameters that must be evaluated in future research [28].

In 2020, a study by Guo et al. evaluated a two-stage process to leach gold with thiourea from a calcine concentrate obtained from a mineral with high arsenic and sulfur content. After the first stage of leaching with thiourea, the leaching liquor is separated from the residue by filtration. Subsequently, the solid is sent to a grinding stage, where its surfaces are reactivated to allow a second stage of leaching with thiourea. As part of the study, iron powder was added to the leaching liquor, to obtain a gold-containing slurry and to recirculate the barren solution to the leaching stages. The optimum reagent concentrations identified for the leaching stages were the following: thiourea, sodium lignosulfonate, urea, and ferric ion concentrations of 6 g/L, 0.9 g/L, 2 g/L and 3 g/L, respectively. Similarly, a stirring speed of 300 rev/min, a pH of 1.2, a temperature of 40°C, 2 hours of leaching time and a liquid-to-solid ratio of 3:1 were considered as optimum parameters. After carrying out the study at laboratory scale, the experiments were developed on a pilot scale, in tanks of 3 m^3 and using 75 kg of calcine sample in each test. Leaching at laboratory scale achieved an extraction of 96.51% of the gold from the concentrate, while at pilot scale 96.43% of gold was extracted, which validates the scaling of this technology [29].

2.2. Gold cementation from pregnant thiourea leach solutions

The recovery of gold and silver from pregnant thiourea leach solutions through cementation was evaluated in 1996 by Lee et al. This study evaluated the cementation of these precious metals (96 ppm of gold and 534 ppm of silver, approximately 5.44 mM of precious metals) after adding zinc (the current reagent of choice for cementation of gold), iron, or aluminum powder to the solution, considering cementation kinetics and overall recovery. The authors indicated that using zinc as the cementing powder improved cementation kinetics at the cost of increasing powder consumption. Zinc requirement (10 kg/m^3) to recovered precious metals was in the molar proportion of ~28.1:1 and achieved 99% of gold recovery after 10 minutes. Cementation with aluminum (2.5 kg/m^3) and iron powder (2.5 kg/m^3) required 60 min to recover 99% and 100% of gold, respectively. Aluminum and iron requirements per mole of precious metals were of ~17.1 moles and ~8.3 moles, respectively. The authors also indicated that purging oxygen from the system with nitrogen increased gold recovery slightly and reduced zinc, aluminum, or iron consumption [30]. If zinc was used for cementation, it can afterwards be separated from gold through sulfuric acid dissolution, which occurs at a rate of 0.22 g of zinc per hour if immersed in a sulfuric acid solution of 2.55 M. Stoichiometrically, sulfuric acid consumption is of ~1.5 g per gram of zinc. [31].

2.3. Pretreatments for gold leaching

Several authors have recently studied tentative pretreatments to reduce the refractoriness of gold-containing minerals or concentrates, to increase the extraction of this metal, or to reduce the consumption of leaching agents. The state of the art of these pretreatments is described below, which have been divided according to the media in which they are developed.

2.3.1. Acid pretreatments

In 2020, a study by Torres et al. evaluated the effect of performing an acid pretreatment at pH 5 with sodium citrate to increase gold extraction from a refractory mineral based on pyrite and quartz using thiourea as a leaching agent. This pretreatment is performed to remove non-precious metals such as iron from the ore before leaching with thiourea. This is beneficial because gold could be inside a refractory iron-containing matrix, which could be attacked with citrate to extract the iron beforehand. In the first pretreatment cycle, fresh sodium citrate is used, which is then recycled a maximum of 3 times, always with an adjusted pH of 5. Subsequently, the solid residue of each of the cycles is recovered by filtration and is leached with thiourea, which increases the extraction of gold after 6 hours, as shown in **Figure 2.2**. The efficiency of the pretreatment is reduced as the acid citrate solution is recycled, so an economical evaluation is in order to assess if it is justified to continue recycling this solution more than 3 times [32].

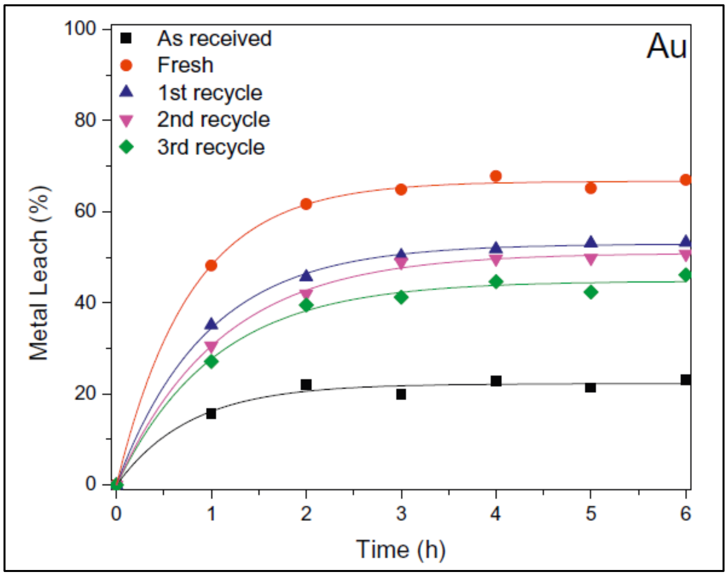

Figure 2.2. Percent extraction of gold as a function of time for a sample that was leached as received (black line) or that was subject to a pretreatment with fresh sodium citrate (red line) or with sodium citrate that was recycled 1 (blue line), 2 (magenta line), or 3 (green line) times [23].

The study found that these pretreatments affect only total extraction, but do not alter the kinetics of leaching, since the curves presented in **Figure 2.2** have the same shape, although they reach different final values of gold extraction [32].

A 2020 study by Ahmed et al. used a sulfuric acid pretreatment to remove uranium, copper, and other non-precious metals from a tailing from the processing of uranium ores, before leaching the pretreated sample to extract gold. The pretreatment consisted of stirring the tailings at 200 rev/min and 60°C for 8 hours, considering a solid/liquid ratio of 1:3 and a sulfuric acid concentration of 1.5 M. The untreated tailings allowed the extraction of 58% of the gold during 1 hour of leaching with thiourea, while the extraction of gold increased to 75% after the pretreatment. Also, adding sodium sulfite during leaching with thiourea increased gold extraction up to 94% in 60 minutes and to 98% in 90 minutes. 1.5 g/L of thiourea, 4 g/L of Na_2SO_3 and 0.02 M of H_2O_2 as an oxidizing agent were used for leaching. The kinetic analysis of the results identified that the leaching of gold with thiourea is controlled by diffusion, regardless of whether sodium sulfite is added [33].

In 2021, a study by Ippolito et al. on the extraction of silver and gold from printed circuit boards via thiourea leaching identified the need for acid pretreatments to increase precious metal extraction. This was necessary to prevent copper from competing with gold for the consumption of thiourea. Direct leaching with thiourea of the circuit boards only managed to remove 8.5% of the gold present in them after an hour. A pretreatment of 1 hour with a 3 M solution of HNO_3 removed all the copper present in the board, which resulted in an 81% gold extraction with thiourea, while a pretreatment with H_2SO_4 and H_2O_2 extracted 81% of the copper in half an hour and 79% of the gold during leaching with thiourea. In both cases, leaching with thiourea was performed for 1 hour, at a pH of 1 and 25°C, considering the use of 0.11 kg of $Fe_2(SO_4)_3$, 0.05 kg of H_2SO_4 and 0.12 kg of thiourea dissolved in 4.83 kg of water per kg of circuit boards fed to the process [34].

2.3.2. Alkaline pretreatments

Alkaline pretreatments to increase the efficiency of gold leaching with thiourea have not been identified as part of the state of the art. However, these pretreatments are commonly used before cyanidation. The main recent studies in this area are described below.

A 2014 study by Alp et al. performed a KOH pretreatment to improve the efficiency of gold and silver leaching from a refractory ore in which precious metals were mainly dispersed in antimony sulfides. The study compared the extraction of various metals during alkaline pretreatment, as well as during leaching with and without the pretreatment. The main results of the study [35] are presented in **Figure 2.3.** The authors indicate that the alkaline pretreatment is effective in removing the arsenic and antimony contained in the mineral. They also report that the pretreatment does not remove any of the other metal species, whose extractions increase significantly when carrying out cyanidation after pretreatment. Specifically, the extraction of gold increases from 49.5% to 87.2% and of silver from 18.7%

to 90.0% during cyanidation. The authors conclude that the substantial increase in the extraction of precious metals is due to the dispersal of antimony sulfides, which degrade during pretreatment [35].

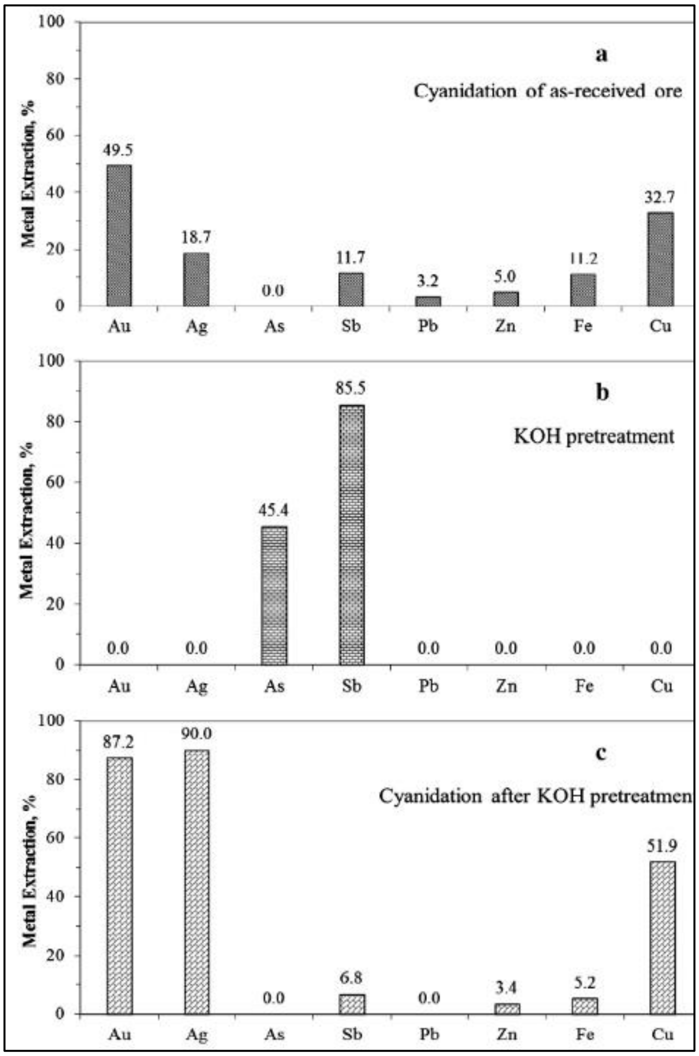

Figure 2.3. Percent extraction of gold, silver, arsenic, antimony, lead, zinc, iron, and copper during (a) cyanidation with no pretreatment, (b) KOH pretreatment, and (c) cyanidation after pretreatment. Pretreatment with 5 M KOH at 80°C for 2 hours and cyanidation with 1.5 g/L NaCN at pH 10.5 for 24 hours [35].

In 2018, a study by Bidari and Aghazadeh evaluated the use of an alkaline pretreatment with NaOH at different concentrations at 80°C for 8 hours to increase gold extraction by cyanidation (25°C, 24 h, KCN concentration of 6 g/L and O_2 flow of 200 mL/min) from a refractory ore in which the precious metal is mainly dispersed in clays and zinc, iron, and arsenic sulfides. The study compared species extraction associated with direct cyanidation without pretreatment with cyanidation preceded by NaOH treatment at 2 M and 4 M [36]. The extraction results of gold, silver, and other species present in the ore during cyanidation with and without pretreatment are presented in **Table 2.3:**

Species	**Extraction with no pretreatment (%)**	**Extraction after NaOH 2 M (%)**	**Extraction after NaOH 4 M (%)**
As	26.30	43.40	5.30
Fe	23.60	29.70	19.20
Zn	7.19	5.73	12.34
S	43.70	29.79	10.34
Au	69.35	62.83	80.66
Ag	44.40	33.30	88.90

Table 2.3. Comparison of the extraction of arsenic, iron, zinc, sulfur, gold, and silver from a mineral during direct cyanidation or cyanidation after alkaline pretreatment with NaOH 2 M or 4 M. Adapted from [36].

Based on the results shown in **Table 2.3** and other findings reported in the study, the authors concluded that the pretreatment with NaOH at 2 M decreased gold extraction in the case of the mineral of interest, since at this concentration the pretreatment attacks arsenic sulfides and makes them susceptible to being leached by cyanide, a reaction that disfavors the formation of gold-cyanide complexes. This can be explained because cyanide will form complexes with arsenic, while consuming the oxygen required for the process. However, doubling the concentration of NaOH during pretreatment does increase the extraction of both gold and silver during cyanidation, since oxidation of the pyrite matrix in which precious metals were dispersed occurs under conditions of very high alkalinity [36].

2.3.3. Other pretreatments

A 2017 study by Choi et al. employed a microwave pretreatment to improve the subsequent leaching of gold with thiourea of a concentrate based on pyrite and quartz. The pretreatment increased the temperature of the ore to 950°C and generated cracks at a microscopic level, facilitating thiourea diffusion during leaching. Since pyrite has a greater ability to capture microwaves than quartz, the treatment managed to thermally decompose a considerable fraction of pyrite, forming pyrrhotite and hematite. Thus, the microwave pretreatment increased the degree of gold liberation and reduced the presence of refractory pyrite, improving the performance of thiourea leaching. This was achieved by reducing the sulfur content from 20.14 g/kg in the original concentrate to 1.12 g/kg after 70 minutes of treatment. It was reported that the direct leaching of the concentrate with a thiourea concentration of 34.7 mM, in the presence of 0.6 mM of Na_2SO_4, and 3.5 mM $Fe_2(SO_4)_3$ achieved a gold extraction of 78.1% after 60 minutes of leaching. However, pretreating the concentrate for 50 minutes and 70 minutes, considering the same concentrations of reagents and conditions, increased gold extraction after 60 minutes to 95.5% and 100%, respectively [37].

In 2017, a study by Oliveira Nunan et al. evaluated the impact of an oxidative treatment by injecting hydrogen peroxide into a sulfide-based mineral pulp (60% solids) on cyanide consumption and gold extraction. The oxidation of the ore attacked the sulfides that encapsulated the gold and increased the oxygen dissolved in the cyanide solution. The study was performed at laboratory scale and at pilot scale, considering the processing of 150 t/h of dry ore, in which case gold extraction during cyanidation increased from 91.3% to 92.5% and cyanide consumption was reduced from 0.52 kg/t to 0.40 kg/t [38].

2.4. Leaching of rare earths

A 2014 study by Panda et al. optimized the parameters of the NaOH decomposition stage of a monazite concentrate, within the framework of the IRE process to extract rare earths. The parameters studied for the pretreatment were NaOH concentration, temperature, and percentage of solids, while acid leaching was carried out for 2 hours at 90°C, with a pulp density of 60 g/L and with an HCl concentration of 6 N. Initially, the concentrate was leached directly with the indicated conditions, which allowed the extraction of only 29.34% of the rare earths present. The authors concluded that the low extraction is due to the presence of phosphates, which are poorly soluble in the acidic medium. However, rare earth extraction can be significantly increased using an alkaline pretreatment. The authors identified that, in the studied ranges for each of the parameters, the optimum conditions for the pretreatment are NaOH concentration of 50% by weight, a pulp density of 100 g/L and a temperature of 100°C. Under these conditions, an almost complete dissolution of phosphates is achieved, forming oxides and hydroxides of rare earths, which are soluble in acid. Thus, it is possible to increase the extraction of rare earths up to 95% [39].

A 2017 study by Liang et al. evaluated the effect of certain parameters on the efficiency of sulfuric acid leaching of rare earths from a phosphate mineral that contained monazite. The authors identified that the leaching liquor that contained rare earths is mainly accompanied by the trivalent anion PO_4, which proves the association of rare earths with the phosphate ion in the mineral monazite. They also studied the effect of adding H_3PO_4 in low concentrations to the ore before leaching with H_2SO_4. The evaluated parameters were the leaching time, initial concentration of H_3PO_4, temperature, stochiometric ratio of H_2SO_4 with respect to CaO in the mineral, and the solid-liquid ratio in the pulp. Of these parameters, the four factors that had the most impact on rare earth extraction were the initial concentration of H_2SO_4 and H_3PO_4, temperature and solid-liquid ratio. Within the evaluated range of parameters, the highest leaching efficiency (52.82%) was achieved when operating at 75°C, with an initial concentration of H_3PO_4 of 17% by weight, an H_2SO_4/CaO ratio of 1.05, and a solid-liquid ratio of 3.5 [40].

In 2019, a study by Cánovas et al. evaluated the extraction of rare earths, uranium, and thorium from a gypsum-based concentrate, which was produced from the acid decomposition of fluoroapatite ($Ca_5(PO_4)_3F$) to obtain phosphoric acid and hydrofluoric acid. The effect of using different leaching agents to extract the metals was compared, which were added to a mineral pulp that had a solid-liquid ratio of 1:20. The reaction systems were kept at room temperature and were subjected to stirring at 500 rpm. 5 different possible leaching systems were used: (1) HNO_3 3M, (2) H_2SO_4 0.5 M, (3) diethylenetriaminopentaacetic acid (DTPA) solution and HNO_3 at pH 3-5, (4) diethylenetriaminopentaacetic acid (DTPA) solution and H_2SO_4 at pH 3-5 and (5) distilled water [41]. The results of extraction of rare earths, uranium and thorium are presented in **Figure 2.4**.

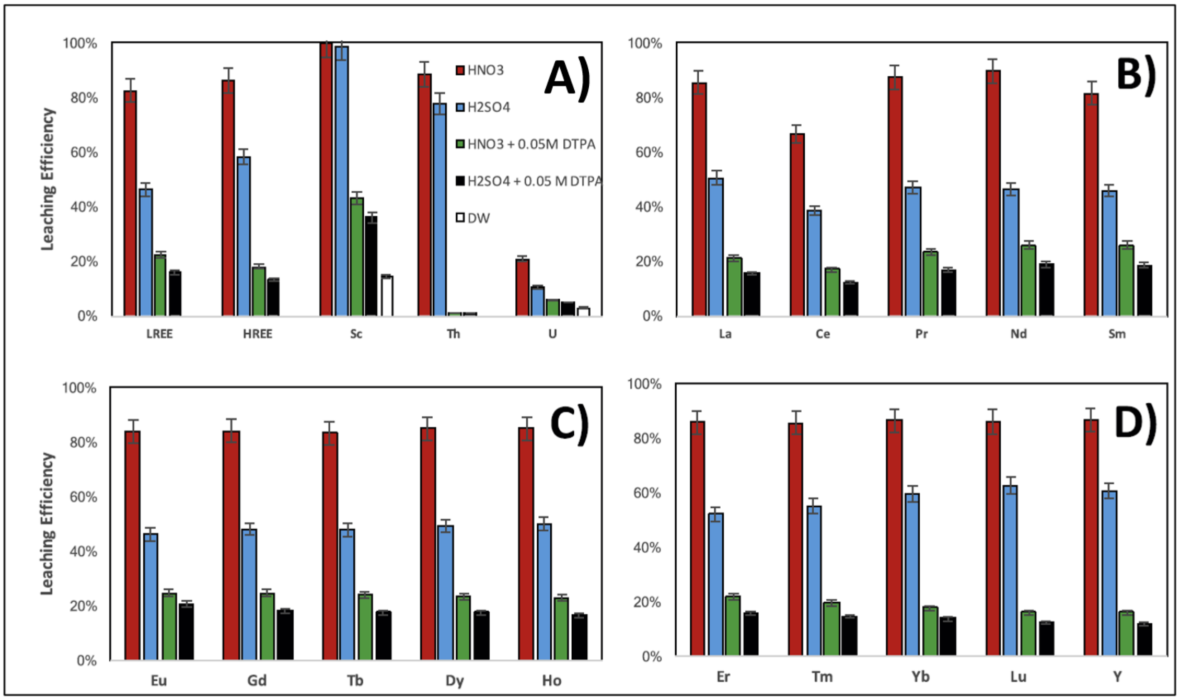

Figure 2.4. Percent extraction of rare earths, thorium, and uranium from a gypsum concentrate when using different leaching agents for 8 hours: HNO_3 3 M, H_2SO_4 0.5 M, solutions at pH 3-5 of HNO_3 or H_2SO_4 with the chelating agent DTPA, and distilled water. LREE and HREE represent the average of extraction of lanthanides between lanthanum and samarium, and between europium and lutetium, respectively. A) LREE, HREE, Sc, Th, and U; B) La, Ce, Pr, Nd, and Sm; C) Eu, Gd, Tb, Dy, and Ho; D) Er, Tm, Yb, Lu, and Y. [41].

The authors conclude that the addition of the chelating agent DTPA does not increase the extraction of rare earths, uranium or thorium when comparing these results with the extraction achieved with aqueous solutions of HNO_3 or H_2SO_4. This reveals that the leaching of rare earths is not limited by the absence of chelating agents. Likewise, the substantial extraction of rare earths by using HNO_3 3 M is linked to the dissolution of impurities of calcium, sulfur, strontium, cadmium, phosphorus and barium, which will remain in the leaching liquor along with rare earths, uranium and thorium [41].

A 2019 study by Amine et al. was based on statistical processing using the response surface methodology of HCl leaching data from a fluoroapatite mineral ($Ca_5(PO4)_3F$). The study sought to identify the effect that HCl concentration, temperature, stirring speed, solid-liquid ratio, and leaching time have on the extraction of rare earths from the ore. Data processing revealed that the parameters that have the greatest impact on leaching efficiency are temperature, HCl concentration and solid-liquid ratio. Likewise, it was determined that the optimal conditions for the leaching of rare earths of the mineral in the studied range of parameters are an HCl concentration of 23% by weight, a temperature of 44°C, a solid-liquid ratio of 43%, a stirring speed of 233 rev/min, and a leaching time of 45 minutes, which results in a 75% extraction of rare earths. However, the authors conclude that greater rare earth extraction could be achieved by reducing the solid-liquid ratio and increasing both HCl concentration and temperature [42].

In 2020, a study by Kim et al. evaluated the development of two pre-leaching treatments of a mineral based primarily on goethite (FeOOH), which contained submicroscopic grains of monazite scattered around the mineral. The ore had a total content of 3.4% by weight of rare earth oxides, which include cerium oxides, lanthanum, neodymium, and yttrium. As a baseline, the authors leached the mineral with HNO_3 at concentrations in the range between 1 M and 3 M, at temperatures between 25°C and 80°C. Despite the high temperatures and concentrations, at most 61%-73% of the different species of rare earths present in the mineral were extracted. Afterwards, a pretreatment with H_2SO_4 was evaluated, in which a mixture of acid and mineral was baked in a furnace at 200°C for 2 hours. Subsequently, the pretreatment residue was leached with water for 3 hours at a solid percentage of 10%. As part of the experiment, different temperatures and proportions by weight of acid-mineral were considered during the water leaching stage. The authors concluded that a higher acid-mineral mass ratio encourages greater phosphate decomposition, which increases rare earth extraction. Likewise, the authors indicated that increasing the temperature during the leaching stage with water is detrimental to extraction, since the solubility of the species of interest decreases with temperature. When applying an acid-mineral ratio of 2.0 and leaching with water at 25°C, it was possible to extract between 96.5% and 100% of the different rare earths present. Finally, the authors considered a process of caustic digestion with NaOH at different concentrations and temperatures for 3 hours, after which the residue was washed with water and leached with HCl at different concentrations for 3 hours at 80°C and at a solid percentage of 20%. The authors identified that a higher concentration of HCl during acid leaching increases extraction, while rare earth extraction is maximum when the concentration of NaOH during the alkaline digestion is 30% (both lower and higher NaOH concentration reduce rare earth extraction). Finally, in the evaluated ranges for the parameters, it was found that a digestion with NaOH at 30% concentration followed by an acid leaching with HCl at 3 M maximizes the leaching of rare earths, which exceeds 98% of extraction [43].

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CHAPTER III

METHODOLOGY

This section describes the experimental methodology and the procedure for analyzing the data obtained from such experiments. The selection and justification of the research designs and their relationship with the specific objectives is presented in **Annex 1**. The laboratory procedure is detailed first, to later establish the bases on which technical and economic decisions were made based on the experimental results.

3.1. Experimental design

The experimental procedure was subdivided into three stages. Each of these stages evaluated the results of independent or linked hydrometallurgical unit processes, subjected to different parameters, all evaluated at two levels. To ensure the accuracy of the experiments, all tests were carried out in duplicate. It was ruled out to perform the experiments in triplicate due to limitations in the availability of the reagents and mineral samples required for each trial. A total of twelve samples of ore were required to carry out the tests.

The evaluated hydrometallurgical unit processes were the following:

a) Alkaline pretreatment with KOH to enhance subsequent gold and/or rare earth extraction in case the rare earths are present as monazite.

b) Acid leaching of rare earths with HCl.

c) Thiourea leaching of gold in acid medium in presence of ferric ion.

To study the effect of each of these unit processes, thiourea leaching was evaluated first, then acid leaching followed by thiourea leaching, and, finally, the concatenation of the three unit processes (alkaline pretreatment, followed by acid leaching and later by thiourea leaching, considering washing the mineral between each stage). In each of these 3 experimental steps, one independent variable that impacts on the performance of each process was modified in 2 levels. The response variables were the consumption of reagents and the extraction of both gold and rare earths. Although temperature can significantly affect the results, it was not considered as an independent variable because safe temperatures for laboratory work were used, so that they can be scaled to an artisanal level. The kinetics of each process was followed by evaluating the response variables in specific control times.

The ore samples were artisanal concentration tailings from a gravimetric table from Madre de Dios. Sampling began with 20 kg of dry ore of density 4,420±0,001 g/cm^3 (determined using an ULTRAPYC 1200e gas pycnometer). The original sample was quartered using a canvas until obtaining four samples of 80 g, four samples of 85 g, and four samples of 95 g, approximately. In addition, other samples were separated to determine the granulometric distribution of the mineral in a Ro-Tap, using ASTM E11 sieves of meshes 70, 100, 140, 200, 270 and 400. The particle size distribution of the samples is detailed in **Annex 2**, from which was determined that the average particle diameter d_{50} was 0.12 mm. Additionally, samples were separated for analysis by multi-element and rare earth inductively coupled plasma (SPECTRO ARCOS® ICP-OES model) and atomic absorption spectroscopy (Perkin-Elmer® Atomic Absorption Spectroscopy 3110 model), tests that were performed in an external laboratory after digestion with *aqua regia*. The elemental composition of the initial sample is detailed in **Annex 3**. Based on these results, the only rare earths evaluated throughout this work are cerium, lanthanum, and yttrium, since these metals are relatively abundant in the samples. While thorium is an actinide and not a rare earth, it was also evaluated due to its abundance in the sample and to its economic value.

For thiourea gold leaching, Sigma-Aldrich thiourea ReagentPlus® (≥99.0%), Himedia ferric sulfate HI-AR™, and JT Baker Analyzed™ (95.0-98.0%) sulfuric acid were used. For thiourea titration, Scharlau EssentQ® soluble potato starch and Scharlau Titrasure® (≥99.4%) potassium iodate were required. JT Baker Analyzed™ (36.5-38%) hydrochloric acid was used for acid leaching, while Biopack potassium hydroxide in pellets, ≥85.0% was required for performing alkaline pretreatments. Additionally, Scharlau Titrasure® (≥99.95%) Potassium Hydrogen Phthalate (KHP) and Fremont phenolphtalein indicator solution (<1.0%) were used for acid-base titrations.

3.1.1. First experimental step

As part of this stage, a total of two different tests of thiourea leaching of gold were performed. This involved the evaluation of one independent variable (thiourea concentration) at two levels. Likewise, the response variables considered at this stage were the consumption of thiourea, H_2SO_4, and ferric sulfate per ton of processed ore, as well as gold extraction. **Figure 3.1** presents a scheme of the first experimental step, which will be described in detail below:

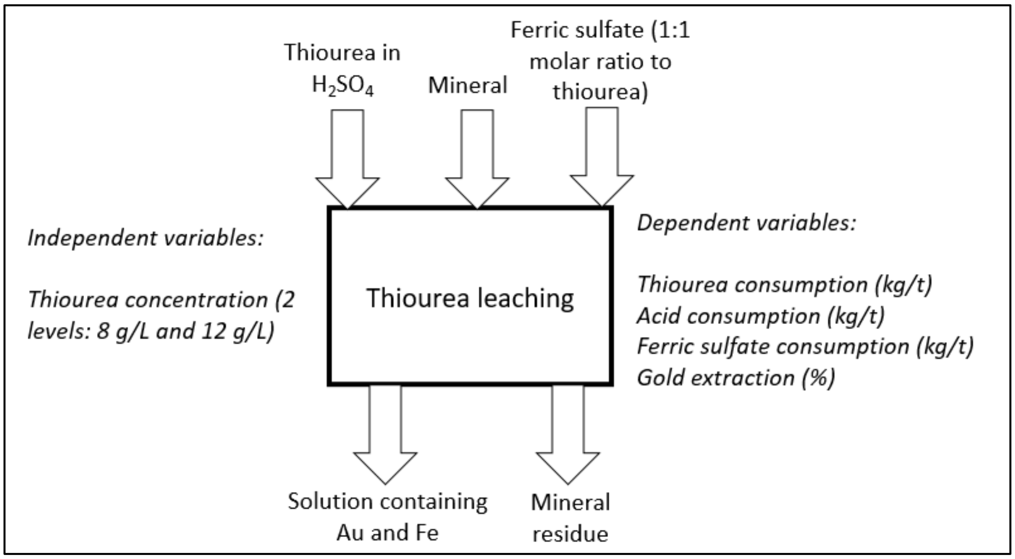

Figure 3.1. Scheme for the first experimental step that involved thiourea leaching of gold.

The following samples were used for the first experimental step, considering the thiourea concentrations detailed in **Table 3.1**:

Sample code	Sample amount (g)	Thiourea concentration (g/L)
E.1.1	78.5	8
E.1.2	81.0	8
E.2.1	79.5	12
E.2.2	80.0	12

Table 3.1. Samples used for the first experimental step.

The first experimental step comprised the following procedure: First, a 500 mL beaker was labeled and weighed. In this beaker, a known mass of dry mineral sample of approximately 80 g was mixed with ~120 mL of water to obtain a 40% solid pulp. Next, either 8 or 12 g of solid thiourea were added per liter of solution (approximately 0.96 g or 1.44 g of thiourea, respectively), as well as a molar equivalent amount (1:1 molar ratio) of ferric sulfate (approximately 5.04 g or 7.56 g of ferric sulfate, respectively). The weighed mass of ore is slowly added to the beaker, the contents of which were stirred lightly. The pH was adjusted to 1.5 by adding H_2SO_4 dropwise. At that moment, the stirring speed was increased, and the time of the experiment began, which had a total duration of 4 hours. The thiourea leaching experiments were performed at room temperature (15°C-22°C). The evaluated thiourea concentrations and the used operation conditions were extracted from the research of Olyaei et al. described in the previous chapter [26].

The experimental system was controlled after 5 min, 15 min, 30 min, 60 min, 120 min, 180 min, and 240 min. As part of each of these controls, two aliquots of pulpless solution were extracted, one of 5 mL for determination of extracted gold by atomic absorption (AA), and another 2 mL for redox titration of thiourea with potassium iodate as a titrant and starch as an indicator, according to the method established by Calla-Choque and Nava-Alonso [44]. The AA analysis was performed using a Shimadzu AA7000 Atomic Absorption Spectrophotometer. The pH of the solution was also measured at each control time. After the measurements, the corresponding mass of water was replenished to account for the extracted aliquots, adding the mass of thiourea and ferric sulfate consumed according to the results of the titration. The mass or volume of each of the added reagents per control were recorded.

Finally, the obtained solid was filtered, the solution was stored and sent for analysis to determine the amount of extracted gold (via AA) and other metals (via ICP at an external laboratory). The solid was washed with distilled water until obtaining an aqueous effluent of pH greater than 6. The solid was then dried on a heating plate at 80°C and stored in case residue analysis was required afterwards.

3.1.2. Second experimental step

The study now focused on the unit process of acid leaching of rare earths and on its effect on the subsequent leaching of gold with thiourea. As part of this step, two different tests were carried out, evaluating one independent variable (HCl concentration during acid leaching) at two levels. On the other hand, the considered response variables were the consumption of HCl and the percent extraction of the rare earths present in the ore. In addition, all the response variables from the first experimental step were also evaluated, given that acid leaching could have an impact on subsequent gold leaching. For this evaluation, the thiourea leaching of the residue was performed using the thiourea concentration that offered the best results (reagent consumption and gold extraction) in the first experimental step, as presented in the next chapter. **Figure 3.2** displays a scheme of the second experimental step:

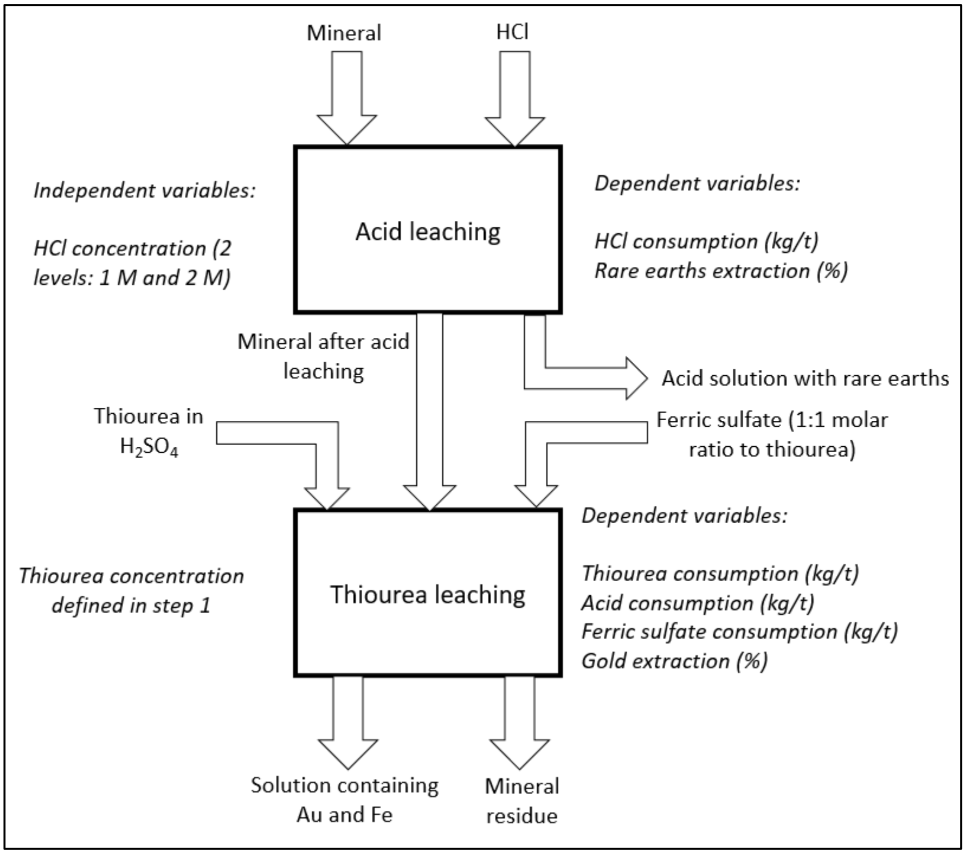

Figure 3.2. Scheme for the second experimental step that involved thiourea leaching of gold preceded by acid leaching of rare earths.

The following samples were used for the second experimental step, considering the HCl concentrations detailed in **Table 3.2**:

Sample code	Sample amount (g)	HCl concentration (M)
E.3.1	85.0	1
E.3.2	85.0	1
E.4.1	85.0	2
E.4.2	85.0	2

Table 3.2. Samples used for the second experimental step. Subsequent thiourea leaching concentration (8 g/L or 12 g/L) was determined from the results of the first experimental step.

For the second experimental step, a labeled and weighed 2 L beaker was required (the beaker size was selected to prevent any spillage due to unexpected reactions with the hot acid), along with a known mass of dry mineral sample of 85 g. This mass was needed to extract solid samples from the acid leaching residue and to still have ~80 g for thiourea leaching afterwards. Then, ~340 mL of HCl solution sufficient to obtain a 20% solid pulp were added to the beaker. The concentration of HCl in the solution was set to either 1 M or 2 M. The HCl solution was covered with a watch glass and heated under stirring to about 80°C. Once the desired temperature was reached, the mineral was added slowly to the beaker, monitoring that the temperature remained constant. From this moment, the time was controlled, ensuring that the stirring provided to the pulp was vigorous. The experimental period was 3 hours. This procedure was based on the methodology followed by Kim et al., the results of which were described in the previous chapter [43].

The experimental system was controlled at 5 min, 15 min, 30 min, 60 min, 120 min and 180 min. As part of each of these controls, the temperature was adjusted to 80°C. Additionally, the concentration of HCl was measured by acid-base titration with a previously standardized (with potassium hydrogen phthalate) KOH solution. For titration, an aliquot of 2 mL of pulpless solution was required. Additionally, another 10 mL aliquot was separated for ICP analysis. To conclude with the control, the mass of solution corresponding to the extracted aliquots was replenished, adding more HCl if the concentration determined by titration was lower than the acid concentration specified for the test (1 M or 2 M). The mass or volume of the reagents that were added at each instant of the experiment was recorded. While aliquots for ICP were extracted at each control time, only the ones from the final control times (180 minutes) were sent to know whether any extraction had taken place or not.

After the 3 hours, stirring and heating was stopped. Immediately afterwards, the pulp was filtered while still hot. The solid residue was washed with distilled water until reaching a pH greater than 6 in the effluent. The solid was then dried on a heating plate at 80°C to separate it into two fractions by quartering. One of the fractions was of ~80 g and the other of ~5 g. The lesser fraction was stored in case further analysis were required, while the greater fraction was leached with thiourea, following the protocol described in the previous section and considering the thiourea concentration that offered more favorable results in the first experimental step.

3.1.3. Third experimental step

The third experimental step focused on the unit process of alkaline pretreatment of the ore, although the effect of this process on the other two hydrometallurgical stages was also studied. A total of two different tests were carried out, considering one independent variable (KOH concentration), which was evaluated at 2 levels. The response variables considered at this step were the consumption of KOH, as well as the dependent variables described for the previous experimental steps. For the subsequent leaching processes, they were performed with the concentration of reagents that offered the best results during the first two experimental steps, which will be described in the following chapter. **Figure 3.3** presents an outline of the third experimental step, which is detailed below:

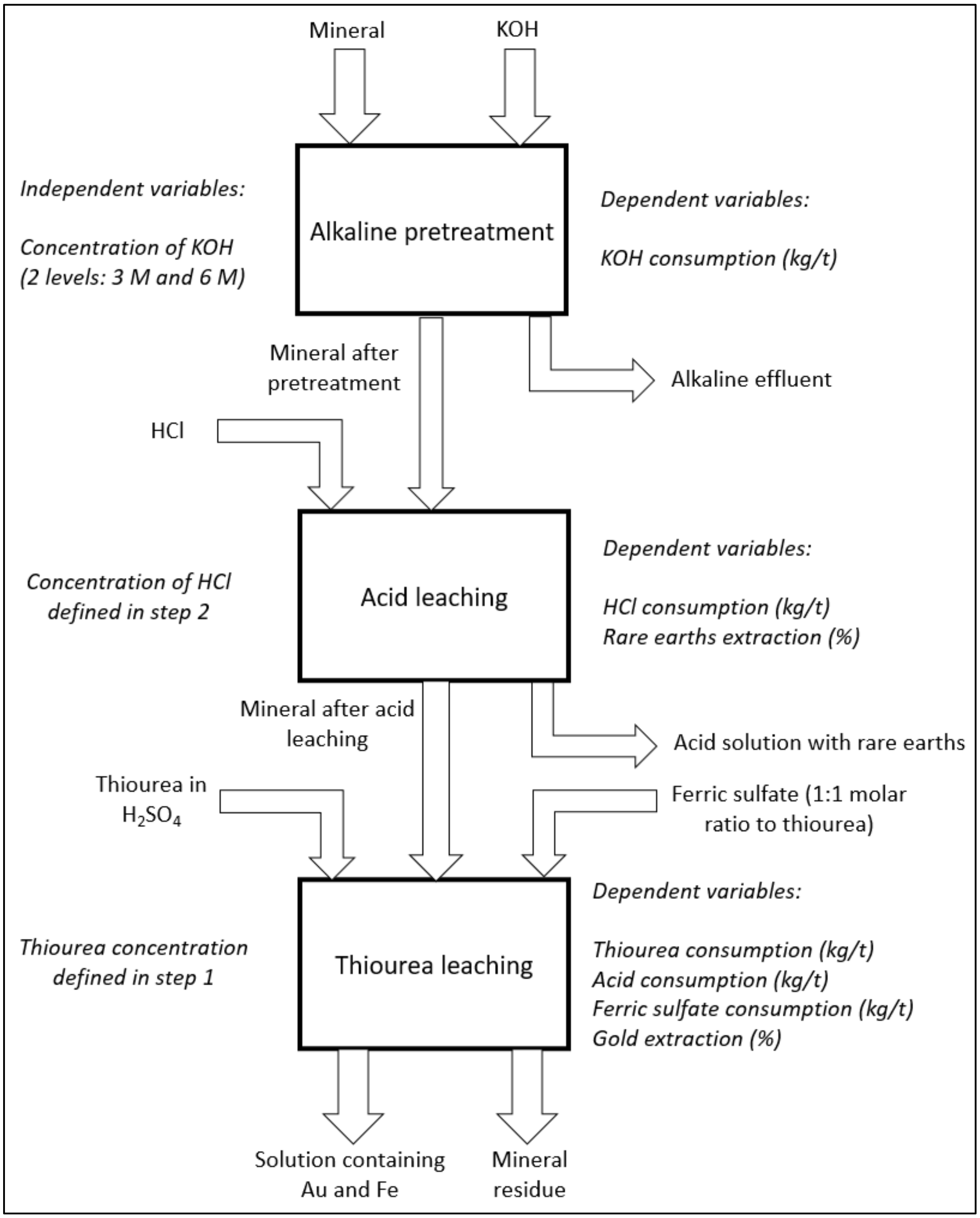

Figure 3.3. Scheme for the third experimental step that involved thiourea leaching of gold preceded by acid leaching of rare earths and an alkaline pretreatment.

The following samples were used for the third experimental step, considering the KOH concentrations detailed in **Table 3.3**:

Sample code	**Sample amount (g)**	**KOH concentration (M)**
E.5.1	95.0	6
E.5.2	95.0	6
E.6.1	95.0	3
E.6.2	95.0	3

Table 3.3. Samples used for the third experimental step. Subsequent acid and thiourea leaching concentrations were determined from the results of the first and second experimental steps.

A previously labeled and weighed 2 L beaker was required (the beaker size was selected to prevent any spillage due to unexpected reactions with the hot KOH aqueous solution) for the third experimental step. Additionally, a known mass of dry mineral sample of approximately 95 g was required, to have ~80 g of sample for thiourea leaching after accounting for solid residues stored after each stage. Then, ~380 mL of KOH solution were added to the beaker such that a 20% solid pulp was obtained after adding the mineral. The KOH concentration in the solution was set to either 3 M or 6 M. The KOH solution was covered with a watch glass and heated under gentle stirring to about 80°C. Once the desired temperature was reached, the mineral was slowly added to the beaker, controlling the temperature. From this moment, the time was measured, ensuring that the stirring provided to the pulp is vigorous. The experimental period was 3 hours. The procedure described was based on the methodology followed by the studies of Kim et al. and Panda et al., whose main results were presented in the previous chapter [39], [43].

The system was controlled at 5 min, 15 min, 30 min, 60 min, 120 min, and 180 min. As part of each of these controls, the temperature was adjusted, as well as the concentration of KOH, which was measured through acid-base titration with a solution of KHP. For such titration, an aliquot of 2 mL of pulpless solution was required. To finish the control, the mass of solution corresponding to the extracted aliquots was replenished, adding more KOH if the concentration determined by titration was lower than the alkali concentration specified for the test (3 M or 6 M). The mass or volume of the inputs added at each instant of the experiment was recorded.

After the experiment, the hot solution was filtered, and the alkaline effluent was sent for analysis by ICP to an external laboratory. The solid was then washed until the effluent had a pH lower than 8. After discarding the washing water, the solids were dried on a heating plate at 80°C. Finally, the dry residue was divided into two fractions of ~90 g and ~5 g. The lesser fraction was stored in case further analysis were required in the future, while the greater one was used for acid leaching with HCl.

3.1.4. Sedimentation time after thiourea leaching

The time required for fine particles to sediment after thiourea leaching was evaluated by adding ~20 mL of pregnant leach solution to a 25 mL test tube. The solution, which had dispersed fine particles, was shaken before introducing it into the test tube. The tube was oriented vertically, and a ruler was placed at its side, in a well-lit space. A picture of the tube was taken immediately after the solution was added. Additional pictures from the same position and angle were taken after 5 min, 15 min, 30 min, 60 min, 90 min, 120 min, 180 min, 240 min, 480 min, 720 min, and 1440 min. The sedimentation time required for the particles to fully settle was taken as the time required to reach a state in which no further sedimentation was observed with passing time. No further analysis was conducted, as the goal was to establish semi-quantitatively the sedimentation time for process design.

3.2. Statistical data processing

The data from the different experiments was statistically processed using Excel 16.0 spreadsheets. In this program, the averages and standard deviations were computed to represent the combination of the duplicate data points. Thus, all the results have an assigned margin of error which is based on their standard deviation.

On the other hand, the experimental results that required graphical representation were processed so the average values of the recorded experimental data could be shown in the graphs, along with error bars, which indicated the standard deviation linked to each data point. Likewise, the program was also used to adjust the data obtained to functions by linear regression, if deemed necessary. For this purpose, the quality criterion of the adjustment was taken as a coefficient of determination (R^2) greater than 0.95.

Hereafter, changes or differences that are described as statistically significant will refer to cases in which there is no overlap in the interval corresponding to a result's standard deviation centered around its mean value and that same interval calculated for a different data point after modifying an independent variable. Likewise, in graphical representations, statistically significant changes will refer to those that present data points whose error bars do not overlap with the error bars of the data point of the same dependent variable before changing the independent one.

3.3. Basis for process design and analysis

The implementation of the studied hydrometallurgical stages was analyzed according to the amounts of gold and rare earths extracted in each of them, as well as on the consumption of reagents and energy in each step. The analysis was based on the scale required to meet the production of an artisanal community from Madre de Dios which operates fourteen gravimetric tables for 8 hours each day. This accounts for ~40 kg of gravimetric tailings produced per day, according to a private communication. Based on this information, it was evaluated whether the concatenation of the three unit processes was technically and economically feasible or if, on the contrary, it was only convenient to implement some of the stages or none at all.

The mass balance of the process was based on heuristic considerations. Fine tailing particles were taken as approximately 10% of all gravimetric table tailings, in accordance with the ASTM E11 -270+400 and -400 fractions from the granulometric distribution presented in **Annex 2**. Purity of technical grade reagents was not taken into consideration for the mass balance, although it was considered for the economic calculations. Water balance was not rigorous since significant water losses may occur during scale-up and water may come along with the gravimetric tailings into the process as a slurry. Thus, an error margin of 20% for water consumption was estimated. Zinc was suggested for cementation, in the molar proportion of ~28.1 moles of zinc per mole of gold (~9.33 g of zinc per gram of gold), although this is a literature-based estimate that should be confirmed for the specific pregnant leach solution. This estimate is based on the conditions for which the literature results were obtained (temperatures between 15°C and 35°C and a pH of ~1.2, which are similar to the operating conditions of the designed process) [30]. The required amount of sulfuric acid that will be used to dissolve zinc will depend on the number of batches that will be processed with the same acid bath. 2.55 M sulfuric acid is required to dissolve zinc particles to recover zinc-free, high purity solid gold (1.5 g of sulfuric acid are required to dissolve 1 g of zinc) [31]. Tentatively, an acid bath will be reutilized for 50 batches. Water consumption, along with all the other reagent requirements, should be validated after scaling up the process. The following sulfuric acid and ferric sulfate neutralization reactions were employed to calculate quicklime requirements for the mass balance [45]:

$$\mathrm{CaO_{(s)} + H_2SO_{4(aq)} = CaSO_{4(s)} + H_2O_{(l)}} \tag{7}$$

$$\mathrm{3CaO_{(s)} + 3H_2O}_{(l)} \mathrm{+ Fe_2(SO_4)_{3(aq)} = CaSO_{4(s)} + Fe(OH)_{3(s)}} \tag{8}$$

Preliminary sizing of the required equipment for the selected unit processes was performed next. Reactor sizing was based on conventional stirring tank geometric parameters (reactor diameter to fluid height proportion of 1:1, impeller diameter to reactor diameter proportion of 1:3, and impeller height to reactor diameter proportion of 1:3) [46]. For stirred reactors, an A310 impeller type was selected, since it is frequently used to suspend solid slurries [47]. The diameter and nominal height of the reactor were calculated by considering only the volume occupied by the main components in each tank (water and mineral particles). However, effective reactor height considered a 1.5 factor to provide sufficient additional volume for the remaining reagents, the stirring system, the vortex that will be formed, and for uncertainties in the calculations.

A sedimentation tank was designed as a cylinder with a height to diameter ratio of 1:4, which is a common ratio for gravity-based settling systems. This proportion was used to calculate the diameter and the nominal height of the sedimentation tank based on the volume of slurry that needs processing [46]. Effective tank height was increased by 50% to account for uncertainties in the calculations.

The volume that the tailings dam is required to hold was calculated based on the total volume of tailings (solids and effluents) produced per batch, which was multiplied by the number of batches that are expected to be processed throughout the period of operation of the project.

To provide a raw estimate of the area required to install all the sized equipment, the cross-sectional area of the reactors and the sedimentation tank will be calculated from their diameters. Afterwards, the total area will be multiplied by a factor of 30 to consider that all pieces of equipment should be separated from one another for safety reasons, to allow the worker to move freely around the area, and to provide space to store all reagents, auxiliary tanks, and buckets. Likewise, to estimate the area required to build the dam, its height will be taken to be ~1 m. Adding these two area estimates, total required surface area will be calculated referentially. A plant layout will not be presented herein since the dam will account for most of the plant area and its details of construction (geometry) lie beyond the scope of the present work, which is focused on process design rather than on plant design.

The energy balance of the process was also based on heuristic considerations and correlations. Energy for slurry transport through pumps is not considered since slurries will be transferred manually using buckets. The only energy requirement is associated to slurry stirring. On that matter, the stirring speed required to suspend a slurry was estimated from the Zwietering correlation [47]:

$$\mathrm{N_{js}} = \mathrm{S}\left(\frac{\mathrm{g}(\rho_S-\rho_L)}{\rho_L}\right)^{0.45}\frac{d_p^{0.2}\nu^{0.1}X^{0.13}}{D^{0.85}} \tag{9}$$

Where:

N_{js}: Stirring speed to ensure particle suspension (rev/s)

S: Zwietering constant (6.39 for A310 impeller type)

g: Acceleration of gravity (9.81 m/s^2)

ρ_S: Solid density (kg/m^3)

ρ_L: Water density (kg/m^3)

d_p: Particle mean diameter (m)

v: Water kinematic viscosity (m^2/s)

X: Mass ratio percent (100×mass of solid/mass of liquid)

D: Impeller diameter (m)

Afterwards, power consumption due to stirring was calculated by using the following equation, including a 70% motor efficiency factor [48]:

$$0.7\mathrm{P}_{\mathrm{js}} = \rho_{SL}\mathrm{N}_{\mathrm{p}}\mathrm{N}^3\mathrm{D}^5 \quad (10)$$

Where:

N_p: Power number (0.3 for A310 impeller type)

N: Stirring speed (rev/s, $N=N_{js}$ for slurry suspension)

ρ_{SL}: Slurry density (kg/m^3)

Once the characteristics of the hydrometallurgical processing stages have been defined, a hazard identification, risk assessment and control measures (HIRAC) matrix was built based on ISO 45001: Occupational health and safety management systems [49]. This matrix evaluated the hazards and risks associated with the development of the hydrometallurgical stages that were finally considered. The risks were assessed as the product of severity of the risk (from 1 to 5) and probability of occurrence (from 1 to 5). Thus, all risks were evaluated in a scale from 1 to 25, where 25 would be the risk of a fatal and probable event occurring. Afterwards, administrative control measures and personal protection equipment (PPE) were suggested, and the risk was reassessed to evaluate how the suggested measures reduced the probability of the event from occurring. Hazard elimination, hazard substitution, and engineering control measures were not considered in the analysis.

To schedule the process, all required activities were listed, mentioning the estimated time required for completion and the equipment required for each of them. Additionally, the activities were classified based on if they require supervision. This information was used to create schedules for two consecutive days (8 hours a day plus an additional hour of lunch break). The considerations for the schedules were that only one activity can occur per equipment at the same time and that only one supervised activity can occur at any given time.

Based on the designed process, the capital expenditure (CapEx) and the operational expenditure (OpEx) linked to the process were evaluated, considering a level of accuracy of a study estimate (preliminary), which corresponds to a margin of error between 20% and 30%. Pricing data and foreign exchange rates (USD 1.00 is equal to PEN 4.00, to INR 74.35, or to GBP 0.74 [50]) were accurate as of 14 November 2021.

Part of the capital investment is related to procuring equipment from Peruvian and international sellers. Since no tank or piece of equipment will be tailor-made for the process, the sizing results will only be taken as estimates, which implies that a design in detail of the required equipment is not needed. Conventional tanks will be acquired and adapted to achieve dimensions close to the calculated ones: ±20% in linear dimensions is acceptable if the tanks can still hold their contents adequately. Installation and location factors are neglected for the analysis, due to the artisanal scale of the project (most pieces of equipment will be acquired locally).

A raw estimate of the capital investment associated to building a tailings dam will be obtained by scaling down data from a technical estimation generated for the construction of a tailings dam for Dynacor Gold Mines in Ayacucho. The estimated cost for a tailings dam expected to hold 94030 m^3 is of $1.26 million. This estimate includes costs associated to designing and building the dam (which includes procuring and installing a drainage system and a geomembrane liner), producing an Environmental Impact Assessment, as well as designing and procuring materials for a mine closure plan after filling the dam [51]. Scaling down this estimate results in a cost of ~$13.40 per cubic meter of tailings. Due to the very different scales of processing between the Dynacor Gold Mines dam and the one required for the process, this estimate will be roughly doubled to account for economies of scale, yielding a cost of $25 per cubic meter of tailings.

Total capital expenditure will be increased by 50% to account for customization of acquired equipment, freight costs, land acquisition cost, and customs fees. For the sake of formalization, the project (including previous stages of gravimetric concentration) should obtain an environmental permit. However, the fees associated to the permit are neglected within the economic evaluation of the project, since this cost should be partially covered by the income from the gravimetric concentration stages.

Operational expenditure was calculated as the addition of variable and fixed operational costs. Variable operational expenditure was estimated per batch and included the cost of raw materials (reagents) and utilities (water and electricity). Fixed operational expenditure considered salary of workers and maintenance expenses [52]. The investment in raw materials was based on international technical grade reagent selling sources. Total price of reagents was increased by 50% to account for freight costs, customs fees, and proper disposal of the empty containers in which reagents (particularly sulfuric acid) were originally acquired. The price of water was estimated from the latest available information for this resource for industrial purposes, as sold by a water provider from Madre de Dios. Likewise, the price of electricity was referentially taken as that indicated by the Peruvian government's electricity regulatory body (OSINERGMIN) for non-residential use in rural areas of Madre de Dios. The salary of the worker was competitively set above Peruvian current minimum monthly wage ($232.50 as of 14 November 2021 [53]). Given the scale of operation, the project would be classified within the *MYPE* (Micro and Small Business by its initials in Spanish) regime under Peruvian legislation, so the only social benefits that must be paid to workers are 15 days of vacation (~4.2% of monthly salary) and affiliation to Peruvian National Health Services (9% of monthly salary) [54]. The assigned salary will be referentially increased by a factor of 20% to account for these social benefits and for transport for the worker. An annual salary rise of 3% was factored to account for inflation [55]. Maintenance expenses were referentially estimated as 5% of the capital investment in the equipment that may require maintenance.

The expected cash flow statement of the process was evaluated based on the previous results for a five-year projection. To account for holidays and unexpected events, 80% of the maximum number of yearly batches (according to the schedule of the process) were considered. The fluctuations of the gold price were neglected for the purpose of the evaluation, for which a referential price of ~$1800 per troy ounce ($57.87 per gram) of gold was taken as a 2021 average [56]. Current artisanal operation neglects the payment of taxes. However, in the sake of formality, taxes and depreciation were considered for the cash flow statement. Gross profit was calculated on a yearly basis by subtracting the operational expenses (fixed and variable) from the gold sales from each year. Afterwards, depreciation charges were subtracted from the gross profit to obtain the taxable income, to which a 29.5% tax is applied, in accordance with Peruvian legislation [57]. The method that was used to calculate depreciation charges was linear depreciation of all capital expenditure over a period of five years. Finally, the cash flow of each year was the result of subtracting the applied tax from the gross profit [52]. The cash flow of the zeroth year was taken as the negative of the total capital expenditure.

From the previous information, the profitability associated to the selected set of hydrometallurgical stages was evaluated by calculating the net present value (NPV) and the internal rate of return (IRR) indicators of the process [52]. To evaluate the NPV, a discount rate of 15% was considered, to account for uncertainties and for the financial risk for prospective investors. Both profitability indicators were calculated by using their respective Excel functions (=NPV and =IRR). A sensitivity analysis was also performed by evaluating how the NPV of the process was affected by varying the total capital expenditure, the price of gold, the production scale (number of batches per year), and the cost of reagents.

CHAPTER IV

RESULTS AND DISCUSSION

This section describes and analyzes the results obtained from performing the three experimental steps presented in the previous chapter. Additionally, it covers the design and evaluation of hydrometallurgical stages for reprocessing the gravimetric table tailings based on technical-economic criteria and safety considerations.

4.1. First experimental step

The scope of the first experimental step was to evaluate only acid thiourea leaching of the mineral, for which all conditions were consistent with the experimental design detailed in the previous chapter.

4.1.1. Thiourea leaching of gold

Gold extraction and reagent consumption results for thiourea leaching will be presented in this section. Firstly, the averaged gold extraction kinetic results during thiourea leaching are shown in **Figure 4.1**, where the whiskers represent the standard deviation of the duplicates for each thiourea concentration. These results were calculated based on the concentration of gold found in the 2 mL aliquots, along with the gold content that was determined in the as-received sample (14.88±0.07 ppm), according to AA results (**Annex 3**). The gold concentration determined for each of the 2 mL aliquots is reported in **Annex 4.** The dilution of the pregnant leach solution during each of the controls, due to the aliquots that were removed and replenished from the experimental system was accounted for in the calculations.

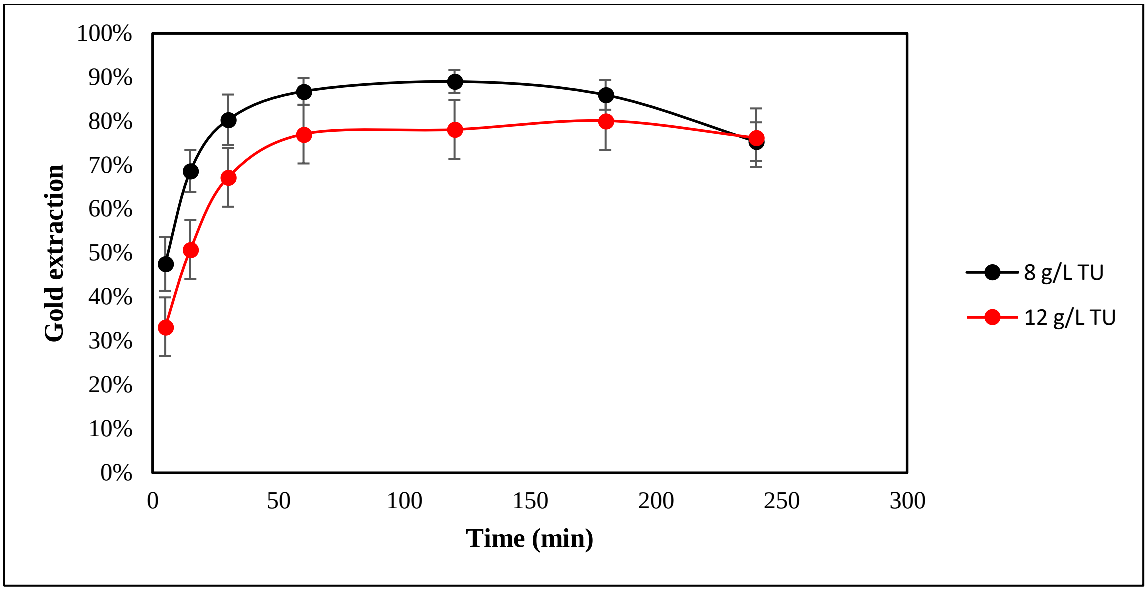

Figure 4.1. Gold extraction kinetics during thiourea leaching for thiourea concentrations of 8 g/L and 12 g/L.

Based on **Figure 4.1**, there is sufficient statistical evidence to indicate that a greater gold extraction can be achieved when using a thiourea concentration of 8 g/L than one of 12 g/L, particularly throughout the first 180 minutes. Additionally, the maximum gold extraction is obtained after 60 minutes, since the slight increase observed after 120 minutes is not statistically significant for either thiourea concentration. A key aspect is that the accumulated gold extraction trend is reversed after 180 minutes. This phenomenon may be explained by either gold adsorption (preg-robbing) over the surface of clays or organic matter present in the sample or because of the progressive formation of stable Fe(III)-thiourea complexes, which can lead to gold precipitation due to consumption of the ligand.

Thiourea consumption kinetics for each of the concentrations was also followed throughout the leaching period, as shown in **Figure 4.2**. These results are based on the measured concentrations of thiourea throughout each of the experiments, information which is displayed in **Annex 5**. **Figure 4.2** considers only the thiourea that was consumed by the reaction, disregarding the quantity required to begin the leaching stage (12 kg/t and 18 kg/t for 8 g/L and 12 g/L of thiourea concentration, respectively). Ferric sulfate consumption was not followed directly, but it is consumed at the same rate as thiourea. Approximately, an estimated 5.25 kg of ferric sulfate are consumed per kg of thiourea.

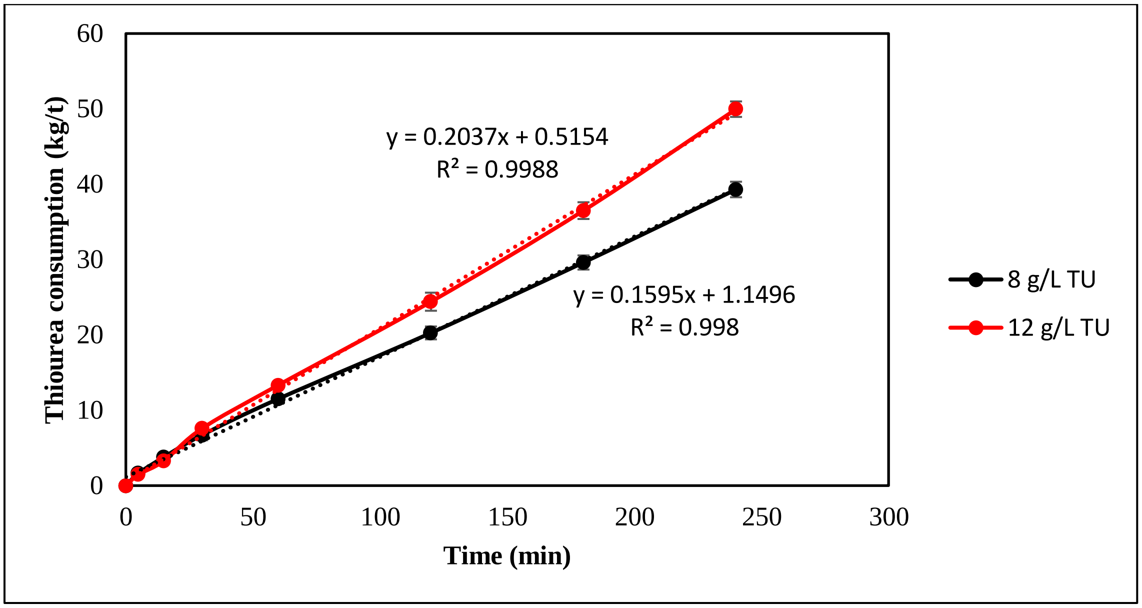

Figure 4.2. Thiourea consumption kinetics during thiourea leaching for thiourea concentrations of 8 g/L and 12 g/L.

Two important findings are observed in **Figure 4.2**. Firstly, thiourea consumption exhibits a linear behavior regarding time. This can be explained by the addition of ferric sulfate in a molar equivalent proportion to thiourea, which promotes the formation of Fe(III)-thiourea complexes, in addition to providing the media required for the leaching process to take place. This suggests that most thiourea consumption is due to the formation of Fe(III) complexes rather than to gold leaching, which can be explained by the relatively high abundance of iron (as ferric sulfate which is already in solution and is continuously added) with regards to gold (as part of a fixed amount of mineral). This is not to say that the ferric sulfate is consuming all thiourea, but rather that it will consume more than gold because it is in a higher concentration. It is also noteworthy that the formation of certain Fe(III)-thiourea complexes is more thermodynamically favored than that of gold-thiourea, as shown by the equilibrium constants in **Equations (1)-(4)**. Secondly, thiourea consumption is higher when the concentration for this reagent is set to 12 g/L than when it is set to 8 g/L. This is expected since a higher concentration of both ferric sulfate and thiourea should favor the reaction kinetics for the formation of the Fe(III)-thiourea complex, while gold leaching is still limited by the amount of gold available in the mineral. However, increasing thiourea concentration did not seem to have an important effect on gold extraction kinetics, although it reduced overall extraction, as was shown in **Figure 4.1**.

Further processing of the data from the first experimental step yields the information shown in **Table 4.1**, in which the results associated to the maximum gold extraction are summarized. Thiourea and ferric sulfate requirements include the amount of reagents consumed as part of the reaction and the quantity required to reach the desired initial concentration. On that matter, the reagent requirements are related to the total reagents that were added until before the 60 minutes control point, which is when the maximum gold extraction was detected for the two thiourea concentrations. The total amount of water and sulfuric acid (scaled from the consumed ~0.25 mL of acid during laboratory experiments) is the same regardless of time and thiourea concentration since these substances were only added in the beginning of each experiment and were not seemingly consumed by the reactions. It is noteworthy that the results displayed in **Table 4.1** cannot be compared with previous experiments from the literature, given that the samples used for these experiments are very different to other minerals, which are often refractory.

Thiourea concentration (g/L)	**Max. gold extraction (%)**	**Time until max. extraction (min)**	**Required reagents for max. extraction**
8	86.8±3.1	60	Thiourea: 18.7±0.7 kg/t Ferric sulfate: 98.2±3.7 kg/t Water: 1500 L/t H_2SO_4 (18 M): ~3.1 L/t
12	77.1±4.4	60	Thiourea: 25.6±0.3 kg/t Ferric sulfate: 134.4±1.6 kg/t Water: 1500 L/t H_2SO_4 (18 M): ~3.1 L/t

Table 4.1. Summarized results for accumulated reagent requirements until maximum gold extraction is achieved in the first experimental step.

The rare earth extraction incapacity of the thiourea leaching stage was confirmed based on an ICP assay of the pregnant leach solution after 240 minutes. The concentration of all rare earths on the solutions was below the detection limit (<1 ppm), regardless of the concentration of thiourea. The concentration of all other valuable metals (aluminum, copper, tin, titanium, zinc, and zirconium) in the leach solution was below 10 ppm for either thiourea concentration, except for the case of iron. However, the high concentration of this metal is due to the addition of ferric sulfate and not because of iron extraction.

4.1.2. Technical decision on gold leaching stage

Based on the previous results, it is apparently convenient to perform the leaching process for only 60 minutes, since the benefit of continuing the process for an additional 2 hours is negligible. Longer times will be detrimental, as it was observed that reaching the fourth hour will result in a poorer gold extraction. Since reagent consumption is high, finishing the process early constitutes a technical and economic advantage. Additionally, it was found that a thiourea concentration of 8 g/L achieves a greater extraction than a 12 g/L concentration. Thus, an 8 g/L thiourea concentration will be considered for the following experimental steps.

Even though the highest gold extraction was identified after 1 hour of leaching, the complete 4 hours process will still be studied in the second and third experimental steps. This is necessary to identify any possible positive or negative effects on gold extraction kinetics of performing the acid leaching and alkaline pretreatment stages before thiourea leaching. Additional exploration is recommended on whether reducing thiourea concentration further or decreasing the molar proportion of ferric sulfate to thiourea increases or maintains overall gold extraction. This would be useful since both strategies yield less reagent consumption.

4.2. Second experimental step

The second experimental step evaluated rare earth acid leaching and a subsequent acid thiourea leaching of the mineral. All conditions for each of the stages were consistent with the experimental design described in the previous chapter. In the case of the thiourea leaching stage, a concentration of 8 g/L of thiourea was considered.

4.2.1. Acid leaching of rare earths

Acid leaching did not offer significant rare earth extraction or of other valuable metals, including gold. This can be observed in **Annex 6** for the detected concentrations of various elements in the extracted aliquots after 180 minutes. Lanthanum will not be followed because its concentration in the aliquots was below the limit of detection provided by the ICP technique, as was the case of gold. Since the determined extractions for rare earths and thorium were not significant, their extraction kinetics were not followed. **Table 4.2** exhibits the percent extraction of cerium, yttrium, and thorium after 180 minutes of leaching. These results were calculated based on the information from **Annex 6**, considering dilution factors due to the replenished aliquots associated to each control.

HCl concentration (M)	**Cerium extraction (%)**	**Yttrium extraction (%)**	**Thorium extraction (%)**
1	4.4±0.8	5.8±0.8	54±7
2	5.0±0.2	5.8±0.1	72±5

Table 4.2. Percent extraction of cerium, yttrium, and thorium after 180 minutes of acid leaching with HCl at concentrations of 1 M and 2 M. The calculations are based on the cerium, yttrium, and thorium concentrations determined in the as-received samples (383.5±16.5 g/t, 82±1 g/t, and 189.5±10.5 g/t, respectively).

As evidenced in **Table 4.2**, cerium, and yttrium extraction during acid leaching of an untreated sample is not significant. This is expected since cerium and yttrium are commonly found as the rare earth phosphate monazite, which is not amenable to acid leaching unless it has received an aggressive alkaline pretreatment [23]. There is not sufficient statistical evidence to indicate that different HCl concentrations affect the extraction of rare earths for an untreated sample. Thorium extraction from the untreated samples was high, particularly for the case of 2 M HCl concentration.

Acid consumption was negligible throughout the rare earth leaching stage, regardless of HCl concentration, as can be observed in **Annex 7**. HCl was only added in each control to account for the extracted and replenished aliquots. Thus, acid is only needed to set the initial concentration, which results in the requirements for water and acid that are displayed in **Table 4.3**.

HCl concentration (M)	**Leaching time (min)**	**Required reagents during 3 hours of HCl leaching**
1	180	Water: ~3667 L/t HCl (12 M): ~333 L/t
2	180	Water: ~3333 L/t HCl (12 M): ~667 L/t

Table 4.3. Summarized results for accumulated reagent requirements during 3 hours of HCl leaching of rare earths of the as-received sample in the second experimental step.

The fact that acid was not consumed throughout the reaction agrees with the poor extraction results. Moreover, it would seem to indicate that no other minerals are being affected significantly by the acid media, which is coherent with the results from **Annex 6**.

4.2.2. Thiourea leaching of gold

Results for gold extraction and reagent consumption during 8 g/L thiourea leaching of the acid leaching residue are presented in this section. The averaged gold extraction kinetic results during thiourea leaching are shown in **Figure 4.3**. These results were calculated based on the concentration of gold found in the 2 mL aliquots, along with the gold content that was determined in the as-received sample (14.88±0.07 ppm), according to AA results (**Annex 3**). Using the gold concentration in the head sample is valid since no gold was extracted from the solid during HCl leaching, according to the results in **Annex 6**. The gold concentration determined through AA for each of the extracted 2 mL aliquots during the 8 g/L thiourea leaching stage from the second experimental step is reported in **Annex 8.** The dilution of the pregnant leach solution during each of the controls, due to the aliquots that were removed and replenished from the experimental system was accounted for in the calculations.

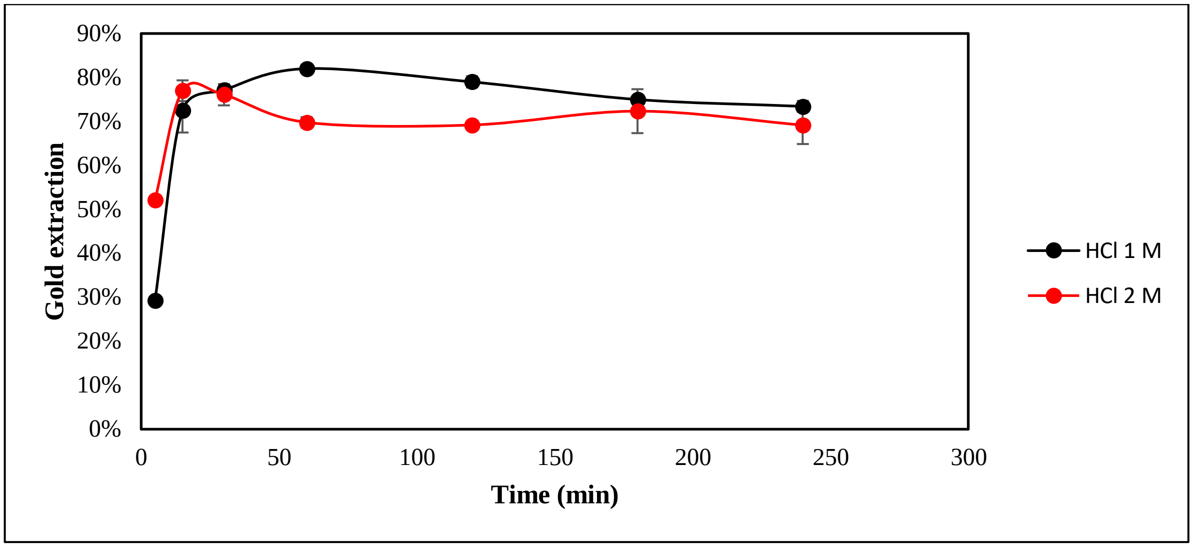

Figure 4.3. Gold extraction kinetics during 8 g/L thiourea leaching after performing 1 M or 2 M HCl leaching for 3 hours.

Based on **Figure 4.3**, there is sufficient statistical evidence to indicate that a greater gold extraction can be achieved after 60 minutes of 8 g/L thiourea leaching after a 180 minutes 1 M HCl treatment than after a 2 M one. However, there is no statistically significant difference between gold extraction after 15 minutes and 30 minutes, regardless of HCl concentration. As observed during the first experimental step, the accumulated gold extraction trend is reversed after reaching a maximum extraction (after 60 minutes and 15 minutes for the samples that were pretreated with 1 M HCl and 2 M HCl, respectively.

Thiourea consumption kinetics after the acid pretreatments was also followed throughout the leaching period, as shown in **Figure 4.4**. These results are based on the measured concentrations of thiourea during the gold leaching stages of the second experimental step, which are displayed in **Annex 9**. **Figure 4.4** considers only the thiourea that was consumed by the reaction, disregarding the quantity required to begin the leaching stage (12 kg/t of thiourea to reach a concentration of 8 g/L).

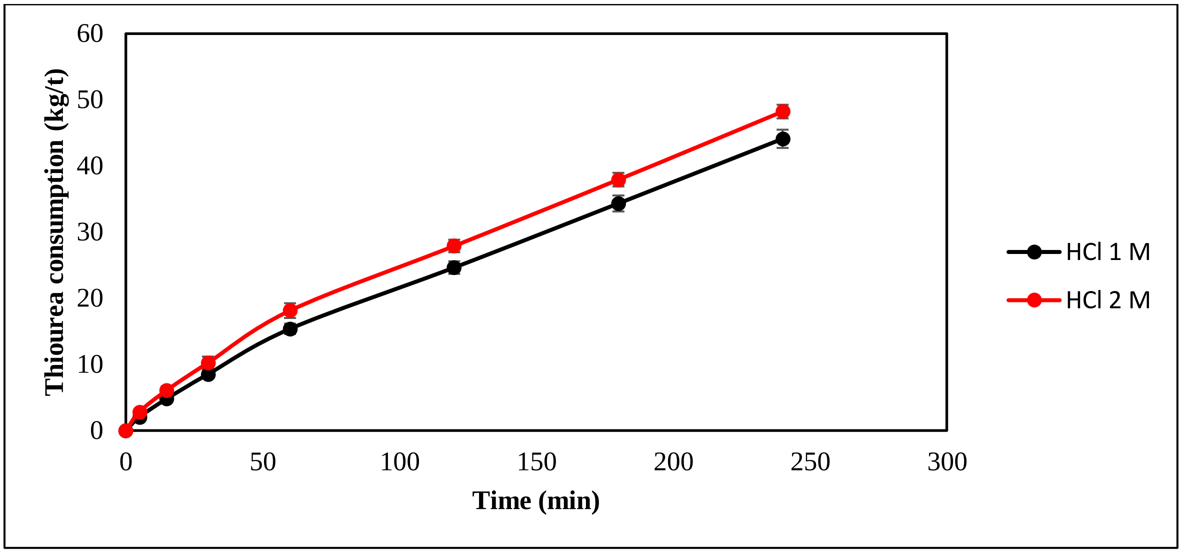

Figure 4.4. Thiourea consumption kinetics during 8 g/L thiourea leaching after performing 1 M or 2 M HCl leaching for 3 hours.

Figure 4.4 reveals that two different thiourea consumption trends exist during the 4-hour leaching period. Regardless of HCl concentration during the pretreatment, the first 60 minutes of thiourea leaching exhibit a greater consumption rate of this reagent than after this time. Moreover, the thiourea consumption rate remains constant after the first 60 minutes. The first observation is likely due to thiourea being consumed by both the leaching reactions with minerals and by its reaction with ferric sulfate to form Fe(III)-thiourea complexes, which agrees with the discussion from the first experimental step. The fact that thiourea consumption increases after an acid pretreatment indicates that HCl activates some minerals, which become amenable to thiourea leaching. After the first 60 minutes, most of the leachable species have already been extracted, so further thiourea consumption is mainly associated to the formation of Fe(III)-thiourea complexes. Again, the linear behavior of thiourea consumption, particularly after 60 minutes, can be explained by the addition of ferric sulfate in a molar equivalent proportion to thiourea in each control, which resets the initial concentrations of both the leaching agent and of the ferric ion.

Further processing of the data from the thiourea leaching stage of the second experimental step produces the information shown in **Table 4.4**. In this table, the results associated to the maximum gold extraction after performing the acid leaching stage are summarized. The displayed thiourea and ferric sulfate requirements include both the mass of reagents required to set the initial concentrations, as well as the consumed amounts after each period. On that matter, the reagent requirements are related to the total reagents that were added until before the 60 minutes and 15 minutes control points for HCl 1 M and HCl 2 M, respectively, which are the periods required to reach maximum gold extraction. The total amounts of water and sulfuric acid were the same regardless of time and HCl concentration during the acid leaching since these substances were not consumed by the reactions.

HCl concentration (M)	**Thiourea leaching time until max. extraction (min)**	**Max. Gold extraction (%)**	**Reagent requirement for max. extraction**
1	60	82.0±0.9	Thiourea: 20.5±0.6 kg/t Ferric sulfate: 107.6±3.2 kg/t Water: 1500 L/t H_2SO_4 (18 M): ~3.1 L/t
2	15	77.0±2.4	Thiourea: 14.8±0.3 kg/t Ferric sulfate: 77.7±1.6 kg/t Water: 1500 L/t H_2SO_4 (18 M): ~3.1 L/t

Table 4.4. Summarized results for accumulated reagent requirements to achieve maximum gold extraction during thiourea leaching following acid leaching at HCl concentrations of 1 M or 2 M.

4.2.3. Technical decision on acid leaching stage

An HCl concentration of 1 M or 2 M yields extraction results that are very similar. The only statistically different results were thorium extraction during acid leaching and gold extraction during thiourea leaching after 60 minutes, following the acid treatment. In that sense, more thorium was extracted after 180 minutes when using the 2 M HCl concentration, while more gold was extracted after 60 minutes of thiourea leaching after 180 minutes of 1 M HCl leaching. Given that gold is more valuable than thorium and that using a lower HCl concentration contributes towards the economic and environmental sustainability of the process, an HCl concentration of 1 M will be considered for the third experimental step.

Since percent extraction of rare earths was low, direct acid leaching of rare earths prior to thiourea leaching of gold is not convenient. Even though acid consumption is negligible, adding the stage and treating its effluents will be more costly than the profit that can be obtained. However, the inclusion of an alkaline pretreatment before the acid leaching stage is evaluated next.

4.3. Third experimental step

The third experimental step evaluated an alkaline pretreatment and its effect on subsequent rare earth acid leaching and acid thiourea leaching. All conditions for each of the stages were based on the experimental design described in the previous chapter. In the case of acid leaching, an HCl concentration of 1 M was considered, while a thiourea concentration of 8 g/L was used for the gold leaching stage.

4.3.1. Alkaline pretreatment

The contents of the alkaline pretreatment solution after 180 minutes of treatment of the as-received samples are presented in **Annex 10.** As expected, no rare earths or gold were extracted during the alkaline pretreatment [23]. On that matter, the only metal apart from sodium and potassium that was detected in significant quantities in the solution is aluminum, although it will not be followed in the present work. The elevated potassium concentration in the solution is due to the use of potassium hydroxide for the pretreatment. The high sodium content is caused by the presence of sodium hydroxide as the main impurity of the acquired potassium hydroxide. This explains why sodium content in the solution was roughly doubled when working at twice the concentration of potassium hydroxide.

Another finding was that very little phosphorus was extracted during the pretreatment, which implies that the rare earth phosphates (monazite) did not undergo the expected reaction presented in **Equation (5)**, with potassium substituting sodium ions**.** If the reaction had taken place, the phosphorus from the formed soluble species potassium phosphate and sodium phosphate would be detected.

While the evaluated experimental parameters for this project were milder than those typically used at an industrial scale (lower temperature, pressure, alkali concentration and higher solid percentage) to reduce energy and reagent requirements, they were not effective at forming rare earth hydroxides. Thus, the alkaline pretreatment that was performed at our selected conditions is not likely to enhance rare earth extraction during HCl leaching. While more extreme operating conditions could be evaluated for our samples, working at temperatures beyond 100°C is neither technically or economically feasible for artisanal or small-scale miners, since working with pressure vessels would be compulsory. Likewise, using greater quantities or concentrations of potassium hydroxide significantly increases overall cost, safety hazards, and the environmental concerns of the process. Thus, these possibilities were not considered as part of the study.

KOH consumption during the alkaline pretreatment stage was negligible, regardless of the set hydroxide concentration, as shown in **Annex 11**. KOH was added in each control only to account for aliquot extraction and replenishment. As a result, KOH is only needed to achieve the initial concentration, which yields the water and KOH requirements displayed in **Table 4.5**. As shown, the amount of KOH required for the pretreatment is very high. For instance, the 6 M KOH pretreatment requires more mass of KOH than of mineral to achieve the desired concentration.

KOH concentration (M)	Pretreatment time (min)	Required reagents during 3 hours of KOH treatment
6	180	Water: ~2931 L/t KOH: ~1069 kg/t
3	180	Water: ~3409 L/t KOH ~591 kg/t

Table 4.5. Summarized results for accumulated reagent requirements during 3 hours of KOH pretreatment leaching of rare earths of the as-received sample.

4.3.2. Acid leaching of rare earths

Acid leaching following the alkaline pretreatment did not offer significant rare earth extraction or of other valuable metals, including gold, regardless of the KOH concentration during the treatment. This can be observed in **Annex 12** for the detected concentrations of various elements in the extracted aliquots after 60 minutes and 180 minutes of 1 M HCl leaching. In this case, gold, lanthanum, and yttrium will not be followed because their concentrations in the aliquots were below the limit of detection. **Table 4.6** presents the percent extraction of cerium and thorium after 60 minutes and 180 minutes of 1 M HCl leaching. These results were calculated based on the information from **Annex 13**, considering dilution factors due to the replenished aliquots associated to each control.

KOH concentration (M) during pretreatment	1 M HCl leaching time (min)	Cerium extraction (%)	Thorium extraction (%)
3	60	4.1±0.8	31±2
3	180	5.6±0.9	59±5
6	60	4.1±0.8	29±3
6	180	6.2±0.3	60±6

Table 4.6. Percent extraction of cerium and thorium after 60 minutes and 180 minutes of 1 M HCl leaching, after 180 minutes of alkaline treatment with 3 M KOH and 6 M KOH. The calculations are based on the cerium and thorium concentrations determined in the as-received samples (383.5±16.5 g/t and 189.5±10.5 g/t, respectively).

As shown in **Table 4.6**, cerium extraction during acid leaching of the samples that underwent a previous alkaline treatment is not significant, regardless of leaching time and of KOH concentration. This is expected based on the results from the alkaline pretreatment, since only traces of phosphorus were extracted during it. Since rare earth phosphates require becoming hydroxides before becoming amenable to acid leaching, poor extraction is more closely related to issues during KOH treatment rather than during HCl leaching. Thorium extraction from the pretreated samples was high, although this result is comparable to the extraction achieved after 180 minutes of 1 M HCl leaching of the untreated sample. In addition, yttrium extraction was negligible during 1 M HCl leaching after pretreating the samples.

There is not sufficient statistical evidence to indicate that different KOH concentrations during the pretreatment affect cerium and thorium extractions. However, there is statistical evidence to support that more cerium and thorium can be extracted if the HCl leaching period is increased. **Figure 4.5** combines the results from **Table 4.2** and **Table 4.6** to compare rare earth and thorium extraction performance after 180 minutes of acid leaching of untreated samples and of samples that underwent a 3 M or 6 M KOH pretreatment.

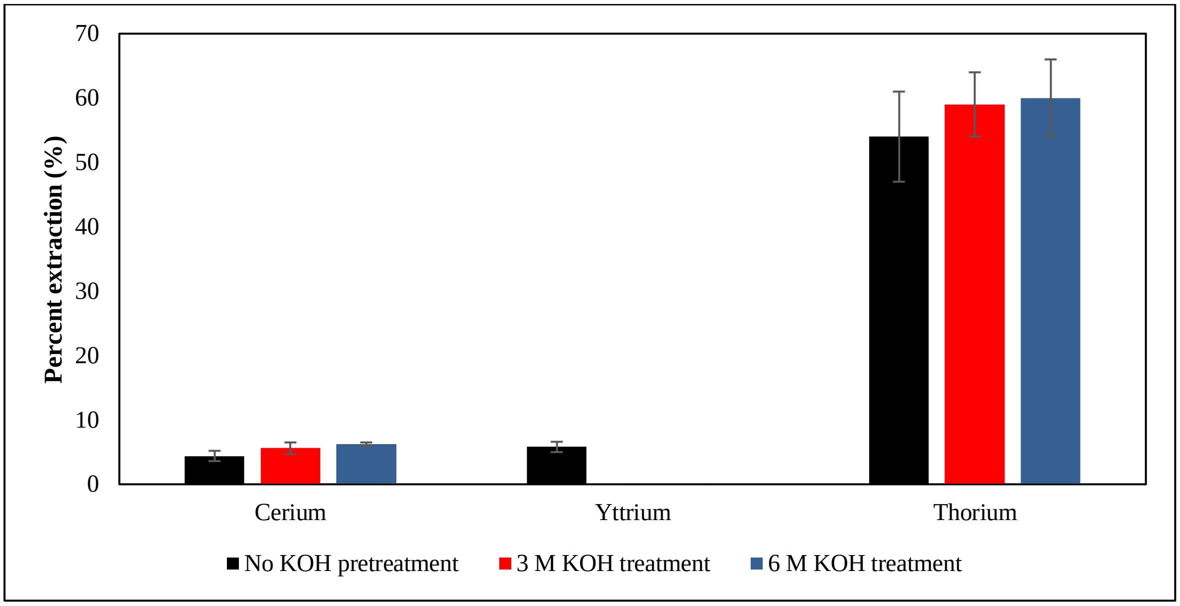

Figure 4.5. Cerium, yttrium, and thorium overall extraction after 180 min of 1 M HCl leaching following no KOH pretreatment, a 3 M KOH pretreatment, or a 6 M KOH pretreatment for 3 hours. Yttrium extraction was negligible during 1 M HCl leaching of the pretreated samples. The calculations are based on the cerium, yttrium, and thorium concentrations determined in the as-received samples (383.5±16.5 g/t, 82±1 g/t, and 189.5±10.5 g/t, respectively).

Figure 4.5 reveals that cerium extraction does not statistically change during 1 M HCl leaching for 180 minutes regardless of whether no pretreatment is considered or if a 3 M KOH pretreatment is performed. However, upon comparison with results from the case with no pretreatment, cerium extraction is slightly higher if a 6 M KOH pretreatment is performed. Based on **Figure 4.5**, yttrium extraction is only achieved if no KOH treatment is performed. Additionally, it suggests that there is no statistical difference on thorium extraction during acid leaching, regardless of whether an alkaline pretreatment (at KOH 3 M or 6 M) was performed or not.

As found for HCl leaching of the as-received samples, acid consumption during 1 M HCl leaching of the pretreated samples was negligible, regardless of KOH concentration during the pretreatment, as observed in **Annex 13**. Thus, HCl was only added in each control to account for aliquot extraction and replenishment. Consequently, water and acid are only needed to set the initial concentration of 1 M HCl, for which ~333 L/t of HCl (12 M) and ~3667 L/t of water are required.

4.3.3. Thiourea leaching of gold

Gold extraction and reagent consumption results during 8 g/L thiourea leaching of the samples that underwent 1 M HCl leaching following a 3 M or 6 M KOH pretreatment will be presented in this section. Firstly, averaged gold extraction kinetic results during thiourea leaching are shown in **Figure 4.6**. These results were based on the concentration of gold found in the 2 mL aliquots, along with the gold content that was determined in the as-received sample (14.88±0.07 ppm), according to AA results (**Annex 3**). Using the gold concentration in the head sample is adequate because gold was not extracted during HCl leaching or during the alkaline pretreatment, according to the results in **Annex 10** and **Annex 12**. Gold concentration for the extracted aliquots during the thiourea leaching stage from the third experimental step is reported in **Annex 14.** Gold extraction calculations accounted for the dilution of the leach solution during the controls, due to the aliquots that were removed and replenished from the experimental system.

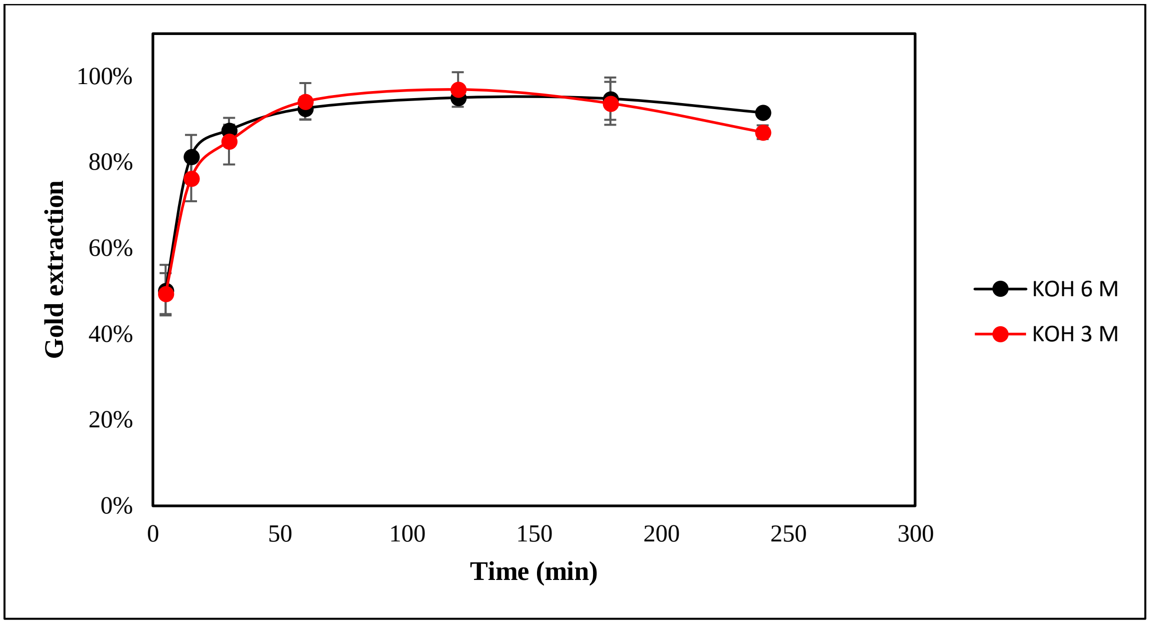

Figure 4.6. Gold extraction kinetics during 8 g/L thiourea leaching after 1 M HCl leaching for 3 hours following 180 minutes of alkaline pretreatment with 3 M or 6 M KOH.

Figure 4.6 reveals that there is no statistical difference in gold extraction at any given time during thiourea leaching following 1 M HCl leaching, regardless of KOH concentration during an initial alkaline pretreatment. In addition, sufficient statistical evidence exists to indicate that gold extraction peaks after 60 minutes of 8 g/L thiourea leaching of the HCl leached and KOH pretreated samples. The effect of performing the alkaline pretreatment on gold extraction during thiourea leaching is noticeable, since a greater amount of gold is leached, as will be detailed afterwards.

Thiourea consumption kinetics after the acid leaching and the alkaline pretreatment steps was followed throughout the leaching period, as shown in **Figure 4.7**. These results are based on the thiourea concentration during the gold leaching stages of the third experimental step, which are displayed in **Annex 15**. It should be considered that **Figure 4.7** includes only the thiourea that was consumed by the reaction, disregarding the amount required to achieve the initial concentration (12 kg/t of thiourea for a concentration of 8 g/L).

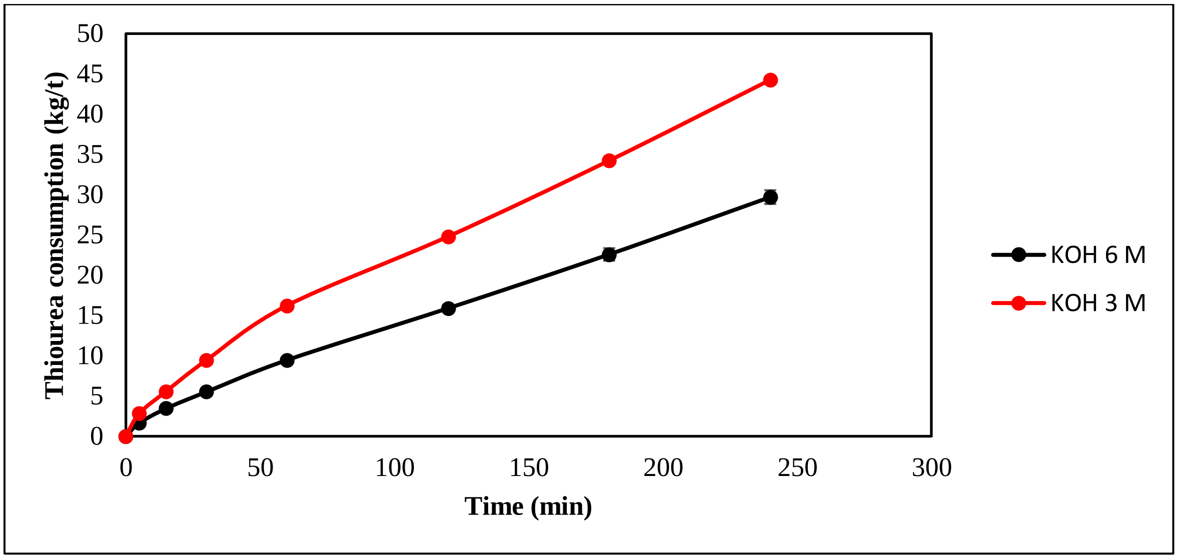

Figure 4.7. Thiourea consumption kinetics during 8 g/L thiourea leaching after performing 1 M HCl leaching for 3 hours following 180 minutes of alkaline leaching with 3 M KOH or 6 M KOH.

Figure 4.7 suggests again that there are two different thiourea consumption trends over the 4-hour leaching period, as discussed before. During the first 60 minutes, both major metal leaching and Fe(III)-thiourea complexes formation take place, while during the remaining period, thiourea is consumed mainly by the formation of Fe(III) complexes, which agrees with the discussion of the results from the first experimental step. Thiourea consumption results for the samples that received the 3 M KOH pretreatment are like those of the samples that did not receive an alkaline treatment (**Figure 4.4**), although thiourea consumption is lower if a 6 M KOH pretreatment is performed before acid leaching and thiourea leaching.

Additional processing of the data from the thiourea leaching stage of the third experimental step yields the information shown in **Table 4.7**, which summarizes maximum gold extraction results after performing a KOH pretreatment and an acid leaching stage. The presented thiourea and ferric sulfate requirements include the mass of reagents required to set the initial concentrations and the consumed amounts after each period. Reagent requirements are related to the added quantities until the 60 minute-mark for all samples, regardless of KOH concentration during pretreatment. The summary includes information for the first 60 minutes since it is the time required to achieve the maximum concentration. The total amounts of water and sulfuric acid are the same since they were only added to begin each experiment.

KOH concentration during pretreatment (M)	Thiourea leaching time until max. extraction (min)	Max. Gold extraction (%)	Reagent requirement for max. extraction
3	60	94.2±4.3	Thiourea: 21.5±0.3 kg/t Ferric sulfate: 112.9±1.6 kg/t Water: 1500 L/t H_2SO_4 (18 M): ~3.1 L/t
6	60	92.6±2.6	Thiourea: 17.5±0.3 kg/t Ferric sulfate: 91.9±1.6 kg/t Water: 1500 L/t H_2SO_4 (18 M): ~3.1 L/t

Table 4.7. Summarized results for accumulated reagent requirements to achieve maximum gold extraction during thiourea leaching following 1 M HCl leaching after alkaline pretreatments with KOH 3 M or 6 M.

4.3.4. Technical decision on alkaline pretreatment stage

The overall effect of performing an alkaline pretreatment on rare earth extraction is not positive, since cerium extraction only increased slightly, while yttrium extraction was reduced significantly, and thorium extraction did not change, as was shown in **Figure 4.5**. Thus, including a KOH pretreatment stage is not justified based on its effect on the subsequent acid leaching stage, regardless of KOH concentration.

On the other hand, the alkaline pretreatment improved gold extraction during 8 g/L thiourea leaching, considering an intermediate 1 M HCl leaching stage. This improvement is contrasted with the baseline of gold extraction during direct thiourea leaching, as displayed in **Figure 4.8.**

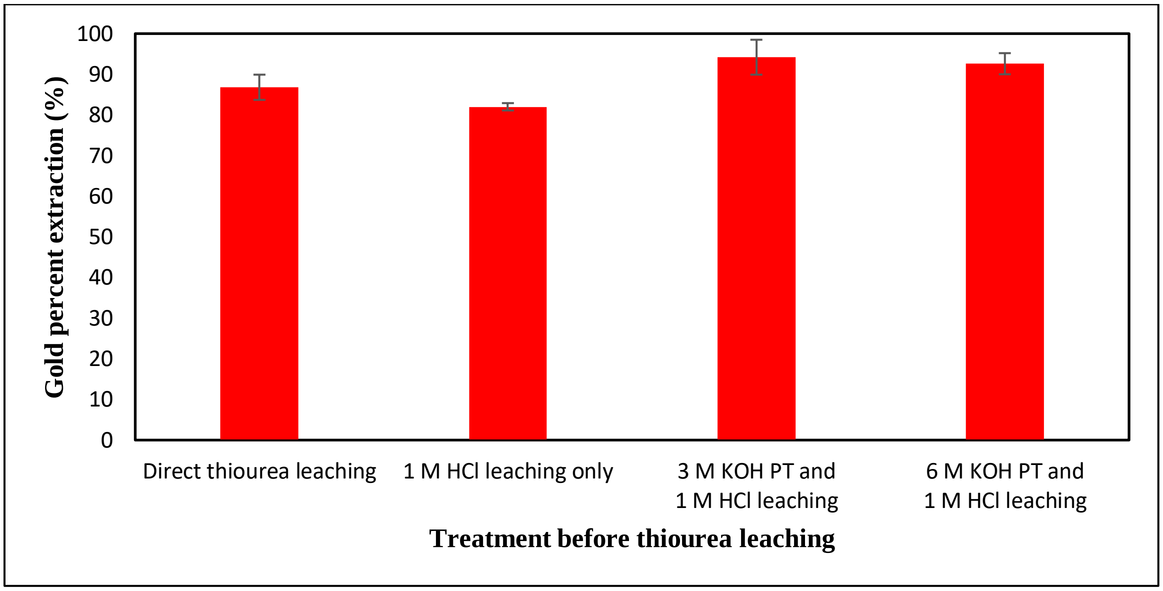

Figure 4.8. Comparison of gold extraction results after 60 minutes of 8 g/L thiourea leaching of as-received samples, of samples that underwent a 180-minute 1 M HCl leaching stage or of samples that underwent 180 minutes of 3 M KOH or of 6 M KOH pretreatment, followed by 180 minutes of 1 M HCl leaching. PT stands for pretreatment.

As presented, gold extraction is favored by performing an alkaline pretreatment, preferably with 3 M KOH solution rather than with a 6 M KOH one. However, the purpose of the alkaline pretreatment was to improve rare earth extraction during acid leaching, which it failed to do. KOH consumption is very high, a temperature of 80°C must be maintained, and the pretreatment does not yield the expected results. Thus, the inclusion of the pretreatment in the overall process is not justified and will not be evaluated further, regardless of the slight increase in gold extraction.

4.4. Sedimentation time after thiourea leaching

The analysis of the sedimentation process is based on the images presented in **Annex 16** for a slurry obtained after 60 minutes of 8 g/L thiourea leaching. As observed, the height of the solution in the tube was ~12.5 cm and most changes occurred over the first 60 minutes of sedimentation time. However, slight changes in the color of the solution occurred until the 240 minute-mark. Thus, sedimentation occurs at an approximate rate of 3.1 cm/h, considering the 4 hours required for the height of the solution to finish settling. The low rate at which sedimentation occurs indicates that tall sedimentation vessels should be avoided, since it would constitute a bottleneck in the process.

4.5. Hydrometallurgical stages design

Based on the experimental results, further evaluation of the alkaline pretreatment and acid leaching stages is not justified for process design, since rare earth extraction was low under the evaluated conditions. Thus, the process whose design is presented next will only include gold extraction through thiourea leaching and its recovery as a solid by cementation with zinc powder followed by zinc dissolution with sulfuric acid to obtain high purity gold. In addition, effluent neutralization stages are considered as well.

4.5.1. Process description and flow diagrams

The process is designed for artisanal miners who currently obtain gold through a small-scale operation. The main inputs of the process are the gravimetric table tailings obtained through batch gravimetric concentration techniques. As a result, the design will also be batch-based.

The base scale of design is 40 kg/day (14.6 t/year) of gravimetric tailings. However, increasing overall processing scale by combining the tailings production from other communities will be evaluated. This analysis will be based on a detailed scheduling of the processing stages, which is included afterwards.

For the sake of comparison, alluvial artisanal mining in Madre de Dios is typically based on the process shown in **Figure 4.9** (according to a private communication). This involves transport of alluvial sands and gravimetric concentration in carpets, sluices, and in tables, from which metallic gold is obtained. Currently, the produced tailings receive no further treatment and are left at the processing site.

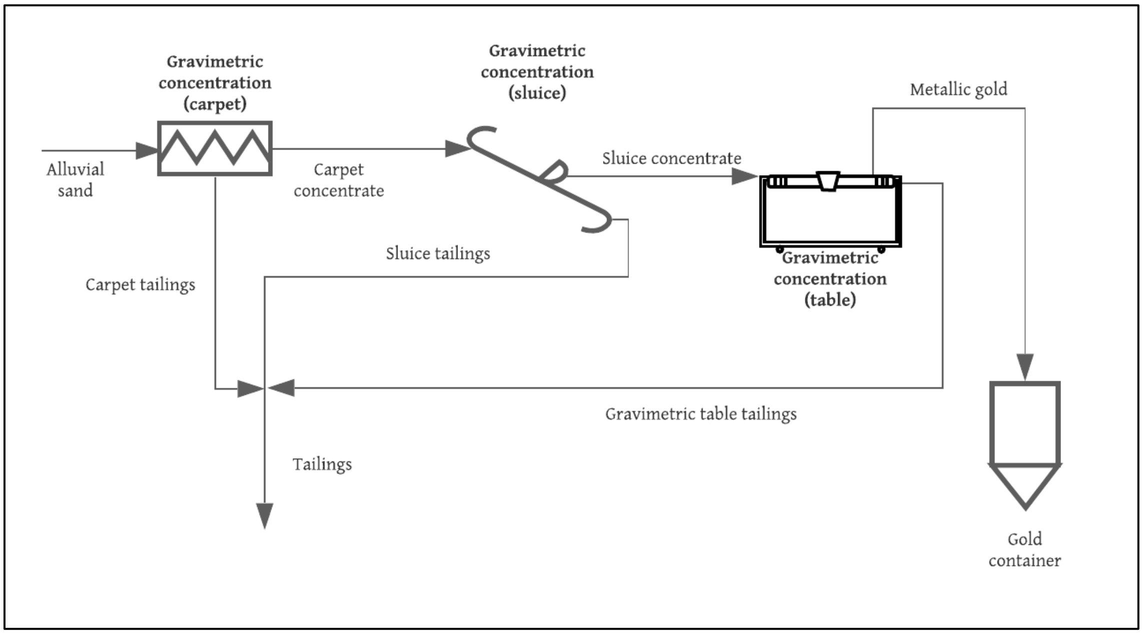

Figure 4.9. Current gold concentration process scheme performed by artisanal alluvial miners in Madre de Dios. Process scheme based on private communications with a community of artisanal miners.

The designed process, which is conducted at ambient conditions of pressure and temperature, is shown in the block flow diagram (BFD) displayed in **Figure 4.10**. The process begins with the tailings from the gravimetric table. These tailings will be subject to 8 g/L thiourea leaching to extract gold, for which water, sulfuric acid, ferric sulfate, and thiourea are needed. The reagents and the slurry will be mechanically stirred for an hour. Thiourea and ferric sulfate will be added periodically to account for their consumption, in accordance to results from **Figure 4.2**. After leaching, sedimentation is performed to separate the slurry from the gold pregnant thiourea solution. This solution undergoes a cementation process in a stirred tank for 10 minutes, for which zinc powder is added in a mass proportion of 9.33:1 regarding complexed gold [30]. Partial or total recycle of the barren leach solution after cementation is not evaluated further herein: the recycled solution would be unable to extract gold since some Fe(III)-thiourea complexes (formed due to ferric sulfate) and zinc-thiourea complex (formed due to zinc powder) are more stable than gold-thiourea. Thus, the barren thiourea solution is sent to effluent neutralization with quicklime before disposal. This process is intended to neutralize all remaining sulfuric acid and to precipitate the oxidizing agent ferric sulfate as ferric hydroxide. Following neutralization, thiourea-based solutions should either be stored in a tailings dam or undergo an effluent treatment before being sent to the Madre de Dios River. Given the low scale of the process, thiourea destruction through additional chemical processes is not recommended.

Solid tailings from the gold leaching process should be adequately disposed alongside tailings from the two previous gravimetric concentration operations. Tailings obtained directly from the gravimetric table (if the designed process is not performed) or those from the leaching process yield similar environmental hazards. This is true since the difference between them is that the elements left in the matrix after leaching will be slightly more concentrated after removing the leachable species. Thus, the process does not raise additional environmental issues regarding solid disposal. An adequate solid tailings disposal strategy is sending the solids to a tailings dam that has been designed to minimize environmental impact.

The produced particles from the cementation process are then submerged in a sulfuric acid bath to dissolve zinc and obtain gold as the only solid product [21]. Due to the small scale of the project, the cemented particles of each batch will be added into the same container which will always be filled with sulfuric acid. This bath will be renewed every 50 batches. Stirring will not be provided continuously.

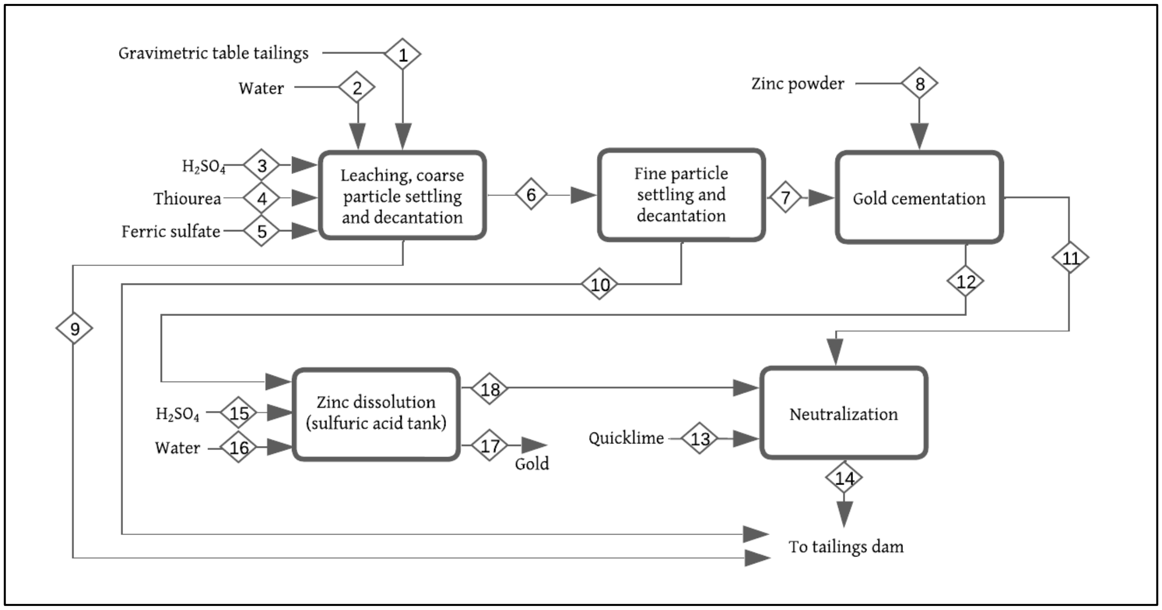

Figure 4.10. Block flow diagram of the designed hydrometallurgical processing stages, representing all unit processes and operations.

A block flow diagram (BFD) was presented before a process flow diagram (PFD) to provide a more thorough understanding of the sequence of unit processes. The artisanal-scale process was designed to minimize equipment requirements. As such, gold leaching and coarse particle settling stages will be performed in the same reactor. This is adequate since the latter stage is fast and does not constitute a bottleneck. The description of each process stream is displayed in **Table 4.8**.

Stream	Description
1	Input: Gravimetric table tailings obtained during artisanal gold concentration.
2	Input: Water to condition the mineral to a 40% solids slurry.
3	Input: Technical grade sulfuric acid to condition pH during leaching.
4	Input: Technical grade thiourea for industrial uses to maintain a concentration of 8 g/L thiourea during leaching.
5	Input: Technical grade ferric sulfate for industrial uses to maintain a ferric sulfate-thiourea 1:1 molar proportion.
6	Pregnant thiourea leach solution with fine particles dispersed.
7	Clear pregnant thiourea leach solution.
8	Input: Industrial-grade zinc powder for cementation.
9	Output: High solid percent slurry of coarse particles in acidified thiourea medium.
10	Output: High solid percent slurry of fine particles in acidified thiourea medium.
11	Barren thiourea leach solution with dispersed fine zinc particles.
12	Gold concentrate that contains zinc impurities.
13	Input: Industrial-grade quicklime for effluent neutralization.
14	Output: Neutralized tailings solution.
15	Input: Technical grade sulfuric acid for the acid bath.
16	Input: Water to obtain a 4.3 M sulfuric acid bath.
17	Output: Gold
18	Acid solution from acid bath

Table 4.8. Description of all the streams displayed in the block flow diagram. Stream description numbering is consistent with **Figure 4.10**.

A process flow diagram (PFD) derived from the previous BFD is presented in **Figure 4.11**. This diagram indicates the equipment distribution and the integration of all process streams. It should be noted that the PFD does not display the operating temperature and pressure of each unit process or operation, since they will all operate at ambient conditions.

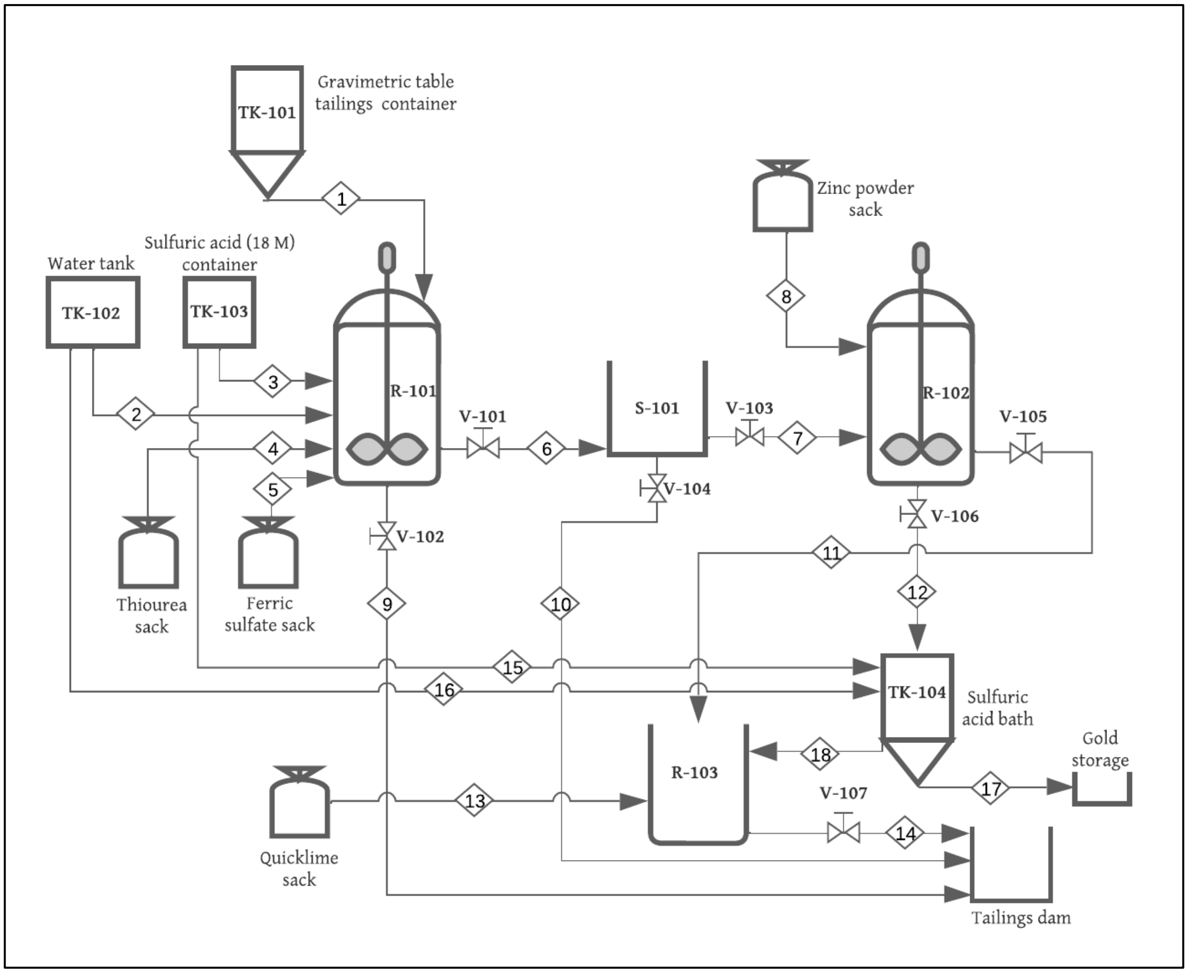

Figure 4.11. Schematic displaying all major equipment and valves and their integration in the designed process.

As presented, the process requires two cylindrical mechanically stirred reactors (R-101 and R-102), one cylindrical reactor without stirring system (R-103), one sedimentation tank (S-101), four containing tanks (TK-101 to TK-104), and seven ball valves (V-101 to V-107). Solid, slurry, and solution transport between reactors and tanks will be conducted manually with buckets and shovels. Pipes and slurry pumps will not be used due to the artisanal nature of the process. Valves will only be used to empty tanks to fill the buckets.

Since the design is to be used by artisanal miners at a small production scale, most of the equipment will be adapted from economic domestic-grade products, such as conventional plastic water tanks that are resistant to chemical attack. Additionally, the scope of design does not include process instrumentation and automatic control schemes. Thus, valves will be manually operated.

4.5.2. Mass balance

Based on 40 kg of gravimetric table tailings per batch (stream 1), 60 kg of water (stream 2) are required to obtain a 40% solids slurry for the thiourea leaching stage. Sulfuric acid, thiourea, and ferric sulfate requirements are calculated based on the reagent consumption results presented in **Table 4.1** for 1 hour of 8 g/L thiourea leaching. Scaling down those results from 1000 kg to a 40 kg batch of gravimetric table tailings yields the following requirements: 0.23 kg, 0.75 kg, and 3.93 kg of sulfuric acid (stream 3), thiourea (stream 4), and ferric sulfate (stream 5), respectively. While the complete sulfuric acid requirement is to be added before leaching begins, only 0.48 kg of thiourea and 2.52 kg of ferric sulfate are added before the process starts, to set the 8 g of thiourea per liter of solution and the 1:1 molar proportion of thiourea to ferric sulfate. The remaining thiourea and ferric sulfate are added proportionally throughout the process, following the linear consumption trend shown in **Figure 4.4.**

After loading and leaching, the reactor should contain ~104.9 kg of a slurry. It should contain the pregnant leach solution (~64.9 kg) and solid gravimetric tailings, which consist of ~36 kg of coarse particles and ~4 kg of fine particles, based on a ~10% fine particle distribution (considering fines to be particles that are able to pass through the openings of a mesh 270 ASTM E11 sieve, according to **Annex 2**). Thus, the slurry obtained after leaching should be ~34.3% coarse tailing particles, ~3.8% fine tailing particles, and ~61.9% pregnant leach solution.

After coarse particle sedimentation, a ~68.9 kg slurry containing ~64.9 kg of pregnant leach solution (~94.2%) and ~4 kg of fine particles (~5.8%) is obtained (stream 6), while ~36 kg of coarse particles are removed through stream 9 and sent to a tailings dam for disposal. Stream 6 is separated through fine particle sedimentation into stream 7 (~64.9 kg of clear pregnant leach solution) and stream 10 (~4 kg of fine particle tailings), which is sent to the tailings dam for disposal as well.

Gold content in the pregnant leach solution is estimated to be ~0.5 g based on 40 kg of gravimetric tailings with a gold concentration of 14.88 ppm (**Annex 3**), of which ~86.8% was extracted (**Table 4.1**). Based on the previously presented requirement of ~9.33 g of zinc per gram of gold [30], ~4.67 g of zinc powder should be added in stream 8. It should be noted that this is an estimate from the literature, which will depend on the presence of other metals in the solution capable of oxidizing zinc. Total gold recovery from the pregnant leach solution is expected after cementation, which consumes a mole of zinc per mole of gold to replace all gold atoms in the thiourea complex. Thus, ~0.17 g of zinc will remain in solution as part of thiourea-zinc complexes, while ~4.50 g of zinc will remain as solids, on which ~0.5 g of gold will cement. From the ~5.0 g of obtained product from stream 12, ~10.0% and ~90.0% will be gold and zinc particles, respectively.

The ~64.9 kg of acid barren leach liquor in stream 11, which contains an additional ~0.17 g of zinc undergoes a neutralization stage to deal with the important quantities of sulfuric acid and ferric sulfate within it. Although stream 18 is also introduced to the neutralization reactor (every 50 batches), its contents are not considered for the following calculations, given that its mass is negligible when compared to stream 11, as will be described afterwards. Experimentally, sulfuric acid consumption during thiourea leaching was found to be negligible so ~0.23 kg of this acid will require neutralization with quicklime, for which ~0.13 kg of quicklime is required, according to **Equation (7)**. Total neutralization of sulfuric acid produces ~0.32 kg of calcium sulfate and ~0.04 kg of water. While ferric ion may have been reduced to ferrous ion throughout the process, the total amount of sulfate anions remains the same and requires neutralization. Thus, the following calculation is based on the ~3.93 kg of ferric sulfate that was introduced to the process through stream 5. To neutralize this amount of ferric sulfate, ~1.65 kg of quicklime is required, according to **Equation (8)**. Total neutralization of ferric sulfate also consumes ~0.54 kg of water and produces ~4.01 kg of calcium sulfate and ~2.10 kg of ferric hydroxide.

Overall, neutralization calculations yield a quicklime requirement of ~1.78 kg in stream 13. Adding the masses of the slurry that required neutralization and of the needed quicklime, a total of ~66.74 kg of neutralized tailings is obtained in stream 14. This neutral solution is comprised of particles of calcium sulfate (~4.33 kg) and ferric hydroxide (~2.10 kg), along with the aqueous effluent based on ~0.75 kg of complexed thiourea in ~59.5 kg of water. Trace amounts of zinc sulfate coming from the dissolution of zinc powder after cementation are expected in this stream as well.

Gold and zinc particles from stream 12 are then sent to a sulfuric acid bath to dissolve zinc and recover gold as the only solid product. It should be noted that zinc would not dissolve if gold prevented sulfuric acid from reaching it. However, this is not likely because there are significantly more zinc particles than gold ones. Given that gold remains unreactive in sulfuric acid, it will only be removed once it is to be commercialized. Since the sulfuric acid bath will be reutilized for 50 batches, 2 L of 4.3 M sulfuric acid will be added to the tank initially. This concentration has been calculated so that when the fiftieth batch is being processed, the concentration of the solution is ~2.55 M and it is still able to dissolve zinc (considering that 1.5 g of sulfuric acid are required per gram of dissolved zinc). This accounts to 0.48 L (0.89 kg) of 18 M sulfuric acid diluted in 1.52 L of water. Although streams 15, 16, 17, and 18 are only introduced or removed from the process every 50 batches, for consistency with the rest of the calculations, they will hereafter be reported in a batch per batch basis. Thus, streams 15 and 16 will referentially require 17.8 g and 30.4 g of 18 M sulfuric acid and water, respectively. Likewise, stream 17 will produce ~0.5 g of gold per batch (50 g of gold are produced each time the acid bath is renewed). Stream 18 will contain the aqueous effluent from the acid bath, which is sent to a neutralization reactor. The amount of quicklime required to neutralize this effluent is negligible when compared to the contents of stream 11.

Mass balance compliance was verified by comparing the total input streams (1-5, 8, 13, 15, and 16) with the total output streams (9, 10, 14, and 17). The combination of all input streams was ~106.74 kg, which was approximately equal to the sum of all output streams. The details of the mass balance for the reprocessing scheme are presented in **Annex 17**, although a summary of the global input and output streams is shown in **Table 4.9**.

Mass and composition (%wt) per batch	
Global inputs	**Global outputs**
Stream 1: 40 kg (100% gravimetric table tailings)	Stream 9: ~36 kg (100% coarse tailings particles)
Stream 2: 60 kg (100% water)	Stream 10: ~4 kg (100% fine tailing particles)
Stream 3: 0.23 kg (100% sulfuric acid, 18 M)	Stream 14: ~66.74 kg (~3.2% ferric hydroxide, ~6.5% calcium sulfate, ~89.2% water, and ~1.1% complexed thiourea, traces of zinc sulfate)
Stream 4: 0.75 kg (100% thiourea)	Stream 17*: ~0.5 g (~100% gold powder)
Stream 5: 3.93 kg (100% ferric sulfate)	
Stream 8: ~4.67 g (100% zinc dust)	
Stream 13: ~1.78 kg (100% quicklime)	
Stream 15*: ~17.8 g (100% sulfuric acid, 18 M)	
Stream 16*: ~30.4 g (100% water)	
Total input mass per batch: ~106.74 kg	**Total output mass per batch: ~106.74 kg**

Table 4.9. Summary of the composition of each global input or output stream for a batch of 40 kg of gravimetric table tailings. Stream numbering is consistent with **Figure 4.10** and **Figure 4.11**. *For compliance with the rest of the mass balance calculations (which are made on a batch per batch basis), streams 15-17 are displayed as if they were also on the same basis. Since these streams are only actively part of the process every 50 batches, their mass per batch is reported in the table as one fiftieth of the amounts required or produced each time the acid bath is renewed.

Considering that all the thiourea that is introduced to the process is consumed by different reactions either during leaching or cementation, it should be noted that only ~0.05% of consumed thiourea is stoichiometrically responsible for gold leaching.

All previous results are only preliminary estimations. Different events during the performance of the reprocessing scheme could occur, such as small spillages of aqueous solutions or the variability of having different humidity contents in the gravimetric table tailings (for this analysis, samples were considered to have a negligible water content, since they had been dried before the experiments) received in each batch. These events would have an impact on the mass balance results, although their effect is not expected to be greater than ±20%.

4.5.3. Sizing of major equipment required for the process

R-101 is the reactor in which batch thiourea leaching occurs. As such, its purpose is to hold and mix the added contents of streams 1-5. This reactor requires a mechanical stirring system to maintain the gravimetric table tailings in a 40% solids suspension. Considering the design has the accuracy of a study estimate, only the main two components will be considered for reactor sizing. The volume occupied by 40 kg of gravimetric table tailings is calculated from the density of the ore (4.42 kg/L), which results in ~9 L. Adding this volume to the required 60 L of water, a total of 69 L of slurry will be processed in R-101. Based on this volume, the tank's diameter and nominal height were calculated to be 0.44 m. Considering the 1.5 factor, the effective height for R-101 is 0.67 m. Finally, the required A310 impeller is 0.15 m in diameter, taken as one third of the tank's diameter, as detailed in the previous chapter.

The cementation of the pregnant thiourea leach solution occurs in R-102. According to the mass balance, ~64.9 kg of leach liquor is fed to R-102, along with ~4.67 g of zinc. Considering that ~60 kg of the liquor is water, the density of the leach solution will be taken as 1 kg/L. Thus, the volume occupied by the slurry will also be approximately 64.9 L. From this volume, the resulting diameter and nominal height of the reactor were 0.44 m. The 1.5 factor yielded an effective height of 0.65 m. The required A310 impeller is also 0.15 m in diameter.

Solution neutralization is performed in R-103. Streams 11, 13, and 18 are fed to the reactor, which accounts for ~66.8 kg. Again, the solution density is taken to be approximately that of water, which results in an occupied volume of ~66.8 L. As a result, the diameter and nominal height of the reactor were determined to be 0.44 m. Using the 1.5 factor results in an effective height of 0.66 m. This reactor will be manually stirred periodically since there is no need to provide continuous stirring.

The sedimentation tank S-101 will process ~64.9 kg of pregnant leach solution (density of ~1 kg/L) with ~4 kg of dispersed fine particles. The dispersed fine particles occupy a volume of ~0.90 L, estimated from the density of the as-received mineral, which results in ~65.8 L of total processing volume. Thus, based on the 1:4 height to diameter proportion, the nominal height and diameter of the settling tank were determined to be 0.17 m and 0.69 m, respectively. Considering the 1.5 factor, the effective height was 0.26 m.

All reactors and the sedimentation tank will be adapted from conventional polyethylene (PE) water tanks or drums.

TK-101 will be used to store the gravimetric table tailings before a new batch is started. The tailings can be stored in any type of open container. For instance, using 10 L buckets is a viable and economic solution for storing and transporting the tailings. ~40 kg per batch of gravimetric table tailings is equivalent to approximately ~9 L of dry tailings. Since the tailings will likely have water content that increases their net volume, using three 10 L buckets would be recommended to store and transport the tailings from the gravimetric concentration station to R-101. Using more buckets than strictly necessary does not elevate the cost of the process significantly, although it ensures safer transport and reduces health hazards for the worker, since each bucket will not be completely full.

TK-102 will hold water before it is used for the process. Since water will be transported to the processing site, it is recommended to store water for multiple batches. As a result, using five 55-gallon drums would reduce the frequency of trips to obtain water. Approximately, these five containers could provide water for over twenty batches of the process.

TK-103 stores the concentrated sulfuric acid required for thiourea leaching. Given the hazardous nature of this substance, it is recommended to store it in the same container in which it was acquired, which is typically a glass bottle. Thus, dimensioning of these containers is not necessary. Sulfuric acid stock should be available to process at least twenty batches at any time.

TK-104 receives the gold-zinc particles obtained from the process. Each batch will yield approximately 5 g of this product, which should be initially received in a small container, such as a 4 L plastic bucket. This bucket will also contain sulfuric acid since it is also where zinc dissolution will occur. After reprocessing 50 batches, ~25 g of gold is collected carefully from the sulfuric acid solution.

Conventional domestic 1" ball valves can be used for V-101 to V-107. PVC is recommended for the valves to withstand corrosion from dilute sulfuric acid in certain stages. Detailed valve design will not be described herein.

The tailings dam must be able to hold all solid residues and effluents generated through the reprocessing of 2500 batches of tailings (500 yearly batches during five years). As part of each batch, streams 9 and 10 jointly send ~40 kg of solid tailings (~9.1 L, considering a density of 4.42 kg/L) to the tailings dam, while stream 14 sends ~66.7 L of neutralized effluents to the dam. Thus, each batch would generate ~75.8 L of tailings, which results in approximately 190 m^3 of tailings over the five-year period.

In addition, five 20 L plastic buckets shall be available to help transport slurries or solutions from one tank to another.

The summary of equipment sizing for the process is presented in **Table 4.10.**

Equipment	Characteristics and dimensions
R-101	Cylindrical reactor adapted from PE water tank or drum (diameter: 0.44 m, height: 0.67 m, standard A310 impeller of diameter 0.15 m).
R-102	Cylindrical reactor adapted from PE water tank or drum (diameter: 0.44 m, height: 0.65 m, standard A310 impeller of diameter 0.15 m).
R-103	Cylindrical reactor adapted from PE water tank or drum (diameter: 0.44 m, height: 0.66 m, no impeller).
S-101	Cylindrical settling equipment adapted from PE water tank or drum (diameter: 0.69 m, height: 0.26 m, no impeller).
TK-101	Three 10 L conventional plastic buckets.

TK-102	Five 55-gallon PE drums.
TK-103	Original sulfuric acid containers
TK-104	One 4 L plastic bucket.
Valves	7 conventional domestic PVC 1" ball valves.
Tailings dam	Capacity of ~190 m^3, with drainage system and geomembrane lining.
Auxiliary equipment	Five 20 L conventional plastic buckets.

Table 4.10. Summary of equipment sizing results for the process. Equipment labels are consistent with **Figure 4.11**.

Considering the surface estimation guidelines provided in the previous chapter, the total cross-sectional area occupied by the three reactors and by the sedimentation tank are calculated to be ~0.83 m^2. This result is then multiplied by a factor of 30, which results in a total area of ~25 m^2 to install all pieces of equipment, auxiliary tanks, and buckets, leaving space for workers to safely transit around the area. Additionally, since the height of the tailings dam is taken as ~1 m, approximately 190 m^2 is required to build this structure. Adding these two quantities, a total surface area of 215 m^2 is required for the whole operation. This result is only a raw estimate, since the area required to build the dam may vary accordingly to a detailed design of this structure.

4.5.4. Energy requirement

All unit processes will be conducted at ambient temperature, and there is no need to supply or remove heat due to reactions (no boilers or cooling systems are required). Likewise, no pumps or compressors will be used as part of the process given that all slurry transport will be conducted using buckets. In addition, there is no need to provide energy to illuminate the work area because the process will operate outdoors during daylight hours. Thus, energy input is only required for the mechanical stirrers in R-101 and R-102 since no auxiliary equipment or operations will need energy.

Required stirring speed for R-101 and R-102 will first be calculated from **Equation (9).** For both cases, water density and kinematic viscosity are referentially taken at 25°C: ρ_L=997 kg/m^3 and υ=8.9×10^{-7} m^2/s [58]. For R-101, particle properties are those from the as-received sample. As a result, particle mean diameter is d_p=1.2×10^{-4} m (**Annex 2**) and solid density is ρ_s=4420 kg/m^3. The mass ratio percent is calculated from the 40% solids slurry that is processed in R-101, which is 100 times the ratio between the mass of solids and the mass of liquids, X=66.67. Thus, the calculated stirring speed to ensure solid suspension in R-101 is ~11 rev/s (~660 rev/min). On the other hand, solid particle properties for R-102 are those of the added zinc particles, which are referentially taken as d_p=7.4×10^{-5} m [30] and ρ_s=7133 kg/m^3 [58]. For R-102, ~4.67 g of zinc require suspension in ~64.9 kg of solution, which results in X=7.2×10^{-3}. Finally, the calculated stirring speed for solid suspension in R-102 is ~3.1 rev/s (~183 rev/min).

Power consumption can now be calculated from the stirring speed using **Equation (10)**. Slurry density for R-101 was ~1448.2 kg/m^3 (estimated considering only water and the tailings), while it was ~997 kg/m^3 for R-102. Thus, for R-101 and R-102, the stirring power requirements are 62.7 W and 2.01 W, respectively. The summary of total energy requirements is presented in **Table 4.11.**

Equipment	**Power requirement**	**Energy requirement per batch (kW.h)**
R-101	62.7 W to achieve 660 rev/min for solid suspension for 1 hour	0.0627
R-102	2.01 W to achieve 238 rev/min for solid suspension for 10 minutes	0.0003
Total energy requirement per batch (kW.h)		**0.063**

Table 4.11. Summary of required energy for the process. Equipment labels are consistent with **Figure 4.11**.

4.5.5. Safety assessment

For the safety assessment, the designed process was divided in six major activities, as detailed in **Table 4.12.** The first activity entails all the instances in which slurries or solutions are extracted from a tank, transported from one vessel to another, or when they are loaded into other containers using buckets. The other five activities include the major unit operations that occur in R-101, S-101, R-102, TK-104, and R-103. Each of these activities were further divided into specific tasks, as displayed in **Table 4.12**.

Activity	Tasks
Loading and unloading tanks with slurries or solutions	Filling buckets with slurries or solutions, transporting buckets, emptying buckets with slurries or solutions.
Thiourea leaching of gold	Addition of sulfuric acid, addition of thiourea, addition of ferric sulfate, waiting for reaction to finish.
Sedimentation of fine particles	Waiting for sedimentation to finish.
Gold cementation with zinc	Addition of zinc powder, waiting for reaction to finish.
Zinc dissolution in acid bath	Addition of sulfuric acid, waiting for reaction to finish
Neutralization of effluents	Addition of quicklime, waiting for reaction to finish.

Table 4.12. List of activities and their respective tasks within the designed process.

Afterwards, hazards and their associated risks were identified, as shown in the six Hazard Identification, Risk Assessment and Control (HIRAC) matrixes presented in **Annexes 18-23** for each of the six activities. These matrixes indicate that the process presents the following risks: skin or eye irritation or burn, acid fume or dust inhalation, back injury, electrocution, and getting cut (which could lead to loss of limb). Apart from the last three risks, the others are associated to working with concentrated sulfuric acid, which is corrosive and releases fumes, and with ferric sulfate, thiourea, fine mineral particles, and zinc powder, which can cause skin, eye, or respiratory tract irritation. The risk of back injury is associated to loading, unloading, and transporting buckets with slurries, solids, or solutions. The risk of electrocution and of being cut are related to the use of electrically powered stirring systems for R-101 and R-102.

The initial construction of these matrixes indicated that all tasks had at least one risk that was ranked over 10 in the scale from 1 to 25, with some tasks having at least one risk ranked at 15 or higher. This finding results in the need to install administrative control measures, as well as issuing mandatory use of personal protection equipment (PPE), such as a back support belt, nitrile gloves, safety goggles, a gas mask, and a dust mask.

Administrative measures included unplugging the stirring systems when unused, always adding sulfuric acid into water slowly, and training personnel to avoid touching the stirring systems and to remain away from the tanks if possible. The details of how each measure addresses a specific risk are presented in **Annexes 18-23**.

The implementation of the described control measures reduces the probability of the risks occurring, which decreases the overall rank of each risk. As a result of the control measures, only one task has a residual rank of 10, while all other risks are now ranked 6 or less.

Based on this assessment, the process is considered safe since all safety and health concerns can be addressed through administrative control measures and the use of PPE. Additionally, fine particle sedimentation and effluent neutralization were found to be the least dangerous activities, which suggests that they do not require monitoring in the interest of safety.

4.5.6. Scheduling

For scheduling purposes, the process was divided in thirteen activities, which are presented in **Table 4.13**. This table also lists the required time and equipment for each activity, as well as if they need supervision. Only those activities that were deemed inherently safe (sedimentation of fine particles and effluent neutralization) will not require supervision, since they do not require any human input either. The allotted times from **Table 4.13** are justified afterwards.

#	Activity	Required equipment	Required time	Supervision
1	Loading R-101	R-101	15 min	Yes
2	Thiourea leaching	R-101	60 min	Yes
3	Sedimentation of coarse particles	R-101	5 min	No
4	Unloading effluent from R-101 and loading S-101	R-101 and S-101	15 min	Yes
5	Sedimentation of fine particles	S-101	340 min	No
6	Unloading coarse tailings from R-101	R-101	5 min	Yes
7	Unloading effluent from S-101 and loading R-102	S-101 and R-102	15 min	Yes
8	Unloading fine tailings from S-101	S-101	5 min	Yes
9	Cementation of gold	R-102	10 min	Yes
10	Unloading effluent from R-102 and loading R-103	R-102 and R-103	15 min	Yes
11	Neutralization of effluents	R-103	20 min	No
12	Unloading R-103	R-103	5 min	Yes
13	Zinc dissolution	TK-104	Continuous	No

Table 4.13. List of activities and their details for scheduling purposes.

Referentially, loading R-101 with water and the gravimetric tailings (activity 1) was predicted to take ~15 minutes. Likewise, all activities that included both unloading a tank and loading another one (4, 7, and 10) were expected to last ~15 minutes. Activities that only included unloading a tank (6, 8, and 12) were estimated to take ~5 minutes. Thiourea leaching (activity 2) time was experimentally determined to be 60 minutes. Coarse particle sedimentation (activity 3) was rapid, as observed during the experimental trials. Thus, ~5 minutes were allotted for this first stage of sedimentation. Fine particle sedimentation (activity 5) was a slow process. Sedimentation speed was experimentally determined to be 3.1 cm/h. Since fluid nominal height in S-101 was 0.17 m, ~329 minutes are required, although 340 minutes were considered to ensure complete sedimentation. Gold cementation (activity 9) is expected to take ~10 minutes, as specified in the literature [30]. The prediction of neutralization time requires a kinetic study that is beyond the scope of this project. Referentially, this reaction (activity 11) has been allotted 20 minutes, although this is subject to evaluation. Zinc dissolution (activity 13) is not assigned a specific period since this activity will be performed continuously: gold-zinc concentrates from multiple batches will be accumulated in the dissolution container.

Tentative schedules for the first two days of operation were prepared based on the information from **Table 4.13**. The schedules for the first and second days are presented in **Figure 4.12** and **Figure 4.13**, respectively. The schedules consider a regular 8-hour workday with an additional hour for lunch break, resulting in 9 active hours per day (540 minutes). Activity 13 is not displayed in either schedule since it occurs continuously in a separate container (TK-104).

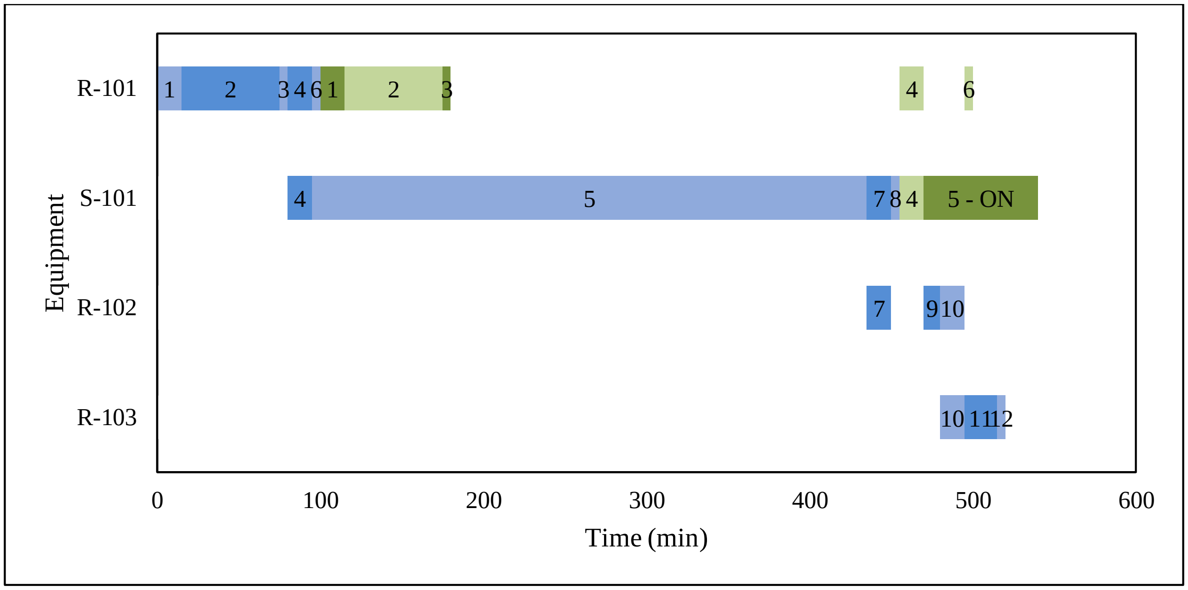

Figure 4.12. Tentative schedule for the first day of operation. The first batch is shown in blue, while part of the second batch is displayed in green. Activity numbering is consistent with **Table 4.13**. ON represents an activity that continues overnight.

During the first day of operation, only one full batch (marked in blue) is finished. However, a second batch (marked in green) begins during the fine particle sedimentation stage of the first one. At the end of the first day, activity 6 of the second batch has been concluded, while fine particle sedimentation (activity 5) is still underway. The worker will leave this activity unsupervised overnight. While activity 5 will finish after ~340 minutes, continuing it for a longer period overnight will not be detrimental to the quality of sedimentation. After 180 minutes, there is an idle period that lasts for 255 minutes. Lunch break should be held at some point during this period. The schedule for the next day is presented in **Figure 4.13**, which starts with the final activities of the second batch.

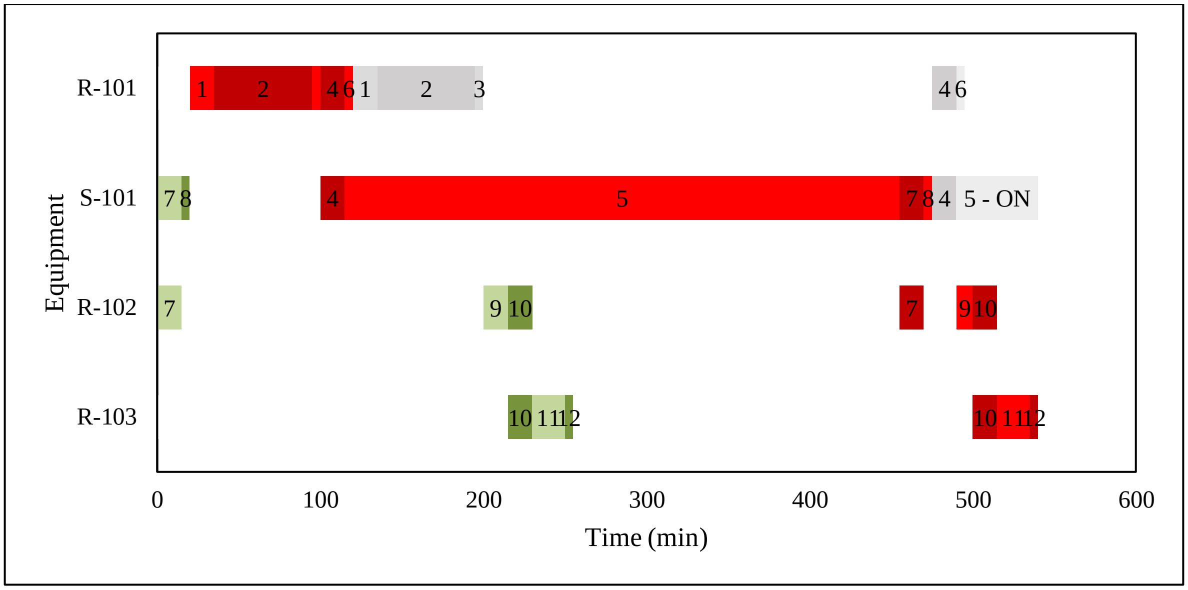

Figure 4.13. Tentative schedule for the second day of operation. Part of the second batch is presented in green; the third batch is shown in red, and part of the fourth batch is shown in grey. Activity numbering is consistent with **Table 4.13**. ON represents an activity that continues overnight.

In the second day of operation, two batches are finished (marked in green and red), while an additional batch (marked in grey) begins during this day. However, this latter batch is left unfinished once the day ends, while the fine particle sedimentation activity is underway. Once again, this activity will be left unattended overnight, to complete the processing of this batch the next day. In the second day, the idle period is shorter: it lasts for

200 minutes, beginning after the 255-minute mark. Lunch break should be held at some point during this period.

The existence of these idle periods indicates that fine particle sedimentation (activity 5) is the bottleneck of the process. Thus, the bottleneck must be addressed to process more batches per day, if desired. An alternative would be to perform two or more fine particle sedimentation activities in parallel, for which acquiring an additional sedimentation tank would be needed. However, further evaluation of this alternative is not discussed further herein.

The progress of the last batch from the second day after finishing work hours is the same as its counterpart from the first day. Hence, all subsequent days will have the same schedule as the second day since they will all begin after overnight completion of fine particle sedimentation. As a result, two batches can be processed daily (except for the first day in which only one batch can be processed), which results in a maximum of approximately 625 batches per year, given that the process is performed from Monday to Saturday.

4.6. Economic assessment

In this section, the designed process will be analyzed from an economic perspective. To do so, the capital and operational expenditure will first be calculated. From this information, a 5-year projection of the cash flow will be presented, from which the profitability indicators net present value (NPV), and internal return rate (IRR) will be calculated. Finally, the effect of different parameters on the projected NPV will be assessed through a sensitivity analysis.

4.6.1. Capital Expenditure (CapEx)

The capital expenditure (CapEx) estimation evaluated the investment required to procure the equipment for the process, as presented in **Table 4.10**. The price of all the equipment was estimated, except for TK-103, which was not sized either, as discussed before.

For cost assessment, R-101 and R-102 were separated into two different components: the vessel and the stirring system (motor and stirrer). Accurate pricing for an A310 impeller was not possible without obtaining a formal quote from the provider. Thus, a referential price was estimated from a manufacturer of stirring systems that sells a high efficiency 316SS impeller, which is geometrically similar to the A310 impeller [59]. Thus, the cost of the stirring systems may not be accurate and should only be considered for the sake of a preliminary study estimate.

The cost of the tailings dam was based on the raw estimate of \$25 per cubic meter of tailings, as described in the previous chapter. This price was multiplied by the 190 m^3 of tailings that are produced over a five-year period, resulting in a total of \$4750.

The cost assessment of all the required equipment and the tailings dam is presented in **Table 4.14.** In this table, the actual characteristics and dimensions of the referentially quoted equipment are displayed, which agree within a 20% margin to the results from **Table 4.10**. Considering the 50% increase in the total preliminary cost of equipment to account for customization, freight costs, and customs fees, total adjusted cost of capital expenditure results in \$8697.84.

Equipment	Quoted characteristics and dimensions	Unit cost (\$)	Amount	Total cost (\$)
R-101 (tank)	30-gallon high density polyethylene cylinder of internal diameter 0.46 m and height 0.76 m [60]	100.00 [60]	1	100.00
R-101 (motor and stirrer)	Customizable dimensions and corrosion resistant. High efficiency impeller 316SS. Low and high RPM [59]	208.50 (INR 15500) [59]	1	208.50
R-102 (tank)	30-gallon high density polyethylene cylinder of internal diameter 0.46 m and height 0.76 m [60]	100.00 [60]	1	100.00

R-102 (motor and stirrer)	Customizable dimensions and corrosion resistant. High efficiency impeller 316SS. Low and high RPM [59]	208.50 (INR 15500) [59]	1	208.50
R-103	30-gallon high density polyethylene cylinder of internal diameter 0.46 m and height 0.76 m [60]	100.00 [60]	1	100.00
S-101	250-liter water tank of external diameter 0.70 m and height: 0.75 m [61]	47.24 (PEN 189.90) [61]	1	47.24
TK-101	13 L plastic bucket [62]	3.78 (PEN 15.20) [62]	3	3.78
TK-102	55-gallon high density polyethylene cylinder [63]	48.00 [63]	5	240.00
TK-104	4 L plastic bucket [64]	2.00 (PEN 8.00) [64]	1	2.00
Valves	PVC ball valves of internal diameter 1" [65]	1.97 (PEN 7.90) [65]	7	13.79
Tailings dam	190 m^3 of capacity	4750.00	1	4750.00
Auxiliary equipment	20 L polyethylene bucket [66]	4.95 (PEN 19.95) [66]	5	24.75
	Total preliminary cost of equipment ($)			**5798.56**
	Total adjusted cost of equipment ($)			**8697.84**

Table 4.14. Equipment cost estimation based on prices and exchange rates from 14 November 2021. Equipment labels are consistent with **Figure 4.11**.

A more detailed evaluation of the capital costs, which would imply contacting, visiting, and bargaining prices with local supply providers, should be performed. This evaluation is likely to produce a significant reduction of overall capital expenditure, particularly in the acquisition of plastic cylinders.

4.6.2. Operational expenditure (OpEx)

The operational expenditure (OpEx) estimation evaluated the investment required for both variable operating expenses (VCOP) and fixed operating expenses (FCOP). VCOP includes the cost of raw materials (reagents) and of utilities (water and electricity) per batch. Likewise, FCOP includes yearly salaries and maintenance fees.

Firstly, reagents were quoted from providers that sell industrial grade thiourea, ferric sulfate, sulfuric acid, zinc powder, and quicklime. The characteristics and cost of each reagent are detailed in **Table 4.15**. Additionally, the effective cost (accounting purity of quoted products) of each reagent is also presented in **Table 4.15**.

Reagent	Quoted characteristics	Cost ($)	Effective cost ($/kg)
Thiourea	Sack of net weight 25 kg of thiourea of purity 99.5% [67]	38.67 (INR 2875) [67]	1.55
Ferric sulfate	HDPE bag of net weight 25 kg of ferric sulfate of purity 71% [68]	22.86 (INR 1700) [68]	1.29
Sulfuric acid	25 L plastic container of net weight 45.8 kg of 18 M sulfuric acid [69]	68.80 (INR 51.00) [69]	1.50
Zinc powder	Bag of net weight 50 kg of industrial grade zinc powder of purity 99% [70]	63.89 (INR 4750) [70]	1.29
Quicklime	PP bag of net weight 50 kg of quicklime powder of purity 90% [71]	3.37 (INR 250) [71]	0.08

Table 4.15. Reagent cost based on prices and exchange rates from 14 November 2021.

The total cost of each reagent per batch is presented in **Table 4.16**. This table combines the information from **Table 4.15** and from the mass balance (**Table 4.10**). After adding each item and multiplying by a 1.5 factor, a total adjusted cost of reagents of $10.14 per batch is obtained.

Reagent	Effective cost ($/kg)	Requirement per batch (kg)	Cost per batch ($)
Thiourea	1.55	0.75	1.16
Ferric sulfate	1.29	3.93	5.07
Sulfuric acid	1.50	0.25	0.38
Zinc powder	1.29	0.0047	0.01
Quicklime	0.08	1.78	0.14
Total preliminary cost of reagents per batch ($)			**6.76**
Total adjusted cost of reagents per batch ($)			**10.14**

Table 4.16. Reagent cost per batch calculation. Information based on prices and exchange rates from 14 November 2021.

The cost of ferric sulfate accounts for ~75.3% of the preliminary cost of reagents. This finding suggests that lowering the consumption of this reagent should be evaluated to increase the profit of each batch. The relative impact of modifying the cost of reagents over the profitability of the project is presented and discussed in the sensitivity analysis.

After calculating reagent prices, the cost of the utilities water and electricity was assessed. Water is to be acquired at $0.94 (PEN 3.757) per 1000 L, as indicated by EMAPAT (local private water provider from Madre de Dios) in 2016 (latest year for which information was available). This price is for water for industrial uses within the consumption range of 0 to 100 m^3 per month [72]. It is noteworthy that this water is not the same than the one used for the performed experiments (distilled water); however, pilot testing in Madre de Dios (or using water from Madre de Dios) is required to assess whether the change in the quality of water will affect gold extraction results. Likewise, electricity cost was estimated from the current price for kW.h of active energy (established by OSINERGMIN) for the Madre de Dios department, which is of $0.21/kW.h (PEN 0.84/kW.h) [73]. For each batch, 60 kg of water are required, as well as 0.063 kW.h of electricity, as shown in **Table 4.9** and **Table**

4.11, respectively. Thus, the utilities cost per batch was estimated to be of $0.07, as presented in **Table 4.17**.

Utility	**Cost**	**Requirement per batch**	**Cost per batch ($)**
Water	$0.94/1000 L [72]	~60 L	0.06
Electricity	$0.21/kW.h [73]	0.063 kW.h	0.01
Total adjusted cost of utilities per batch ($)			**0.07**

Table 4.17. Utilities cost per batch calculation. Information based on exchange rates from 14 November 2021.

Monthly salaries for the first year of operation were considered to be $350.00, which is more than the Peruvian minimum monthly wage [53]. Due to the small scale of operation, only one worker will be required to perform and control the reprocessing scheme. However, considering the 20% factor to account for transport and social benefits (15 days of paid vacation and affiliation to Peruvian National Health Services, as detailed in the previous chapter), a monthly total of $420.00 is needed during the first year to pay salaries, which results in a yearly total of $5040.00. However, the salaries will increase yearly by 3% to account for inflation [55]. It should be noted that other workers at the site, namely those attending gravimetric concentration operations, will be trained to help in case of emergencies that may occur during the reprocessing scheme.

Lastly, yearly maintenance expenses are estimated as 5% of the nominal price of the equipment that may require being repaired, which are the stirring systems of R-101 and R-102. Since the price of the two stirring systems is $417.00, a total of $20.85 per year is necessary to cover maintenance expenses.

Finally, the estimated variable and fixed operating expenses are summarized in **Table 4.18**.

Item	Cost
Raw materials ($/batch)	10.14
Utilities ($/batch)	0.07
Variable operating expenses subtotal ($/batch)	**10.21**
Salaries on first year* ($/year)	5040.00
Maintenance ($/year)	20.85
Fixed operating expenses subtotal ($/year)	**5060.85**

Table 4.18. Summary of variable and fixed operating expenses. Information based on exchange rates from 14 November 2021. Salaries will increase by 3% yearly.

As shown, the two most critical aspects of the operational expenditure are the cost of reagents per batch and the yearly cost of salaries. While reagent cost will be evaluated as part of the sensitivity analysis, the cost of salary will not be analyzed further, since the suggested salary was competitively selected.

4.6.3. Expected cash flow

Each batch produces ~0.5 g of zinc-free solid gold, which yields ~$28.94 (according to a gold price of $57.87/g, which is a referential 2021 gold price average) [56]. Considering that twelve batches can be produced weekly (two per day from Monday to Saturday), approximately 625 batches can be processed yearly. However, only 80% of this number (500 batches per year) is considered for the projected cash flow. As a result, $14467.5 are obtained each year from selling the gold. **Table 4.19** displays the calculation of the yearly gross profit. CapEx, FCOP and VCOP are based on the summaries from **Table 4.14** and **Table 4.18.** It should be noted that FCOP increases due to the 3% yearly rise in salary. VCOP results are also scaled to the production of 500 batches.

Year	Gold sales ($)	CapEx ($)	FCOP ($)	VCOP ($)	Gross profit ($)
0	-	8697.84	-	-	-
1	14467.5	-	5060.85	5105	4301.65
2	14467.5	-	5212.05	5105	4150.45
3	14467.5	-	5367.79	5105	3994.71
4	14467.5	-	5528.19	5105	3834.31
5	14467.5	-	5693.41	5105	3669.09

Table 4.19. Projected gross profit results over five years.

The cash flow is calculated from the gross profit, from which taxes (29.5%) were deducted after subtracting linear depreciation charges. The cash flow from each of the projected five years is presented in **Table 4.20**.

Year	Gross profit ($)	Depreciation charge ($)	Taxable income ($)	Taxes ($)	Cash flow ($)
0	-	-	-	-	-8697.84
1	4301.65	1739.57	2562.08	755.81	3545.84
2	4150.45	1739.57	2410.88	711.21	3439.24
3	3994.71	1739.57	2255.15	665.27	3329.45
4	3834.31	1739.57	2094.74	617.95	3216.36
5	3669.09	1739.57	1929.52	569.21	3099.88

Table 4.20. Projected cash flow results over five years.

Although the cash flow decreases each year (due to the yearly salary rise), it remains positive over the evaluated period. Moreover, the project could tentatively be extended for additional years. However, depreciation charges would no longer be deducted from gross profit after the fifth year since all assets would already be completely depreciated, except for the tailings dam, which would require expansion. Yearly cash flow is relatively low; however, this is sufficient for artisanal, small-scale operation.

4.6.4. Profitability indicators (NPV and IRR)

The projected net present value (NPV) after five years was $2555.37, considering a 15% discount rate. Likewise, the internal rate of return (IRR) was determined to be 27.2%.

The positive NPV and the high IRR, which was greater than the discount rate, indicate that the project is profitable. Moreover, since the IRR was high, the project is considered highly attractive to potential investors.

4.6.5. Sensitivity analysis

The sensitivity of the projected NPV regarding the capital expenditure, the price of gold, the amount of batches per year and the cost of reagents was evaluated next. The effect on the NPV of these parameters is shown in **Figure 4.14**.

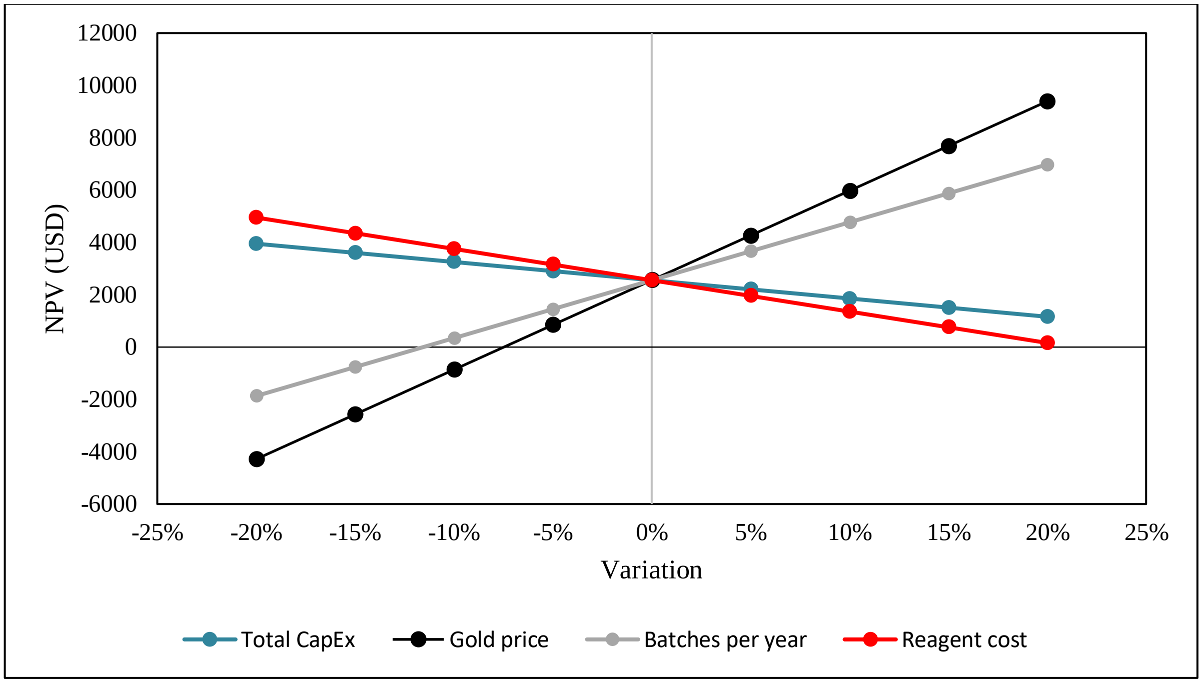

Figure 4.14. Sensitivity analysis of the 5-year projected NPV regarding total CapEx, gold price, scale of operation, and reagent cost.

The effect of varying the capital expenditure on the projected NPV is lower than the effect of the other evaluated factors. As observed, increasing the capital investment reduces the projected NPV moderately. The total capital expenditure would need to be approximately 1.37 times higher to yield a null NPV. This ensures that the project will remain profitable if total CapEx is increased by less than 37% of its current estimation, which leaves a relatively small margin for error in the calculations of capital investment.

Gold price is not a variable that can be manipulated for the sake of the process. However, since gold price fluctuations occur frequently in the international market [74], it is important to understand how they could affect the profitability of the project. **Figure 4.14** reveals that gold price has a critical effect on the projected NPV, since reducing gold price slightly would yield a negative NPV. In fact, gold price per gram would only need to be \$53.54 (~7.5% reduction) to obtain a null NPV. Since the price of gold per gram has reached values lower than the calculated price at some points throughout the last 5 years [74], gold price should be a concern for potential investors. As a result, storing the unprocessed gravimetric table tailings when the price of gold is not suitable and waiting until its price reaches values that would provide profit is a reasonable option. Alternatively, the reprocessing scheme could be performed on the tailings even when gold price is low, although the produced gold should be stored and sold only when price rises again. It should be noted, however, that any of these strategies would result in periods when money is either not being invested or when investments are made with no recovery in the short term.

The number of batches produced per year has also an important impact on the NPV of the process. As observed, increasing the amount of batches results in a higher NPV. However, it should be noted that increasing the yearly batches beyond 625 (a 25% increase) would defy the previously presented schedule. Increasing the scale of production further would require procuring additional equipment, expanding the tailings dam, and hiring at least one more worker, which would increase both the capital expenditure and the fixed operational expenses. On the other hand, the breakeven point (minimum amount of batches that must be processed to obtain a null profit) was determined to be 443 batches (~11.4% reduction). Thus, the project would not be profitable if only one batch was processed daily.

Varying the cost of reagents has a significant effect on the projected NPV: increasing the cost of reagents decreases the NPV. Increasing the cost of reagents by a factor of 1.21 yields a null NPV. This margin allows the process to remain profitable even if variable operational expenses were slightly higher than expected from the study estimate. On that matter, decreasing the cost of reagents through the optimization of ferric sulfate consumption (~75.3% of the cost of raw materials is due to ferric sulfate) is an attractive approach to increase the projected NPV.

CONCLUSIONS

- The gold extraction performance and reagent consumption during thiourea leaching of gravimetric concentration tailings were experimentally evaluated. After contrasting 8 g/L and 12 g/L of thiourea during leaching, it was determined that the lower thiourea concentration consumed less reagents and yielded a greater gold extraction of (86.8±3.1)% after one hour of leaching at ambient temperature. To achieve this extraction, ~18.7 kg/t of thiourea, ~98.2 kg/t of ferric sulfate, 1500 L/t of water, and ~3.1 L/t of sulfuric acid were required. From a technical standpoint, these results justify the inclusion of this stage as part of the process.

- Both direct rare earth acid leaching and acid leaching preceded by an alkaline pretreatment yielded similarly poor extraction results, regardless of acid or alkali concentration during the processes. In all cases, no rare earth (cerium or yttrium) exhibited an extraction higher than 7%. This contrasts with the energy required to maintain the temperature of these processes at 80°C and the consumption of additional reagents to perform the processes and neutralize their effluents. These results do not justify the inclusion of rare earth leaching stages as part of the process.

- The strategy for downstream processing of thiourea leach liquor to recover extracted gold is based on cementation using zinc powder after solid sedimentation and separation. The selection of these unit processes was based on literature review and on the mass balance assessed upon the evaluation of the experimental results of gold extraction. From this evaluation, all extracted gold (~0.5 g per batch of 40 kg of gravimetric table tailings), is to be recovered as a solid after two hours of cementation, which requires 4.67 g of zinc powder. This operation should be followed by a sulfuric acid bath to obtain zinc-free, high purity solid gold.

- The economic assessment of the process revealed that it is profitable over a five-year projection given that 500 batches are reprocessed yearly. The net present value and the internal rate of return were determined to be $2555.37 and 27.2%, respectively. Additionally, a sensitivity analysis revealed that the project remains profitable even with changes within a 20% range of total capital expenditure and cost of reagents, while gold price and scale of production are factors that cause the process to become unprofitable if they are reduced by factors of 7.5% and 11.4%, respectively.

RECOMMENDATIONS

- It is recommended to optimize the operating parameters for thiourea leaching of gold through additional experiments. As identified in this work, the consumption and cost of thiourea and ferric sulfate were high. Performing intensive experimentation to evaluate the impact on gold extraction of altering thiourea concentration, solids percentage, and thiourea to ferric sulfate proportion is suggested. Although this evaluation is beyond the scope of this study, its impact on the sustainability of the process is noteworthy. In addition to reducing variable operation expenses, consuming less thiourea and ferric sulfate decreases the environmental impact of the process.

- The design of the downstream processing strategies should be validated through experiments on the unit processes of gold cementation with zinc and zinc dissolution with sulfuric acid. Parameters such as the required mass of zinc and sulfuric acid were taken from literature-based estimates at conditions that were similar but not identical to those of the designed process. Apart from validating the downstream processing strategies, additional experiments should focus on the optimization of parameters such as pH, temperature, thiourea concentration, and zinc content during cementation of gold, as well as of pH, temperature, and sulfuric acid concentration during zinc dissolution.

- Performing a mineralogical characterization through X-ray diffraction and polarization microscopy of the gravimetric table tailings is recommended for future studies. While this characterization was not considered as part of the objectives of the project, it would yield important information to comprehend the mineral better and search for strategies to optimize the process. This additional evaluation could lead to a better understanding of why rare earth leaching was unsuccessful and provide knowledge to address the extraction of these valuable metals. Likewise, performing a valued mesh analysis would provide understanding on the distribution of gold relative to particle size fraction. This information would be useful to increase the efficiency of the process since sieving the process input would isolate the fractions of mineral that contain gold so as not to address all the mineral as part of the reprocessing scheme.

- After gold extraction, the solid tailings still contain rare earths and other valuable metals such as iron, aluminum, and titanium. Future studies on this matter could take two routes. A first approach could evaluate additional or more intensive processes to extract these metals. Alternatively, another approach would be to quote these tailings to estimate their economic value, since they might be sold directly instead of disposing of them as waste.

- Effluent treatment beyond neutralization should also be evaluated in future studies. In this work, neutralized effluents were sent to a tailings dam. However, it should be determined if the effluents could be partially recycled to the thiourea leaching stage. Nevertheless, this evaluation should also consider whether the additional process to regenerate the effluent is environmentally more convenient than sending it to a tailings dam.

- A detailed environmental impact study of the project should be performed in future research. This study should address both the designed process and the gravimetric concentration stages that precede it, given that they are two parts of a broader project. This assessment should evaluate the effect of performing the processes over the landscape, as well as on the land and aquatic environments of the Madre de Dios basin. As a result, it should also consider in detail all effluent and solid tailing handling strategies. These strategies must include containment measures in case of leakages or filtrations of the aqueous effluents due to unexpected events. As part of future studies, reforestation of the mining and reprocessing sites should also be considered as a strategy to diminish the environmental impact of the process.

- A raw estimate of the required area to install the operation was provided as part of this work. However, this estimate was based on a series of assumptions that should be verified after the tailings dam is designed in detail, aspect that was beyond the scope of this study. As a result, future works should focus on the design of this structure, which would allow for a more accurate surface area requirement estimation. In addition, once this information is available, a plant layout should be drafted to provide guidelines for construction and installation of all equipment, including the tailings dam.

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ANNEXES

ANNEX 1: Research design type selection for specific objectives

Specific objectives	**Design type**	**Justification**
To determine experimentally the extraction performance and reagent consumption when employing thiourea as a leaching agent to extract gold from concentration tailings.	Pure experimental design: -Laboratory based -3 experimental steps (single independent variable, multiple dependent variables)	-The objective explicitly mentions the word "experimentally". -The 2 independent variable (thiourea concentration) levels will be applied to 2 groups (each in duplicate) that are equivalent (a detailed quartering (random, probabilistic) sampling method was used).
To establish the rare earths extraction performance during acid leaching of concentration tailings on an experimental basis.	Pure experimental design: -Laboratory based -3 experimental steps (single independent variable, multiple dependent variables)	-The objective explicitly mentions the word "experimental". -The 2 independent variable (HCl concentration) levels will be applied to 2 groups (each in duplicate) that are equivalent (a detailed quartering (random, probabilistic) sampling method was used).
To develop downstream processing stages to recover the valuable metals extracted during leaching.	It is not linked to a specific experimental or non-experimental research design.	This objective was fulfilled through literature review.
To evaluate the implementation of the reprocessing scheme of gravimetric table tailings through an economic analysis.	Cross-sectional correlational design: -Not laboratory based. -Study will only require experimentation indirectly to validate the analysis.	The technical analysis is based on the results from the previous two objectives. Economic analysis will include NPV and IRR calculations and a sensitivity analysis (independent variables: scale of production and reagent requirements; dependent variable: the NPV of the process.

Table A.1. Matrix of analysis of coherence between specific objectives and selected research design types.

ANNEX 2: Granulometric distribution of the as-received mineral

ASTM E11 sieve	Particle size (geometric mean, mm)	Retained mass (assay 1, g)	Retained mass (assay 2, g)	Retained fraction (assay 1)	Retained fraction (assay 2)	Average retained fraction
70	0.212	4	4.5	2.09%	2.26%	(2.2±0.1) %
-70+100	0.178	25	28.5	13.09%	14.32%	(13.7±0.9) %
-100+140	0.126	52	56.5	27.23%	28.39%	(27.8±0.8) %
-140+200	0.089	52	58.5	27.23%	29.40%	(28±1.5) %
-200+270	0.063	37	29.5	19.37%	14.82%	(17±3) %
-270+400	0.044	16	16	8.38%	8.04%	(8.2±0.2) %
-400	0	5	5.5	2.62%	2.76%	(2.7±0.1) %
Total		191	199	100%	100%	

Table A.2. Granulometric distribution of the as-received mineral sample.

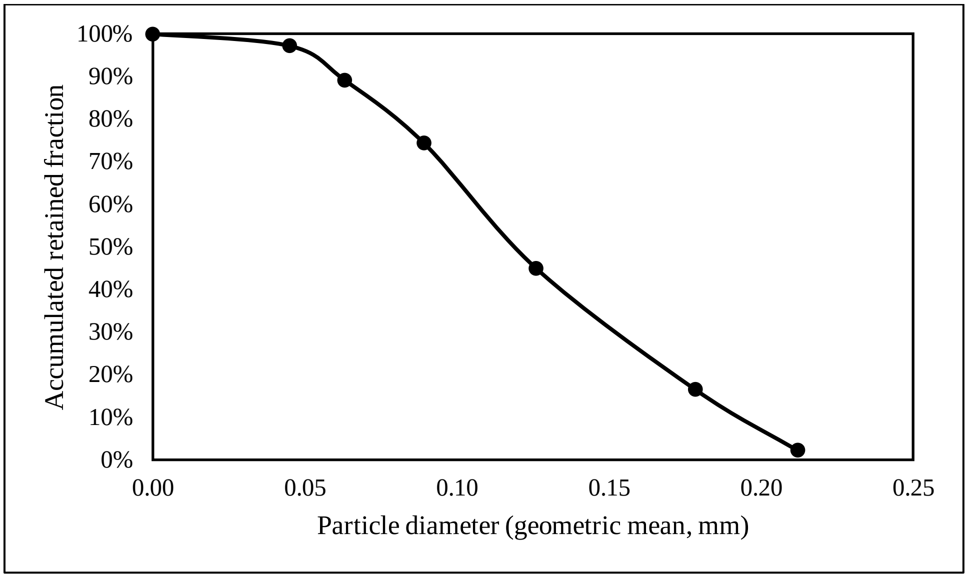

Figure A.2. Accumulated retained fraction in sieves according to particle size. Approximately, d_{50}=0.12 mm.

ANNEX 3: Elemental characterization of the as-received mineral

Element	Determination method	Assay 1 result (ppm)	Assay 2 result (ppm)	Average content (ppm)
Au	AAS	14.95	14.81	14.88±0.07
Ce	RE-ICP	367	400	383.5±16.5
Dy	RE-ICP	<10	<10	<10
Er	RE-ICP	<10	<10	<10
Eu	RE-ICP	<5	<5	<5
Gd	RE-ICP	<20	<20	<20
Ho	RE-ICP	<5	<5	<5
La	RE-ICP	136	162	149±13
Lu	RE-ICP	<5	<5	<5
Nd	RE-ICP	<10	<10	<10
Pr	RE-ICP	<20	<20	<20
Re	RE-ICP	<10	<10	<10
Sc	RE-ICP	12	13	12.5±0.5
Sm	RE-ICP	36	40	38±2
Tb	RE-ICP	<10	<10	<10
Th	RE-ICP	179	200	189.5±10.5
Tm	RE-ICP	<10	<10	<10
Y	RE-ICP	81	83	82±1
Yb	RE-ICP	<5	<5	<5
Ag	ME-ICP	<1	<1	<1
Al	ME-ICP	6700	6600	6650±50
As	ME-ICP	<5	<5	<5
Ba	ME-ICP	53	54	53.5±0.5
Be	ME-ICP	1	1	1
Bi	ME-ICP	317	287	302±15

Ca	ME-ICP	3700	3700	3700
Cd	ME-ICP	9	9	9
Co	ME-ICP	185	177	181±4
Cr	ME-ICP	257	202	229.5±27.5
Cu	ME-ICP	100	100	100
Fe	ME-ICP	>50000	>50000	>50000
K	ME-ICP	1500	1500	1500
Mg	ME-ICP	2300	2200	2250±50
Mn	ME-ICP	6600	6300	6450±150
Mo	ME-ICP	<5	<5	<5
Na	ME-ICP	800	800	800
Ni	ME-ICP	29	29	29
P	ME-ICP	385	420	402.5±17.5
Pb	ME-ICP	<100	<100	<100
Sb	ME-ICP	8	8	8
Sn	ME-ICP	<5	<5	<5
Sr	ME-ICP	28	28	28
Ti	ME-ICP	>50000	>50000	>50000
V	ME-ICP	493	481	487±6
W	ME-ICP	<1	<1	<1
Zn	ME-ICP	100	100	100
Zr	ME-ICP	427	354	390.5±36.5

Table A.3. Elemental characterization of the as-received mineral sample. AAS, ME-ICP, RE-ICP refer to atomic absorption spectroscopy, multi-element inductively coupled plasma, and rare earth inductively coupled plasma, respectively.

ANNEX 4: Gold concentration on extracted aliquots during thiourea leaching stage on first experimental step.

Sample	E.1.1	E.1.2	E.2.1	E.2.2
Sample that underwent thiourea leaching (g)	78.5	81.0	79.5	80.0
Thiourea concentration (g/L)	8	8	12	12
Au 5 min (ppm)	5.07	3.92	2.78	3.24
Au 15 min (ppm)	6.24	5.66	4.14	4.21
Au 30 min (ppm)	7.02	6.32	5.32	5.38
Au 60 min (ppm)	6.97	6.81	6.29	5.51
Au 120 min (ppm)	6.74	6.67	5.62	5.71
Au 180 min (ppm)	6.16	5.95	6.24	4.83
Au 240 min (ppm)	4.96	4.55	5.41	4.38

Table A.4. Gold concentration determined by atomic absorption spectroscopy on the extracted aliquots during acid thiourea leaching of the as-received samples on the first experimental step.

ANNEX 5: Thiourea concentration during acid thiourea leaching stage on first experimental step.

Sample	**E.1.1**	**E.1.2**	**E.2.1**	**E.2.2**
Sample that underwent thiourea leaching (g)	78.5	81.0	79.5	80.0
Thiourea concentration (g/L)	8	8	12	12
5 min (g/L)	6.74	7.08	11.07	10.96
15 min (g/L)	6.39	6.74	10.85	10.73
30 min (g/L)	5.94	6.17	9.25	9.02
60 min (g/L)	5.02	4.57	8.11	8.22
120 min (g/L)	1.83	2.51	5.25	4.00
180 min (g/L)	1.71	1.83	3.88	4.00
240 min (g/L)	1.48	1.60	2.97	3.08

Table A.5. Concentration of thiourea during acid thiourea leaching of the as-received samples on the first experimental step. After each control, thiourea was added to achieve a concentration of 8 g/L or 12 g/L, accounting for replenished aliquots.

ANNEX 6: Elemental characterization of the pregnant leach solution of acid leaching of untreated mineral samples (second experimental step, after 180 min)

Element	Determination method	Concentration after HCl 1 M (ppm)	Concentration after HCl 2 M (ppm)
Au	AAS	<0.1	<0.1
Ce	RE-ICP	3.5±0.5	4
Dy	RE-ICP	<1	<1
Er	RE-ICP	<1	<1
Eu	RE-ICP	<1	<1
Gd	RE-ICP	<1	<1
Ho	RE-ICP	<1	<1
La	RE-ICP	<1	<1
Lu	RE-ICP	<1	<1
Nd	RE-ICP	<1	<1
Pr	RE-ICP	<1	<1
Re	RE-ICP	<1	<1
Sc	RE-ICP	<1	<1
Sm	RE-ICP	<1	<1
Tb	RE-ICP	<1	<1
Th	RE-ICP	21.5±1.5	28.5±0.5
Tm	RE-ICP	<1	<1
Y	RE-ICP	1	1
Yb	RE-ICP	<1	<1
Ag	ME-ICP	<1	<1
Al	ME-ICP	248±22	259.5±11.5
As	ME-ICP	<1	<1
Ba	ME-ICP	2	2
Be	ME-ICP	<1	<1

Bi	ME-ICP	<1	<1
Ca	ME-ICP	121.5±13.5	123±3
Cd	ME-ICP	<1	<1
Co	ME-ICP	1	1
Cr	ME-ICP	5±1	8.5±0.5
Cu	ME-ICP	<1	6
Fe	ME-ICP	2319.5±215.5	6002.5±617.5
K	ME-ICP	16±2	16.5±0.5
Mg	ME-ICP	92±7	94±3
Mn	ME-ICP	10±1	16.5±1.5
Mo	ME-ICP	<1	<1
Na	ME-ICP	<1	<1
Ni	ME-ICP	1	2
P	ME-ICP	35±4	35.5±0.5
Pb	ME-ICP	3	1
Sb	ME-ICP	<1	<1
Sn	ME-ICP	<1	<1
Sr	ME-ICP	1	1
Ti	ME-ICP	40±4	97.5±9.5
V	ME-ICP	5.5±0.5	15±1
W	ME-ICP	<1	<1
Zn	ME-ICP	2.5±0.5	3
Zr	ME-ICP	<1	<1

Table A.6. Elemental characterization of the pregnant leach solution obtained after 180 minutes of acid leaching of untreated mineral samples (averages of E.3.1, E.3.2, and of E.4.1, E.4.2), corresponding to the second experimental step. AAS, ME-ICP, RE-ICP refer to atomic absorption spectroscopy, multi-element inductively coupled plasma, and rare earth inductively coupled plasma, respectively.

ANNEX 7: HCl concentration during acid leaching of rare earths stage on second experimental step.

Sample	E.3.1	E.3.2	E.4.1	E.4.2
Sample that underwent HCl leaching (g)	85.0	85.0	85.0	85.0
HCl concentration (M)	1.00	1.00	2.00	2.00
5 min (M)	1.00	1.00	2.03	2.01
15 min (M)	1.00	1.00	2.01	1.99
30 min (M)	1.00	1.00	2.01	2.01
60 min (M)	1.01	1.01	2.03	2.03
120 min (M)	1.01	1.00	2.01	2.01
180 min (M)	1.03	1.02	2.01	1.99

Table A.7. Concentration of HCl during acid leaching of the as-received samples on the second experimental step. After each control, HCl was added to achieve a concentration of 1 M or 2 M, accounting for replenished aliquots.

ANNEX 8: Gold concentration on extracted aliquots during thiourea leaching stage on second experimental step.

Sample	E.3.1	E.3.2	E.4.1	E.4.2
Sample that underwent thiourea leaching (g)	76.7	76.8	74.2	76.2
HCl concentration during previous acid leaching (M)	1	1	2	2
Thiourea concentration (g/L)	8	8	8	8
Au 5 min (ppm)	2.74	2.80	4.84	4.78
Au 15 min (ppm)	6.25	6.32	6.58	6.19
Au 30 min (ppm)	6.38	6.29	6.12	5.75
Au 60 min (ppm)	6.33	6.49	5.11	4.98
Au 120 min (ppm)	5.66	5.89	4.61	4.79
Au 180 min (ppm)	5.07	5.11	4.67	4.72
Au 240 min (ppm)	4.56	4.76	4.47	3.82

Table A.8. Gold concentration determined by atomic absorption spectroscopy on the extracted aliquots during acid thiourea leaching of the previously HCl leached residue during the second experimental step.

ANNEX 9: Thiourea concentration during acid thiourea leaching stage on second experimental step.

Sample	E.3.1	E.3.2	E.4.1	E.4.2
Sample that underwent thiourea leaching (g)	76.7	76.8	74.2	76.2
HCl concentration during previous acid leaching (M)	1	1	2	2
Thiourea concentration (g/L)	8	8	8	8
5 min (g/L)	6.51	6.74	5.94	6.28
15 min (g/L)	6.05	6.28	5.59	6.05
30 min (g/L)	5.36	5.71	5.02	5.48
60 min (g/L)	3.31	3.54	2.62	2.85
120 min (g/L)	1.71	1.94	1.60	1.37
180 min (g/L)	1.37	1.71	1.26	1.37
240 min (g/L)	1.37	1.60	1.14	1.14

Table A.9. Concentration of thiourea during acid 8 g/L thiourea leaching of samples that underwent HCl leaching at 1 M or 2 M HCl concentration during the second experimental step. After each control, thiourea was added to achieve again a concentration of 8 g/L, accounting for replenished aliquots.

ANNEX 10: Elemental characterization of the alkaline pretreatment solution after treating the as-received mineral samples (third experimental step, after 180 min)

Element	Determination method	Concentration after KOH 6 M (ppm)	Concentration after KOH 3 M (ppm)
Au	AAS	<0.1	<0.1
Ce	RE-ICP	<1	<1
Dy	RE-ICP	<1	<1
Er	RE-ICP	<1	<1
Eu	RE-ICP	<1	<1
Gd	RE-ICP	<1	<1
Ho	RE-ICP	<1	<1
La	RE-ICP	<1	<1
Lu	RE-ICP	<1	<1
Nd	RE-ICP	<1	<1
Pr	RE-ICP	<1	<1
Re	RE-ICP	<1	<1
Sc	RE-ICP	<1	<1
Sm	RE-ICP	<1	<1
Tb	RE-ICP	<1	<1
Th	RE-ICP	<1	<1
Tm	RE-ICP	<1	<1
Y	RE-ICP	<1	<1
Yb	RE-ICP	<1	<1
Ag	ME-ICP	<1	<1
Al	ME-ICP	121±7	105.5±1.5
As	ME-ICP	<1	<1
Ba	ME-ICP	5.5±0.5	5
Be	ME-ICP	<1	<1

Bi	ME-ICP	3.5±0.5	3.5±0.5
Ca	ME-ICP	<1	<1
Cd	ME-ICP	2	2
Co	ME-ICP	3	3
Cr	ME-ICP	<1	<1
Cu	ME-ICP	11	10
Fe	ME-ICP	<1	<1
K	ME-ICP	>10000	>10000
Mg	ME-ICP	<1	<1
Mn	ME-ICP	4	3
Mo	ME-ICP	2	2
Na	ME-ICP	1002±71	521±5
Ni	ME-ICP	3	2
P	ME-ICP	2±1	2
Pb	ME-ICP	1	<1
Sb	ME-ICP	<1	<1
Sn	ME-ICP	3±1	2.5±0.5
Sr	ME-ICP	<1	<1
Ti	ME-ICP	<1	<1
V	ME-ICP	5	5
W	ME-ICP	4±1	1
Zn	ME-ICP	<1	<1
Zr	ME-ICP	1.5±0.5	1

Table A.10. Elemental characterization of the alkaline pretreatment solution obtained after 180 minutes of KOH treatment at 80°C of 95.0 g of untreated mineral samples (averages of E.5.1, E.5.2, and of E.6.1, E.6.2), corresponding to the third experimental step. AAS, ME-ICP, RE-ICP refer to atomic absorption spectroscopy, multi-element inductively coupled plasma, and rare earth inductively coupled plasma, respectively.

ANNEX 11: KOH concentration during alkaline pretreatment on third experimental step.

Sample	**E.5.1**	**E.5.2**	**E.6.1**	**E.6.2**
Sample that underwent alkaline pretreatment (g)	95.0	95.0	95.0	95.0
KOH concentration (M)	6.00	6.00	3.00	3.00
5 min (M)	6.04	6.04	2.96	2.96
15 min (M)	6.08	6.00	3.08	3.08
30 min (M)	6.04	6.00	3.00	3.00
60 min (M)	6.04	5.96	3.04	2.96
120 min (M)	6.04	6.00	2.96	2.96
180 min (M)	6.04	6.00	2.96	2.96

Table A.11. Concentration of KOH during alkaline pretreatment of the as-received samples on the third experimental step. After each control, KOH was added to achieve a concentration of 6 M or 3 M, accounting for replenished aliquots.

ANNEX 12: Elemental characterization of the pregnant leach solution during HCl leaching at 1 M after performing alkaline pretreatment at 6 M or 3 M (third experimental step, after 60 min and 180 min of HCl leaching)

Element	**Determination method**	**After KOH 6 M pretreatment**		**After KOH 3 M pretreatment**	
		HCl 1 M after 60 min (ppm)	**HCl 1 M after 180 min (ppm)**	**HCl 1 M after 60 min (ppm)**	**HCl 1 M after 180 min (ppm)**
Au	AAS	<0.1	<0.1	<0.1	<0.1
Ce	RE-ICP	3.5±0.5	5	3.5±0.5	4.5±0.5
Dy	RE-ICP	<1	<1	<1	<1
Er	RE-ICP	<1	<1	<1	<1
Eu	RE-ICP	<1	<1	<1	<1
Gd	RE-ICP	<1	<1	<1	<1
Ho	RE-ICP	<1	<1	<1	<1
La	RE-ICP	<1	<1	<1	<1
Lu	RE-ICP	<1	<1	<1	<1
Nd	RE-ICP	<1	<1	<1	<1
Pr	RE-ICP	<1	<1	<1	<1
Re	RE-ICP	<1	<1	<1	<1
Sc	RE-ICP	<1	<1	<1	<1
Sm	RE-ICP	<1	<1	<1	<1
Tb	RE-ICP	<1	<1	<1	<1
Th	RE-ICP	12.5±0.5	24±1	13	23.5±0.5
Tm	RE-ICP	<1	<1	<1	<1
Y	RE-ICP	<1	<1	<1	<1
Yb	RE-ICP	<1	<1	<1	<1
Ag	ME-ICP	<1	<1	<1	<1

Al	ME-ICP	55±10	125.5±2.5	74±6	158.5±1.5
As	ME-ICP	<1	<1	<1	<1
Ba	ME-ICP	7	7	7	8
Be	ME-ICP	<1	<1	<1	<1
Bi	ME-ICP	2	1	2	1
Ca	ME-ICP	89±7	114±1	107.5±0.5	143±5
Cd	ME-ICP	2	2	2	2
Co	ME-ICP	3	3	3	3
Cr	ME-ICP	<1	3±1	<1	1
Cu	ME-ICP	9	9	9	9.5±0.5
Fe	ME-ICP	1064±25	2607±96	1387±114	3283±91
K	ME-ICP	215±109	153±43	61.5±3.5	69.5±3.5
Mg	ME-ICP	22±2	55.5±2.5	32±2	67±3
Mn	ME-ICP	10	15	11	16
Mo	ME-ICP	1	1	1	1
Na	ME-ICP	45	44.5±0.5	44±1	45±1
Ni	ME-ICP	3	3.5±0.5	3	3
P	ME-ICP	12.5±0.5	13.5±0.5	16.5±0.5	17
Pb	ME-ICP	2	3	2.5±0.5	3
Sb	ME-ICP	<1	<1	<1	<1
Sn	ME-ICP	2	2	2	2
Sr	ME-ICP	2	2.5±0.5	2	2
Ti	ME-ICP	54.5±1.5	78.5±1.5	40.5±0.5	70±1
V	ME-ICP	5	9	6	10
W	ME-ICP	<1	<1	<1	<1
Zn	ME-ICP	2.5±0.5	3	2	3
Zr	ME-ICP	1	1	1	1

Table A.12. Elemental characterization of the pregnant leach solution during 1 M HCl leaching at control times 60 min and 180 min for the samples that underwent alkaline pretreatment with KOH 6 M and KOH 3 M for 180 minutes at 80°C, corresponding to the third experimental step (averages of E.5.1, E.5.2, and of E.6.1, E.6.2). 86.2±0.1 g and 85.1±0.01 g of pretreated mineral were used for the experiments after KOH 6 M and after KOH 3 M, respectively. AAS, ME-ICP, RE-ICP refer to atomic absorption spectroscopy, multi-element inductively coupled plasma, and rare earth inductively coupled plasma, respectively.

ANNEX 13: HCl concentration during acid leaching of samples that underwent an alkaline pretreatment on third experimental step.

Sample	**E.5.1**	**E.5.2**	**E.6.1**	**E.6.2**
Sample that underwent HCl leaching (g)	86.1	86.3	85.0	85.0
KOH concentration during pretreatment (M)	6.00	6.00	3.00	3.00
HCl concentration (M)	1.00	1.00	1.00	1.00
5 min (M)	0.98	0.98	1.01	1.01
15 min (M)	1.02	1.00	1.00	1.01
30 min (M)	1.02	1.01	1.01	1.01
60 min (M)	0.99	1.01	1.02	1.01
120 min (M)	1.01	1.02	1.02	1.02
180 min (M)	1.02	1.02	1.02	1.03

Table A.13. Concentration of HCl during acid leaching of samples that underwent alkaline pretreatment with 6 M and 3 M KOH. After each control, HCl was added to achieve a concentration of 1 M, accounting for replenished aliquots.

ANNEX 14: Gold concentration on extracted aliquots during thiourea leaching stage on third experimental step.

Sample	E.5.1	E.5.2	E.6.1	E.6.2
Sample that underwent thiourea leaching (g)	75.9	76.0	76.7	75.0
KOH concentration during alkaline pretreatment (M)	6	6	3	3
HCl concentration during previous acid leaching (M)	1	1	1	1
Thiourea concentration (g/L)	8	8	8	8
Au 5 min (ppm)	5.31	4.19	5.00	4.12
Au 15 min (ppm)	6.97	6.94	6.78	5.90
Au 30 min (ppm)	6.95	7.24	7.16	6.30
Au 60 min (ppm)	7.34	6.94	7.45	6.83
Au 120 min (ppm)	6.95	6.94	7.25	6.70
Au 180 min (ppm)	6.92	6.13	6.52	6.06
Au 240 min (ppm)	5.83	5.88	5.39	5.30

Table A.14. Gold concentration determined by atomic absorption spectroscopy on the extracted aliquots during acid thiourea leaching of the previously KOH pretreated and HCl leached residue during the third experimental step.

ANNEX 15: Thiourea concentration during acid thiourea leaching stage on third experimental step.

Sample	**E.6.1**	**E.6.2**	**E.6.1**	**E.6.2**
Sample that underwent thiourea leaching (g)	75.9	76.0	76.7	75.0
KOH concentration during alkaline pretreatment (M)	6	6	3	3
HCl concentration during previous acid leaching (M)	1	1	1	1
Thiourea concentration (g/L)	8	8	8	8
5 min (g/L)	6.96	6.85	6.17	6.05
15 min (g/L)	6.85	6.74	6.17	6.17
30 min (g/L)	6.74	6.51	5.59	5.25
60 min (g/L)	5.37	5.37	3.31	3.65
120 min (g/L)	3.77	3.65	2.17	2.40
180 min (g/L)	3.77	3.31	1.60	1.83
240 min (g/L)	3.31	3.20	1.26	1.37

Table A.15. Concentration of thiourea during acid 8 g/L thiourea leaching of samples that underwent HCl leaching at 1 M HCl concentration after being 3 M or 6 M KOH pretreated during the third experimental step. After each control, thiourea was added to achieve again a concentration of 8 g/L, accounting for replenished aliquots.

ANNEX 16: Results of sedimentation test of fine particles in pregnant thiourea leach solution.

					
0 min	5 min	15 min	30 min	60 min	90 min
					
120 min	180 min	240 min	480 min	720 min	1440 min

Table A.16. Results of the sedimentation test of fine particles present in pregnant thiourea leach solution obtained after 60 minutes of 8 g/L of thiourea.

ANNEX 17: Summary of the composition of each process stream per batch.

Stream	Mass per batch	Stream composition (%wt)
1	40 kg	100% gravimetric table tailings
2	60 kg	100% water
3	0.23 kg	100% sulfuric acid (18 M)
4	0.75 kg	100% thiourea (0.48 kg are added initially, the rest is added throughout the leaching process)
5	3.93 kg	100% ferric sulfate (2.52 kg are added initially, the rest is added throughout the leaching process)
6	~68.9 kg	~5.8% fine tailing particles, ~94.2% pregnant leach solution (~0.5 g of gold)
7	~64.9 kg	100% pregnant leach solution (~0.5 g of gold)
8	~4.67 g	100% zinc dust
9	~36 kg	100% coarse tailing particles
10	~4 kg	100% fine tailing particles
11	~64.9 kg	100% barren leach solution (~0.17 g of zinc)
12	~5.0 g	~10.0% gold particles, ~90.0% zinc particles
13	~1.78 kg	100% quicklime
14	~66.74 kg	~3.2% ferric hydroxide, ~6.5% calcium sulfate, ~89.2% water, ~1.1% complexed thiourea, traces of zinc sulfate
15*	~17.8 g	100% sulfuric acid (18 M)
16*	~30.4 g	100% water
17*	~0.5 g	~100% gold powder
18*	~52.7 g	Solution from acid bath

Table A.17. Summary of the composition of each process stream for a batch of 40 kg of gravimetric table tailings. Stream numbering is consistent with **Figure 4.10**. *For compliance with the mass balance calculations (which are made on a batch per batch basis), streams 15-18 are displayed as if they were also on the same basis. These streams are only actively part of the process every 50 batches.

ANNEX 18: Hazard Identification, Risk Assessment and Control (HIRAC) matrix for loading and unloading tanks with slurries or solutions.

Identification of risks and hazards			Initial risk			Control measures		Residual risk		
Task	Risk	Hazard	Sever.	Freq.	Risk	Administrative measures	PPE	Sever.	Freq.	Risk
Filling buckets with slurries or solutions	Back injury or muscular strain	Low position of valves	2	2	**4**		Back support belt	2	1	**2**
	Skin or eye irritation	Dilute sulfuric acid, thiourea and ferric sulfate solution	3	5	**15**		Nitrile gloves, long-sleeved shirts, pants, safety goggles	3	2	**6**
	Acid fume inhalation	Dilute sulfuric acid	3	2	**6**		Gas mask (when transporting the hazard)	3	1	**3**
	Electrocution	Electric stirring systems	5	2	**10**	Unplugging stirring system during task		5	1	**5**
	Dust inhalation	Fine mineral or reagent particles	4	3	**12**		Dust mask (when transporting the hazard)	4	1	**4**

Transporting buckets with slurries or solutions	Back injury or muscular strain	Heavy loads	3	4	**12**		Back support belt	3	2	**6**
	Skin or eye irritation	Dilute sulfuric acid, thiourea and ferric sulfate solution	3	5	**15**		Nitrile gloves, long-sleeved shirts, pants, safety goggles	3	2	**6**
	Acid fume inhalation	Dilute sulfuric acid	3	2	**6**		Gas mask (when transporting the hazard)	3	1	**3**
	Dust inhalation	Fine mineral or reagent particles	4	3	**12**		Dust mask (when transporting the hazard)	4	1	**4**
Emptying buckets with slurries or solutions	Back injury or muscular strain	Low position of valves	2	2	**4**		Back support belt	2	1	**2**
	Skin or eye irritation	Dilute sulfuric acid, thiourea and ferric sulfate solution	3	5	**15**		Nitrile gloves, long-sleeved shirts, pants, safety goggles	3	2	**6**
	Acid fume inhalation	Dilute sulfuric acid	3	2	**6**		Gas mask (when transporting the hazard)	3	1	**3**

	Electrocution	Electric stirring systems	5	2	**10**	Unplugging stirring systems during task		5	1	**5**
	Dust inhalation	Fine mineral or reagent particles	4	3	**12**		Dust mask (when transporting the hazard)	4	1	**4**

ANNEX 19: Hazard Identification, Risk Assessment and Control (HIRAC) matrix for thiourea leaching of gold.

Identification of risks and hazards			Initial risk			Control measures		Residual risk		
Task	Risk	Hazard	Sever.	Freq.	Risk	Administrative measures	PPE	Sever.	Freq.	Risk
Addition of sulfuric acid	Skin or eye burn	Concentrated sulfuric acid	5	5	**25**	Add sulfuric acid slowly after loading water	Nitrile gloves, long-sleeved shirts, pants, safety goggles	5	2	**10**
	Acid fume inhalation	Concentrated sulfuric acid	4	4	**16**		Gas mask (when adding the hazard)	4	1	**4**
	Electrocution	Electric stirring systems	5	3	**15**	Train workers to not touch stirring system		5	1	**5**
	Cuts (could lead to loss of limb)	Stirring system impeller	5	3	**15**	Train workers to not touch stirring system		5	1	**5**

Addition of thiourea	Skin or eye irritation	Thiourea	3	5	**15**		Nitrile gloves, long-sleeved shirts, pants, safety goggles	3	2	**6**
	Electrocution	Electric stirring systems	5	3	**15**	Train workers to not touch stirring system		5	1	**5**
	Cuts (could lead to loss of limb)	Electric stirring systems	5	3	**15**	Train workers to not touch stirring system		5	1	**5**
	Dust inhalation	Fine reagent particles	4	3	**12**		Dust mask (when adding the hazard)	4	1	**4**
Addition of ferric sulfate	Skin or eye irritation	Ferric sulfate	3	5	**15**		Nitrile gloves, long-sleeved shirts, pants, safety goggles	3	2	**6**
	Electrocution	Electric stirring systems	5	3	**15**	Train workers to not touch stirring system		5	1	**5**

	Cuts (could lead to loss of limb)	Electric stirring systems	5	3	**15**	Train workers to not touch stirring system		5	1	**5**
	Dust inhalation	Fine reagent particles	4	3	**12**		Dust mask (when adding the hazard)	4	1	**4**
Waiting for reaction to finish	Skin or eye irritation	Dilute sulfuric acid, thiourea and ferric sulfate solution	3	5	**15**	Remain away from R-101 if possible	Nitrile gloves, long-sleeved shirts, pants, safety goggles	3	1	**3**
	Acid fume inhalation	Dilute sulfuric acid	3	2	**6**	Remain away from R-101 if possible	Gas mask (when close to the reactor)	3	1	**3**
	Electrocution	Electric stirring systems	5	2	**10**	Remain away from R-101 if possible		5	1	**5**
	Cuts (could lead to loss of limb)	Electric stirring systems	5	2	**10**	Remain away from R-101 if possible		5	1	**5**

ANNEX 20: Hazard Identification, Risk Assessment and Control (HIRAC) matrix for sedimentation of fine particles.

Identification of risks and hazards			Initial risk			Control measures		Residual risk		
Task	Risk	Hazard	Sever.	Freq.	Risk	Administrative measures	PPE	Sever.	Freq.	Risk
Waiting for sedimentation to finish	Skin or eye irritation	Dilute sulfuric acid, thiourea and ferric sulfate solution	3	5	**15**	Remain away from S-101 if possible	Nitrile gloves, long-sleeved shirts, pants, safety goggles	3	1	**3**
	Acid fume inhalation	Dilute sulfuric acid	3	2	**6**	Remain away from S-101 if possible	Gas mask (when close to the settling tank)	3	1	**3**

ANNEX 21: Hazard Identification, Risk Assessment and Control (HIRAC) matrix for gold cementation with zinc.

Identification of risks and hazards			Initial risk			Control measures		Residual risk		
Task	Risk	Hazard	Sever.	Freq.	Risk	Administrative measures	PPE	Sever.	Freq.	Risk
Addition of zinc powder	Eye irritation	Zinc powder	2	5	**10**		Safety goggles	2	2	**4**
	Electrocution	Electric stirring systems	5	3	**15**	Train workers to not touch stirring system		5	1	**5**
	Cuts (could lead to loss of limb)	Electric stirring systems	5	3	**15**	Train workers to not touch stirring system		5	1	**5**
	Dust inhalation	Fine zinc particles	4	3	**12**		Dust mask (when adding the hazard)	4	1	**4**
Waiting for reaction to finish	Skin or eye irritation	Dilute sulfuric acid, thiourea and ferric sulfate solution	3	5	**15**	Remain away from R-102 if possible	Nitrile gloves, long-sleeved shirts, pants, safety goggles	3	1	**3**

	Acid fume inhalation	Dilute sulfuric acid	3	2	**6**	Remain away from R-102 if possible	Gas mask (when close to the reactor)	3	1	**3**
	Electrocution	Electric stirring systems	5	2	**10**	Remain away from R-102 if possible		5	1	**5**
	Cuts (could lead to loss of limb)	Electric stirring systems	5	2	**10**	Remain away from R-102 if possible		5	1	**5**

ANNEX 22: Hazard Identification, Risk Assessment and Control (HIRAC) matrix for zinc dissolution in acid bath.

Identification of risks and hazards			Initial risk			Control measures		Residual risk		
Task	Risk	Hazard	Sever.	Freq.	Risk	Administrative measures	PPE	Sever.	Freq.	Risk
Addition of sulfuric acid	Skin or eye burn	Concentrated sulfuric acid	5	5	**25**	Add sulfuric acid slowly after loading water	Nitrile gloves, long-sleeved shirts, pants, safety goggles	5	2	**10**
	Acid fume inhalation	Concentrated sulfuric acid	4	4	**16**		Gas mask (when adding the hazard)	4	1	**4**
Waiting for reaction to finish	Skin or eye irritation	Concentrated sulfuric acid	4	5	**20**	Remain away from TK-104 if possible	Nitrile gloves, long-sleeved shirts, pants, safety goggles	4	1	**4**

	Acid fume inhalation	Concentrated sulfuric acid	4	2	**8**	Remain away from TK-104 if possible	Gas mask (when close to the reactor)	4	1	**4**

ANNEX 23: Hazard Identification, Risk Assessment and Control (HIRAC) matrix for neutralization of effluents.

Identification of risks and hazards			Initial risk			Control measures		Residual risk		
Task	Risk	Hazard	Sever.	Freq.	Risk	Administrative measures	PPE	Sever.	Freq.	Risk
Addition of quicklime	Eye or skin irritation	Quicklime	3	5	**15**		Safety goggles	3	2	**6**
	Dust inhalation	Fine quicklime particles	4	3	**12**		Dust mask (when adding the hazard)	4	1	**4**
Waiting for neutralization to finish	Skin or eye irritation	Dilute sulfuric acid, thiourea and ferric sulfate solution	3	5	**15**	Remain away from R-103 if possible	Nitrile gloves, long-sleeved shirts, pants, safety goggles	3	1	**3**
	Acid fume inhalation	Dilute sulfuric acid	3	2	**6**	Remain away from R-103 if possible	Gas mask (when close to the reactor)	3	1	**3**