

Volume 21 | Issue 4 Article 5

2022

Prospects for thiourea as a leaching agent in Colombian gold small-scale mining: A comprehensive review

Author(s) ORCID Identifier:

Johana Borda: (D) 0000-0002-0540-0519 Robinson Torres: (D) 0000-0002-4033-0827

Follow this and additional works at: https://jsm.gig.eu/journal-of-sustainable-mining

Part of the Explosives Engineering Commons, Oil, Gas, and Energy Commons, and the Sustainability Commons

Recommended Citation

Borda, Johana and Torres, Robinson (2022) "Prospects for thiourea as a leaching agent in Colombian gold small-scale mining: A comprehensive review," *Journal of Sustainable Mining*: Vol. 21: Iss. 4, Article 5. Available at: https://doi.org/10.46873/2300-3960.1364

This Review is brought to you for free and open access by Journal of Sustainable Mining. It has been accepted for inclusion in Journal of Sustainable Mining by an authorized editor of Journal of Sustainable Mining.

Prospects for thiourea as a leaching agent in Colombian gold small-scale mining: A comprehensive review

Abstract

Thiourea, as an alternative medium, is one of the most promising leaching agents for gold recovery by its commercial benefits and research challenges associated with performance and environmental impacts. This review article describes the operational conditions for the use of Thiourea vs cyanide, its chemistry, limitations, toxicity factors, environment, and recovery processes. Although thiourea gold extraction processes have not been applied on a large scale due to the instability of the reagent, its potential to overcome the limitations of cyanide is attractive to the process; with pH, potential, oxidant dosage, and temperature control, solubilized gold thiourea species are achieved. These can be recovered from the pregnant leach solution through methods such as activated carbon absorption and adsorption, polyurethane foams, ion exchange, and electrodeposition.

Keywords

mining, gold, cyanide, thiourea.

Creative Commons License



This work is licensed under a Creative Commons Attribution-Noncommercial-No Derivative Works 4.0 License.

Prospects for Thiourea as a Leaching Agent in Colombian Gold Small-Scale Mining: A Comprehensive Review

Johana Borda*, Robinson Torres

Universidad Pedagógica y Tecnológica de Colombia, Facultad de Ingeniería, Escuela de Ingeniería Metalúrgica, Tunja, Colombia

Abstract

Thiourea, as an alternative medium, is one of the most promising leaching agents for gold recovery by its commercial benefits and research challenges associated with performance and environmental impacts. This review article describes the operational conditions for the use of Thiourea vs cyanide, its chemistry, limitations, toxicity factors, environment, and recovery processes. Although thiourea gold extraction processes have not been applied on a large scale due to the instability of the reagent, its potential to overcome the limitations of cyanide is attractive to the process; with pH, potential, oxidant dosage, and temperature control, solubilized gold thiourea species are achieved. These can be recovered from the pregnant leach solution through methods such as activated carbon absorption and adsorption, polyurethane foams, ion exchange, and electrodeposition.

Keywords: mining, gold, cyanide, thiourea

1. Introduction

S ince colonial times and the 19th century, gold was the main export product in Colombia [1], which allowed the equilibrium of the country's low trade balance; in this way, and through the arrival of foreign investors, technology, capital, and the promotion of other activities such as banking, transportation, agriculture, and state financing for gold exports, Colombia was able to integrate as an independent republic into the world economy [2].

This is why in Colombia, large and small-scale gold mining is considered a key engine for the economic development of the country [3]; in addition, its reserves forecast average annual growth of 2.4% in the extraction of the metal [4].

Colombia is the fourth gold producer in Latin America, according to the United States Geological Survey (USGS) and the Mining Authorities of Peru, Mexico, Brazil, Colombia and Argentina, and is the fifteenth gold producer in the world with 61.8 tons [5]. Due to the above and the increase in gold prices,

these mining activities have been expanding over time.

The most important gold deposits in the country are concentrated in three regions between the Western and Central, Central and Eastern Cordilleras, and the lowlands of the Pacific coast [6,7]. These deposits are genetically related to areas of igneous activity in felsic, sedimentary, metamorphic rock deposits, alluvial deposits, and supergene concentration.

Gold can be found in nature in three forms: as a free metal, occluded in the other minerals' crystal structures or combined with other elements forming alloy compounds or minerals such as sulfosalts, tellurides and selenides. In its native state, gold is usually alloyed with silver, copper, bismuth, mercury, and sometimes platinum group elements such as platinum, palladium, ruthenium, and iridium [7].

The gold and platinum-gold placements (alluvial deposits), seams and veins, Skarn deposits, and massive sulfides are the deposits with the greatest potential for this precious metal extraction [8]. In recent years, the departments of Antioquia and

Received 12 May 2022; revised 6 July 2022; accepted 11 July 2022. Available online 19 November 2022

* Corresponding author.

E-mail address: angelajohana.borda@uptc.edu.co (J. Borda).

Chocó have reached around 40 and 25% of total national production, respectively [4]; they are considered the main gold-producing locations in the country.

Today, there are many gold extraction activities, either by large companies or by traditional and informal miners; the latter is the most common practice in gold production since it is a source of income for the rural population. However, this artisanal mining is characterized by being carried out in a very elementary way without technical assistance and with the use of toxic substances (mercury and cyanide) for the concentration and extraction of the metal. Although cyanidation allows favourable gold dissolutions, the potential for toxicity that characterizes cyanide is undeniable. The growth of these mining practices leads to the affectation of rural areas due to environmental degradation, displacement of communities, and loss of livelihood opportunities for farmers [9]. Through the alluvial gold exploitation (EVOA), illegal mining corresponds to 64% of the country's illicit exploitation [10,11]; Failure to comply with the technical and environmental commitments established by the entities in charge makes these productions one of the biggest problems of water resources contamination in Colombia [12]. These contamination problems are due to the fact that over time methylmercury accumulates in aquatic life in higher concentrations and levels [13]; Studies reveal that 1150 water sources in the country cross municipalities with the presence of illegal gold mining. Of these, 232 water sources pass through municipalities in which mercury poisoning cases occurred [12]. This is why it is necessary to venture into the use of alternative and environmentally safe agents for the extraction of gold or in the mitigation of the impacts of cyanide in the leaching of precious metals. Previous studies have shown that thiourea as an organic sulfur compound can generate favourable extractions with better acceptance by environmental control entities [14-16], however, REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) has reported the possible carcinogenicity of this agent, although only in situations of extraordinarily high or prolonged exposure. This literature review comprehensively analyzes the main challenges of thiourea as an alternative reagent to cyanide in the Colombian gold mining sector; technical, environmental, and social aspects will be addressed, as well as the initiatives developed to face current commercial requirements based on a more sustainable gold mining in the country.

2. Traditional gold leaching: cyanide

The use of mercury in the extraction of gold was prohibited in Colombia due to its serious consequences for biota and human health [17,18]. In 2023 this element will be prohibited in all industries in the country. Colombia ratified the Minamata Convention, an international treaty that seeks to reduce global mercury emissions and their effects on health and the environment. The challenge now will be to control this element in illegal mining [19].

As an alternative to this amalgamation method, gold mining has been working with cyanidation for gold leaching because it has internationally approved protocols for its proper management, however, cyanide toxicity potential is undeniable. Currently, the gold mining sector in Colombia is made up of three main subsectors: formal largescale, small-scale, and artisanal mining. Cyanidation work in artisanal mining requires intervention of mining associations for the gold ore processing in order to prevent private individuals from being exposed to cyanide manipulation [20]. Cyanidation is the predominant gold extraction process in large-scale mining and a viable alternative in small-scale mining; around the world, about 90% of gold is recovered using this method [21]; due to its advantages of low cost and high leaching efficiency [20]. In environmental terms, the use of sodium cyanide (NaCN) in Colombia can release between 55,000 and 90,000 T of hydrogen cyanide (HCN) annually into the atmosphere, a moderately significant amount compared to the two million tons that are released globally [22]; and even though some authors have affirmed that cyanide in small doses does not lead to chronic health problems due to its slow metabolization in the body [23,24], others report the need to monitor the atmosphere, waters, and soils exposed to this chemical compound. Its chemical bond is very stable and difficult to remove 25,26].

Water bodies, for example, must be protected from cyanide in any of its forms before being discharged into the environment through advanced oxidation technologies (AOT); chemical oxidation with caustic chlorine [27] or UV photo-chemicals and with H₂O₂ [28] have been used for the degradation of CN⁻ complexes. However, secondary byproducts, residues, and sludge can sometimes be produced that require additional treatment as they are highly toxic and carcinogenic. In addition cyanide-metal complexes can be concentrated in soils generating a potential danger to groundwater [29]. The high operating chemical equipment and

maintenance costs are attributed as disadvantages to these controlled destruction processes [28–30].

Due to economics and technical simplicity, cyanide is the reagent that has long been used as the main agent for gold leaching. However, different authors have worked on various non-toxic alternatives for the process (chlorides, bromides, iodides, thiosulfate, thiocyanate, thiourea, glycine) [31] because of the difficulty that cyanide presents in extracting gold from complex minerals that are difficult to treat, the long leaching times, the considerable interaction with other non-ferrous metals present in gold ores, and for safety and the environment [32]. However, all of these systems that have been investigated for years require both an agent to oxidize the gold and a ligand to form a complex with it in solution. These leachants have not been widely used because they also have some disadvantages; for example, the stability of the KSCN and SCN solutions occurs at potentials below 0 V; otherwise, the agents tend to oxidize forming: sulfates, carbonates, ammonia, and ammonia. In alkaline systems such as Thiosulfate $(S_2O_3^{2-})$, oxidation occurs by itself, forming sulfides, which complicates the gold leaching system [31].

3. Gold leaching with thiourea

The gold dissolution through the use of thiourea has been investigated for several years with promising results [33]. Acidic working conditions and the presence of suitable oxidants are required for thiourea to dissolve gold, forming a cationic complex, through a rapid chemical reaction, which allows the extraction of approximately 90% of the precious metal [34]. The initial concentration of thiourea concerning that of the oxidants and its oxidation kinetics are relevant factors that affect the reaction chemistry of gold under acidic conditions. In addition, the thiourea process is characterized by advantages such as its minimal degree of toxicity to the environment and its selectivity in the extraction of gold [35].

However, due to the complicated chemical composition of gold ores, conventional thiourea leaching cannot efficiently extract precious metal from refractory calcined samples of gold concentrate [36]. Most refractory minerals contain large amounts of sulfides in composition that influence the stability of the thiourea system under different conditions [37]. This is why pretreatments such as roasting and mechanical activations are necessary [38,39], generating sulfide concentrates for the physical benefit of the mineral [40] or by removing the mineral's base metals through citrate leaching

and recoveries by electrolysis and pH adjustment [41], to increase leaching performance from complex refractory minerals. However, mineral roasting as a pretreatment is highly contaminant because it produces SO₂ and gasses.

The use of halide ions in the process has also been effective because it generally involves halogen species that act as both an oxidant and a ligand [42]. Whitehead et al. [43] demonstrated that the leaching of gold with thiourea in chloride ionic liquid depends on the oxidant used. For example, with HSO₅, they achieved favourable extractions compared to those achieved with Fe (III). Yang et al. [44] showed that the addition of small amounts of thiourea to thiocyanate-ferric solutions achieves a synergistic effect on the dissolution of gold through the formation of a mixed ligand complex Au(Tu)₂SCN; in this way, they achieved favourable extraction rates compared to those obtained by conventional cyanidation.

Today, urban mining is also a potential source for gold mining; emerging investigations from different types of residues have achieved promising recoveries using combinations of thiourea with microbial consortia [45], thiourea, and Fe³⁺ at ambient conditions, under studies of particle size, S/L ratio, and concentrations of the reagent and oxidant [46].

4. Comparison of thiourea and cyanide in gold mining

Gold dissolution occurs in oxidizing solutions in the presence of some complexing ligands, such as cyanide and thiourea; this allows extraction to be selective from generally low-grade minerals.

Although thiourea gold mining has been investigated since 1960, only in the last 20 years has it been seriously considered an alternative to the cyanidation process [33]. Gold leaching by thiourea has been considered due to the rapid reaction with gold [41] and its low price, as well as a lower environmental impact compared to cyanide.

4.1. Limitations of the processes. Chemical aspects

The overall dissolution of gold in aerated, alkaline cyanide solutions, Cyanide ions (CN-) form complexes with the gold contained in the ore, forming a "pregnant solution" from which gold is later extracted.

$$4Au + 8CN^{-} + O_{2} + 2H_{2}O \rightarrow Au(CN)^{-}_{2} + 4OH^{-}(1)$$

In cyanide solutions, the oxidation potential is low, which facilitates the dissolution of gold (Fig. 1).

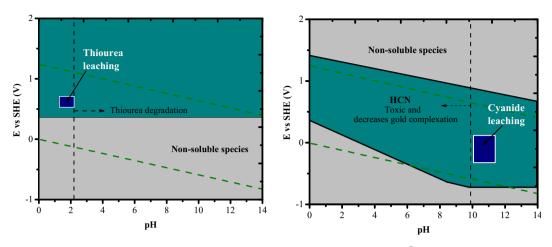


Fig. 1. Indicative ranges of Eh-pH used in industrial gold extraction processes. Designed with MEDUSA® software, with information from the NIST database (Database 46 – Vers. 8.0) [47,48].

The only stable complex in the aqueous solution is Au(CN)₂, and even though said stability does not depend on pH, at values close to 10, there is the least oxidizing zone and, therefore, the most favourable for the process. The formation of HCN at pH values less than 10 decreases the amount of available cyanide ion for gold complexation, affecting the precious metal oxidation potential.

Thermodynamically, cyanide is unstable in water and undergoes spontaneous oxidation. Its power to dissolve gold is effective, but its kinetics are too slow due to the low solubility of oxygen in the solution. The HCN formation at pH values less than 10, decreases the amount of available cyanide ion for gold complexation and affects the gold oxidation potential On the other hand, thiourea can be oxidized to formamidine disulphide (NH₂(NH)CSSC(NH) (NH₂)) in an acidic solution. When there are oxidants in the system (oxygen, Fe³⁺ or H₂O₂), gold can dissolve in the solution rapidly by forming complexing ion with thiourea.

$$Au + 2SC (NH_2)_2 + 1/4O_2 + H^+$$

 $\rightarrow Au [SC(NH_2)_2]_2^+ + 1/2H_2O$ (2)

Au + 2SC (NH₂)
$$_2$$
 + Fe³⁺
 \rightarrow Au [SC(NH₂) $_2$] $_2^+$ + Fe³⁺ (3)

$$2Au + 4SC (NH2)2 + H2O2 + 2H+$$

 $\rightarrow 2Au [SC(NH2)2]2 + 2H2O (4)$

The figure shows that at high redox potentials (greater than 500 mV), the stabilization of both the complex and the formamidine disulfide are

favoured. Lower potentials are good for reducing the consumption of thiourea, but at the same time, they also lead to a decrease in the dissolution of gold. In the same way, the dissolution speed is benefited from these potential values. Therefore air and oxygen are inadequate oxidants for high extractions in short time scales. The use of strong oxidants such as Fe (III), hydrogen peroxide and/or ozone is required. Leaching rates in thiourea solutions are very fast, much faster than those achieved by cyanide. The kinetics in these processes is controlled by the diffusion of reagents to the surface of the gold and, therefore, is linked to the concentrations of Fe (III), formamidine disulfide and thiourea species. Generally, one should work at pH values of 1.4-1.8 to avoid thiourea oxidation [49].

Chemically, thiourea is unstable and, under alkaline conditions, can easily break down into other compounds. Furthermore, the leaching rate of the gold depends on the dosage of the oxidant. Inadequate amounts of oxidant can also result in the oxidation of thiourea to formamidine disulfide, sulfate, sulfite, and elemental sulfur. These species, obtained by the decomposition of the reagent, have the potential to passivate the leaching by forming coating layers on the surface of the metal, which reduces its dissolution [46,50]. Due to the above and the catalytic decomposition by some impurities in the minerals (such as pyrite and soluble ferric oxide), high consumption of thiourea occurs during the process [36,51].

This is why the reagent must be used under relatively restricted conditions. Leaching is normally carried out under careful optimization and control of pH, redox potential, concentration and consumption of thiourea, as well as working time and process temperature [52]. Due to poor reagent stability, the high reaction temperature can cause thiourea to be thermally decomposed [33].

The efficiency of large-scale thiourea leaching operations is also limited, mainly due to the lack of profitability compared to conventional cyanide [53]. The economy of thiourea leaching is determined by the consumption of reagents. Therefore, its reduction is the most considerable problem to be solved to improve the viability of the process. That is why the authors have sought to stabilize thiourea additives such as sulfate, sodium hexametaphosphate (SHMP), sodium lignosulfonate (CMN), and amino acids, among others, to reduce reagent consumption effectively [39].

The consumption of thiourea when complexing with cyanicidal metals is low compared to cyanide; therefore, there is the possibility of recirculating and regenerating it since the other metals, products of secondary reactions, do not contaminate it [36].

4.2. Extraction

The gold stability is reduced in the presence of certain complexing ligands, such as cyanide, chloride, thiourea, thiocyanate, and thiosulfate ions, through the formation of stable complexes. As a result, gold can dissolve in relatively mild oxidizing solutions, for example, aerated aqueous cyanide solutions. Normally when cyanide solutions are used, they are very dilute, typically between 0.01% and 0.05% cyanide (100–500 parts per million) [54]. The stability constants show that some complex ligands form more stable complexes with Au(I) and others with Au(III). It all depends on the mineralogy of the mineral and extractants used. For example, the United States Bureau of Mines (USBM) in 1988 conducted agitation leaching tests on 14 precious metal ores using sodium cyanide (NaCN) and thiourea [(NH₂)₂CS] as leaching reagents [55]. The objective was to compare the results of the two extractants. Cyanide was used at a concentration of 2 g/L with and without H₂O₂ as oxidant, while thiourea was used at concentrations of 2 and 20 g/L, and the solution potential was controlled with a standard hydrogen electrode from 390 to 420 mV. With both reagents at 2 g/L, cyanide extracted more gold than thiourea of all minerals. At 20 g/L thiourea compared to 2 g/L cyanide, thiourea extracted more gold from two ores (Table 1). Cyanide extracted more gold than thiourea from 10 of the 14 ores tested.

It' is important to mention that this comparison was made from an industrial rather than a stoichiometric perspective. On a molar basis, the

Table 1. Extraction of Au from gold ores [55].

| Sample | NaCN (2 g/L) | $NaCN + H_2O_2$ (2 g/L) | Thiourea (2 g/L) | Thiourea (20 g/L) |
|--------|-----------------|-------------------------|---------------------|----------------------|
| 1 | 92% | 96% | 70% | 70% |
| 2 | 82% | 93% | 0% | 60% |
| 3 | 75.5% | _ | 50% | 50% |
| 4 | 82% | 89% | 78% | 100% |
| 5 | 100% | 100% | 0% | 82% |
| 6 | 86% | _ | 0% | 80% |
| 7 | 67% | 100% | 0% | 100% |
| 8 | 67% | 100% | 0% | 0% |
| 9 | 83.5% | _ | 0% | 44% |
| 10 | _ | _ | _ | _ |
| 11 | 64% | 83% | 18% | 49% |
| 12 | 4% | 5% | 1% | 4% |
| 13 | 32% | 34% | 1% | 18% |
| 14 | 18% | _ | 0% | 11% |

thiourea solution is weaker (0.026 M) than the cyanide (0.041 M) because of the higher molecular. The operating conditions were not the same for both reagents of Molar concentration terms. In addition, the oxidant dosage is not specific and is used only for one of the two reagents. Therefore, further studies will be necessary to technically compare the extraction of gold from cyanide and thiourea. Increasing the concentration from 2 to 20 g/L of thiourea improved the metal extraction, which may indicate that base metals consuming extractants. Torres and Lapidus [41] showed that the pretreatment of ore by leaching with citrate solutions to remove and recover base metals from complex refractory ores shows a great improvement in the extraction of gold with thiourea 0.4 M (Table 2) in relation to the untreated ore (as-received).

4.3. Recovery

The behaviour of the complexes formed by gold with cyanide and thiourea is different. The high stability granted by cyanide requires a strong reducing agent such as zinc, while thiourea can be reduced with milder agents such as nitrite and sulfite ions. Previous studies have found that the gold—thiourea complexes can be absorbed on activated carbon without undergoing chemical changes, as well as the adsorption of some ions involving anions such as ClO₄, Cl⁻ o HNO₃. However, the concentration of thiourea ions must be high enough to ensure adequate performance in the recovery

Table 2. Extraction of Au from complex refractory gold ore. Taken from [41].

| Mineral as received | Previous citrate leaching | |
|---------------------|---------------------------|--|
| 20% | 65% | |

process [55]. Furthermore, it should be noted that the adsorption of gold thiourea complex on activated carbon is not as selective since thiourea competes for the surface sites. These adsorptions of gold on activated carbon have been worked through the use of CIP (carbon in pulp), CIL (carbon in leach), and CIC (carbon in column or carbon in clear solution) processes depending on the leaching technique used in the solid-liquid extraction and the physical and chemical properties of the mineral [56].

Gönen et al. [55] showed that the CIL process avoids the easy degradation of thiourea and passivation of the mineral surface, disadvantages found in common leaching processes suitable for CIP and CIC. By simultaneously dissolving and adsorbing in the same tank adding activated carbon during leaching, the CIL process has the advantage of being more economical. However, the reports that propose these processes do not discuss the desorption step [57].

Other recovery methods studied once the gold has been solubilized in acid thiourea are the use of polyurethane foam loaded with tributylphosphate, however, this technique was worked with low concentrations of gold, which may limit its application to real samples [58]. The use of ion exchange resins (Dowex M-33 y Ionac C-249) has also been used, with the disadvantage of considerable time consumption, since the increase in recovery occurs when the contact time is increased from 48 to 96 h [56]. Direct electrodeposition has benefits such as reducing the number of unit operations and maximizing reagent recirculation; however, copper ions limit the potential range where the selective gold deposit is formed [59].

Solvent extraction has stood out within the techniques described above for industrial application in the recovery and purification of metals from leaching liquors, especially from electronic waste, due to its simplicity, high processing speed, and wide applications [60]. This technique has also been used to purify gold or silver from cyanidation solutions [57].

Gold solutions with cyanide have been treated by zinc cementation, achieving recoveries greater than 97%, in addition to being characterized by their low investment, maintenance, and operation costs. The problems lie in what pre-precipitation treatments are necessary, that the process is sensitive to ion interference, and that zinc consumption per ounce of precipitated metal increases if a solution with a low concentration of gold is treated. As with thiourea, activated carbon adsorption is also used to recover gold from cyanide solutions; however, even though no pre-treatments are needed here, its investment cost is higher than zinc cementation operations [61].

The technical simplicity of operations with cyanide about thiourea is remarkable, especially in the task of reaching high gold dissolutions; however, many recovery processes have been investigated and have yielded promising results to make this little-known technology a good alternative for industrial precious metal recovery; Additionally, one of the greatest advantages of thiourea is its ability to be reused, once the precious metals are removed, if the proper recovery method is used [62].

4.4. Cyanide limitations. Social factors

Artisanal gold extraction has become a source of income for the Colombian rural population. Approximately 200,000 miners are dedicated to the search for the precious metal through different processes such as amalgamation or cyanidation. These small-scale mining operations occur in informal conditions. The labour force does not have social or labour security, and they also do not have legal environmental permits. Additionally, these operations have generated spontaneous settlements over the years characterized by precarious living conditions [63].

These informal processes are commonly carried out in mining regions isolated from urban centres, for example, in special management areas such as the territories of ethnic communities. The La Oficina de las Naciones Unidas contra la Droga y el Delito (UNODC) and the Government of Colombia reported that in 49% of the black communities' collective territories, alluvial gold is exploited with machinery on land [64,65].

The modest government management that the Colombian gold zones present is one of the main responsible for this population's scarce resources of public services, health, and education. This is why mining activities are attributed to problems of violence and social conflicts, such as drug trafficking networks and illegal armed groups. Some affirm that the profits due to the production of informal gold are slightly more than double those obtained with cocaine and heroin together because, since it is legal, the precious metal traffic is easier. The lack of regulation in gold mining by the Colombian government generates large profits from the illicit market, benefiting mainly the armed groups, however, the country's financial system has also been affected bythis type of commercialization [63]. Illegal mining in Colombia has grown notably and progressively along with the State's concern to promote the country's extractive sector. However,

this momentum has affected small and mediumsized companies that lack the licenses and financial resources required for a fair share in large-scale mining.

The violence associated with illicit mining is closely related to Colombian politics, which have historically been violent. In addition, some armed groups have resorted to forced displacement to take over the gold exploitations, to combine them in turn with drug trafficking. Guerrilla groups such as the Fuerzas Armadas Revolucionarias de Colombia (FARC), the Ejército de Liberación Nacional (ELN), and paramilitary groups such as the Autodefensas Unidas de Colombia (AUC) have used illegal mining since the mid-1990s as a financing source [66]. This situation has brought social implications since it equates rural communities who have carried out small-scale mining as subsistence strategies with those illegal armed groups.

These mafias have subjected traditional miners for years and have controlled their production and extorted money in exchange for protection and permission to work; this link is, unfortunately, one of the arguments used by the Colombian government to justify the outlawing of their work [63]. Therefore, these communities have been intervened by the army and the police, where they have closed mines, captured people and seized machinery, equipment and explosives [67,68].

In addition to suffering these military interventions, small mining has suffered the aggression of criminal groups that dispute the resource rents. As a consequence of these armed confrontations, the number of homicides and massacres victims in these communities has increased [69].

Gold has undoubtedly become the main commercial interest of armed groups, above drugs and kidnapping. Its powerful economic interests increase in the context of a government that has not prioritized the phenomenon as a great threat to the security of the surrounding population. The reality is that traditional gold mining is linked to violence and illegal acts in very poor areas, although rich in gold.

4.5. Environmental and toxicity factors

Thiourea has been worked as an alternative to cyanide to treat sulfurous minerals that consume it and to mitigate the environmental impacts that they generate and, therefore, restrict its use. Thiourea is a relatively non-toxic agent which behaves like a plant fertilizer in the environment, giving the impression that it could be an attractive alternative to cyanide in environmentally sensitive areas [39].

The environmental impacts generated by gold mining with cyanide are considerable; Artisanal and small-scale gold mining commonly generates changes in the landscape structure, extended degradation to different ecosystem types and potentially arable land [70]. The operations area expansion and the increase in mining settlements also lead to primary and secondary deforestation [71]. Additionally, cyanide leaching accidents have caused water contamination, soil and direct impact on terrestrial ecosystems. The costs of repairs due to improperly draining acid from the mines can be higher than those obtained by extractions [20]. Moreover, as informality is the main way of obtaining the metal, there is little caution and concern for taking corrective actions in this regard.

After one of the most serious environmental disasters in Europe (the Baia Mare cyanide spill in 2000), the International Cyanide Management Code ICMC was developed as a voluntary program in order to improve gold practices by mining companies, as well as for the regulation of producers and transporters [20]. Colombian gold mining has the great challenge of adapting its gold production to ICMC based on safe cyanide management, cyanidation mill tailings, and leaching solutions, however, the challenge is intricate due to a large number of illegal operations in the country, which maintains the risk of possible accidents and deaths from cyanide.

The thiourea reagent has the ability to be used as a leaching agent. Respect to de cyanide, the thiourea has the lack that is less stable than cyanide. The copper ion can act as the cyanide equivalent by forming complexes with four thiourea molecules. High concentrations of cupric and ferric ions can also degrade reagent [72]. However, some progress has already been reported in controlling thiourea degradation in these complex solutions by operating in a specific potential range and adding sequestering agents for both cupric and ferric ions [62,73]. The initiative to improve extractions in terms of safety and health, social and environmental conditions in the gold mining sector could be achieved if work continues in the search for favourable conditions for the implementation of this alternative agent; as a traditional method, cyanide leaching hardly achieves clean production because of its high consumption of auxiliary materials, inefficient production, and high environmental pollution.

It has been shown that small-scale mining has some disadvantages that influence gold extraction, despite being metallurgically efficient. For example, the economic limitations for the producers, are reflected in the lack of technology for the ore benefit

REVIEW ARTICLE

process and the lack of technical and technological training of the miners [74]. Additionally, the treatment of gold-bearing minerals under these conditions is usually unprofitable (due to low extraction) and leads to the use of recovery methods, which are aggressive to the environment. In addition to the social impact, there is concern about the magnitude of the environmental impacts associated with small-scale mining, such as alterations in the hydrogeological regime due to the natural course of the rivers deviation [70], water sources contamination and the food chain alteration due mercury and possibly cyanide accumulation [75].

One of the main problems for the extractive industry in Colombia is the high cost of robust equipment and large quantities of inputs, in addition to the environmental licenses that mining projects must have. The thiourea use as a substitute lixiviant in the gold extraction process makes up for the use of cyanide environmental disadvantages. This would allow small-scale producers to more easily obtain the environmental authorizations established by Colombian legislation [76,77].

5. Conclusions

Cyanide is the reagent used with predominance to leach gold thanks to its strong complexing power with the metal and the technical simplicity of the leaching process. It does not require greater control, only that it must be worked at alkaline pH values, and it is economical both in leaching and in the recovery process from the cyanide solution. However, the use of cyanide can bring challenges in terms of environmental, social, health and safety aspects. Its leaching kinetics is slow, and in the presence of refractory minerals, carbonaceous matter, and gold minerals with copper content, it generates a high reagent consumption which increases processing costs.

Thiourea leaching has been used as an alternative to cyanide, and it has the advantages of fast leaching rate, low toxicity, high efficiency, environmentally friendly, fewer interfering ions, easier reagent handling, and higher selectivity towards gold. The thiourea disadvantage is that it oxidizes and is consumed very quickly, and it can degrade if there is no rigorous control of the conditions required for leaching, which results in higher costs compared to cyanidation.

Subsequent research will be necessary to establish optimal conditions that allow the extraction of gold

with thiourea solutions at an industrial level to mitigate socioeconomic and environmental impacts that have affected the Colombian gold areas over the years.

Due to a large amount of material processed and the rapid kinetics of thiourea, this reagent could help small businesses to be more competitive against large gold producers.

Ethical statement

The authors state that the research was conducted according to ethical standards.

Funding body

None.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgment

The authors are grateful for the support received from the VIE-SGI project to carry out this research, as well as the Grupo Metalurgia No Ferrosa of the Universidad Pedagógica y Tecnológica de Colombia UPTC.

Appendix I.

Reported values of the complex stability constants of metal ions with thiourea and cyanide [47,48].

| Species | log K |
|--------------------------------|-------|
| AuTu ₂ ⁺ | 21.96 |
| $Au(CN)_2^-$ | 41.8 |
| HCN | 9.23 |
| Au(cr) | 30.93 |

References

- [1] Cigüenza-Riaño. Noelia (20 de julio de 2019). En 200 años, la economía colombiana pasó del oro colonial al petróleo. La República. https://www.larepublica.co/economia/en-200-anos-la-economia-colombiana-paso-del-oro-colonial-al-petroleo-2886953. [Accessed 13 July 2021].
- [2] Molina Londoño LF. La" industrialización" de la minería de oro y plata en Colombia en el siglo XIX: sociedad de zancudo y compañía minera de Antioquia. Biblioteca Virtual Biblioteca Luis Ángel Arango. Credencial Historia; 2011 (258), https://www.udea.edu.co/wps/wcm/connect/udea/57455fdb-3a2c-4597-bfa7-49ff41d056a9/mineria-industrializacion-paismirada-antioquia-economia.pdf?MOD=AJPERES. [Accessed 6 June 2021].
- [3] Rudas G. La locomotora minera: crecimiento compatible con la adaptacion al cambio climatico? Bogota 2013. http://www.

- indepaz.org.co/wp-content/uploads/2013/04/La_Locomotora_ Minera_Crecimiento_compatible_con_la_adaptacion_al_ cambio_climatico_1_.pdf. [Accessed 10 July 2021].
- [4] Betancur-Corredor B, Loaiza-Usuga JC, Denich M, Borgemeister C. Gold mining as a potential driver of development in Colombia: challenges and opportunities. J Clean Prod 2018;199:538–53. https://doi.org/10.1016/j.jclepro.2018.07.142.
- [5] Agencia Nacional de Minería, 01 de Julio de. Colombia mejora ranking de producción de oro. 2022. https://www.anm.gov.co/?q=colombia_mejora_ranking_de_producci% C3%B3n_oro.
- [6] Prieto R, Guatame G, y Cárdenas CL, S. C. (comps). Recursos minerales de Colombiavol. 2. Bogotá: Servicio Geológico Colombiano; 2019. https://doi.org/10.32685/9789585246980.
- [7] Arias A, y López J. Oro. En: recursos minerales de Colombia, vol. 2. Bogotá: Servicio Geológico Colombiano; 2019.
- [8] Ingeominas. Zonas potenciales para metales preciosos en Colombia. 2005. Bogota.
- [9] Specht D, Ros-Tonen M. Gold, power, protest. Digital and social media and protests against large-scale mining projects in Colombia. New Media Soc 2017;19(12):1907e1926.
- [10] Veiga MM, Marshall BG. The Colombian artisanal mining sector: formalization is a heavy burden. The Extractive Industries and Society; 2018. https://doi.org/10.1016/j.exis.2018. 11.001.
- [11] ILO, International Labour Organization. FORLAC: trends in informal employment in Colombia. 2014. p. 2009–13. http:// www.ilo.org/wcmsp5/groups/public/— americas/—ro-lima/ documents/publication/wcms_245885.pdf. [Accessed 6 June 2021].
- [12] Gafner-Rojas CM. La contaminación hídrica por mercurio y su manejo en el derecho colombiano. Tratado de derecho de aguas. En: tomo I: derecho de aguas colombiano para el siglo XXI. Bogotá D.C, Universidad Externado de Colombia; 2018. p. 493–526.
- [13] Esdaile LJ, Chalker JM. The mercury problem in artisanal and small-scale gold mining. Chem Eur J 2018;24(27): 6905–16. https://doi.org/10.1002/chem.201704840.
- [14] Eisele JA, Hunt AH, Lampshire DL. Leaching gold-silver ores with sodium cyanide and thiourea under comparable conditions. BuMinesR.I 1988;9181.
- [15] Carrillo M, Delgado J, Córdoba E. Lixiviación con tiourea de dos minerales auroargentíferos santandereanos. Rev Colomb Mater 2014;(5):319–24. https://revistas.udea.edu.co/index. php/materiales/article/view/19478.
- [16] Gönen N. Leaching of finely disseminated gold ore with cyanide and thiourea solutions. Hydrometallurgy 2003;69(1–3):169–76. https://doi.org/10.1016/s0304-386x(03)
- [17] Ley 1658 de 2013. Por medio de la cual se establecen disposiciones para la comercialización y el uso de mercurio en las diferentes actividades industriales del país, se fijan requisitos e incentivos para su reducción y eliminación y se dictan otras disposiciones. 15 de julio de 2013. https://www.minambiente.gov.co/index.php/component/content/article?id=600:plantilla-asuntos-ambientales-y-sectorial-y-urbanasin-galeria-51. [Accessed 23 June 2021].
- [18] Gallo-Corredor Jose, Pérez Humberto, Figueroa Ricardo, Figueroa-Casas Apolinar. Water quality of streams associated with artisanal gold mining; Suárez, Department of Cauca, Colombia. Heliyon 2021;7:e07047. https://doi.org/10. 1016/j.heliyon.2021.e07047.
- [19] Paz-Cardona AJ. Colombia bans the use of mercury in mining. Mongabay; 2018. https://news.mongabay.com/2018/ 08/colombia-bans-the-use-of-mercury-in-mining/.
- [20] Brüger A, Fafilek G, Restrepo BOJ, Rojas-Mendoza L. On the volatilisation and decomposition of cyanide contaminations from gold mining. Sci Total Environ 2018;627:1167–73. https://doi.org/10.1016/j.scitotenv.2018.01.320.
- [21] Holley EA, Smith NM, Delgado Jimenez JA, Cabezas IC, Restrepo-Baena OJ. Socio-technical context of the

- interactions between large-scale and small-scale mining in Marmato, Colombia. Resour Pol 2020;67:101696. https://doi.org/10.1016/j.resourpol.2020.1016.
- [22] Li H, Long H, Zhang L, Yin S, Li S, Zhu F, et al. Effectiveness of microwave-assisted thermal treatment in the extraction of gold in cyanide tailings. J Hazard Mater 2020; 384:121456.
- [23] NICNAS -National Industrial Chemicals Notification and Assessment Scheme. Commonwealth of A, 2010. Sodium cyanide. Sydney, Australia.
- [24] ŚWA -Safe Work Australia. Guide for preventing and responding to cyanide poisoning in the workplace. Commonwealth of Australia; 2013. https://www.safeworkaustralia.gov.au/system/files/documents/1702/guide-cycanide-poisoning-workplace.pdf. [Accessed 22 July 2021].
- [25] Cicerone RJ, Zellner R. The atmospheric chemistry of hydrogen cyanide (HCN). J Geophys Res 1983;88:10689.
 [26] Kleinböhl A, Toon GC, Sen B, Blavier J-FL, Weisenstein DK,
- [26] Kleinböhl A, Toon GC, Sen B, Blavier J-FL, Weisenstein DK, Strekowski RS, et al. On the stratospheric chemistry of hydrogen cyanide. Geophys Res Lett 2006;33(11). https://doi. org/10.1029/2006gl026015.
- [27] Botz MM. Overview of cyanide treatment methods. London, UK: Mining Environmental Management. Mining Journal Ltd; 2001. p. 28–30.
- [28] Ozcan E, Gok Z, Yel E. Photo/photochemical oxidation of cyanide and metal—cyanide complexes: ultraviolet A versus ultraviolet C. Environ Technol 2012;33:1913—25.
- [29] Shehong L, Baoshan Z, Jianming Z, Xiaoying Y. The distribution and natural degradation of cyanide in goldmine tailings and polluted soil in arid and semiarid areas. Environ Geol 2005;47:1150–4.
- [30] Dash RR, Gaur A, Balomajumder C. Cyanide in industrial wastewaters and its removal: a review on biotreatment. J Hazard Mater 2009;163(1):1–11. https://doi.org/10.1016/j. jhazmat.2008.06.051.
- [31] Zheng S, Wang Y, Chai L. Research status and prospect of gold leaching in alkaline thiourea solution. Miner Eng 2006;19(13):1301–6. https://doi.org/10.1016/j.mineng.2005.12.009.
- [32] Muir DM, Aylmore MG. Thiosulphate as an alternative to cyanide for gold processing issues and impediments. Miner Process Extr Metall (IMM Trans Sect C) 2004;113(1): 2—12. https://doi.org/10.1179/037195504225004661.
- [33] Hilson G, Maconachie R. Artisanal and small-scale mining and the sustainable development goals: opportunities and new directions for sub-saharan Africa. Geoforum 2019-111
- [34] Yannopoulos JC. The Extractive Metallurgy of Gold 1991. https://doi.org/10.1007/978-1-4684-8425-0.
- [35] Zhang XM, Senanayake G. A review of ammoniacal thiosulfate leaching of gold — an update useful for further research in non-cyanide gold lixiviants. Miner Process Extr Metall Rev 2016. https://doi.org/10.1080/08827508.2016. 1218872
- [36] Qin H, Guo X, Tian Q, Yu D, Zhang L. Recovery of gold from sulfide refractory gold ore: oxidation roasting pretreatment and gold extraction. Miner Eng 2021;164:106822. https://doi. org/10.1016/j.mineng.2021.106822.
- [37] Qin H, Guo XY, Tian QH, Zhang L. Recovery of gold from refractory gold ores: effect of pyrite on the stability of the thiourea leaching system. Int J Miner Metall Mater 2021;28: 956-64. https://doi.org/10.1007/s12613-020-2142-9.
- [38] Zhang L, Guo X, Tian Q, Li D, Zhong S, Qin H. Improved thiourea leaching of gold with additives from calcine by mechanical activation and its mechanism. Miner Eng 2022;178:107403. https://doi.org/10.1016/j. mineng.2022.107403.
- [39] Guo X, Zhang L, Tian Q, Qin H. Stepwise extraction of gold and silver from refractory gold concentrate calcine by thiourea. Hydrometallurgy 2020;105330. https://doi.org/10.1016/j. hydromet.2020.105330.

- [40] Murthy DS, Kumar V, Rao K. Extraction of gold from an Indian low-grade refractory gold ore through physical beneficiation and thiourea leaching. Hydrometallurgy 2003;68(1–3):125–30. https://doi.org/10.1016/s0304-386x(02)00197-4.
- [41] Torres R, Lapidus GT. Base metal citrate pretreatment of complex ores to improve gold and silver leaching with thiourea. Hydrometallurgy 2020:105461. https://doi.org/10.1016/j.hydromet.2020.105461.
- [42] Tran T, Lee K, Fernando K. Halides as alternative lixivants for processing gold and silver? An update. In: Young CA, Twidwell LG, Anderson CG, editors. Cyanide: social, industrial and economic aspects. The minerals. Warrendale PA: Metals & Materials Society; 2001. p. 501–8.
- [43] Whitehead JA, Zhang J, McCluskey A, Lawrance GA. Comparative leaching of a sulfidic gold ore in ionic liquid and aqueous acid with thiourea and halides using Fe(III) or HSO5— oxidant. Hydrometallurgy 2009;98(3–4):276–80. https://doi.org/10.1016/j.hydromet.2009.05.012.
- [44] Yang X, Moats MS, Miller JD, Wang X, Shi X, Xu H. Thiourea—thiocyanate leaching system for gold. Hydrometallurgy 2011;106(1–2):58–63. https://doi.org/10.1016/j.hydromet. 2010.11.018.
- [45] Sheel Anvita, Pant, Deepak Pant. Thiourea Bacillus combination for gold leaching from waste lithium-ion batteries. Bioresource Technology Reports 2021;15:100789. https://doi.org/10.1016/j.biteb.2021.100789.
- [46] Jing-ying L, Xiu-li X, Wen-quan L. Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones. Waste Manag 2012;32(6):1209–12. https://doi.org/10.1016/j.wasman.2012.01.026.
- [47] NIST. Critically selected stability constants of metal complexes. NIST Standard Reference Database 2004;46. Version 8 0
- [48] Eriksson G. An algorithm for the computation of aqueous multicomponent, multiphase equilibria. Anal Chim Acta 1979;112:375–83.
- [49] Groenewald T. Potential applications of thiourea in the processing of gold. J S Afr Inst Min Metall 1977;77:217–23.
- [50] Jeffrey MJ, Watling K, Hope GA, Woods R. Identification of surface species that inhibit and passivate thiosulfate leaching of gold. Miner Eng 2008;21(6):443–52. https://doi.org/10. 1016/j.mineng.2008.01.006.
- [51] Yang X, Moats MS, Miller JD. Gold dissolution in acidic thiourea and thiocyanate solutions. Electrochim Acta 2010; 55(11):3643–9. https://doi.org/10.1016/j.electacta.2010.01.105.
- [52] Lapidus-Lavine, Terri Gretchen. Modelado matemático de la lixiviación de argentita con sulfato férrico y tiourea. Doctorado en Ciencias. México: Universidad Autónoma Metropolitana-Unidad Iztaoalapa; 1992.
- [53] Zhang Y, Cui M, Wang J, Liu X, Lyu X. A review of gold extraction using alternatives to cyanide: focus on current status and future prospects of the novel eco-friendly synthetic gold lixiviants. Miner Eng 2022;176:107336. https://doi.org/10.1016/j.mineng.2021.107336.
- [54] Wang C, Chen S, Chen Y, Zi F, Hu X, Qin X, et al. Modification of activated carbon by chemical vapour deposition through thermal decomposition of thiourea for enhanced adsorption of gold thiosulfate complex. Separ Purif Technol 2020:116632. https://doi.org/10.1016/j.seppur. 2020.116632.
- [55] Zhang H, Ritchie IM, La Brooy SR. The adsorption of gold thiourea complex onto activated carbon. Hydrometallurgy 2004;72(3-4):291-301. https://doi.org/10.1016/s0304-386x(03) 00182-8.
- [56] Marsden J, House I. The chemistry of gold extraction (Second). Society for Mining, Metallurgy, and Exploration, Inc; 2009.
- [57] Gönen N, Körpe E, Yõldõrõm ME, Selengil U. Leaching and CIL processes in gold recovery from refractory ore with thiourea solutions. Miner Eng 2007;20(6):559–65. https://doi.org/10.1016/j.mineng.2006.11.003.

- [58] Mensah-Biney R, Reid KJ, Hepworth MT. The loading capacity of selected cation exchange resins and activated carbons for gold-thiourea complex. Miner Eng 1995;8(1–2): 125–46. https://doi.org/10.1016/0892-6875(94)00108-o.
- [59] Gamiño-Arroyo Z, Pareau D, Buch A, Gomez-Castro FI, Sánchez-Cadena LE, Stambouli M, et al. Design of multistage extraction system for simultaneous separation of silver and gold from thiourea solutions. Chemical Engineering and Processing - Process Intensification 2021; 164(September 2020):1–8. https://doi.org/10.1016/j.cep.2021. 108391.
- [60] Braun T, Farag AB. The recovery of gold from thiourea solutions with open-cell polyurethane foams. Anal Chim Acta 1973;66(3):419–26. https://doi.org/10.1016/s0003-2670(01) 82561-7.
- [61] Poisot-Díaz ME, González I, Lapidus GT. Electrodeposition of a silver-gold alloy (DORÉ) from thiourea solutions in the presence of other metallic ion impurities. Hydrometallurgy 2008;93(1–2):23–9. https://doi.org/10.1016/j.hydromet.2008. 02.015.
- [62] El-Nadi YA. Solvent extraction and its applications on ore processing and recovery of metals: classical approach. Separ Purif Rev 2017;46(3):195–215. https://doi.org/10.1080/ 15422119.2016.1240085.
- [63] Mpinga CN, Bradshaw SM, Akdogan G, Snyders CA, Eksteen JJ. Evaluation of the Merrill-Crowe process for the simultaneous removal of platinum, palladium and gold from cyanide leach solutions. Hydrometallurgy 2014;142:36–46. https://doi.org/10.1016/j.hydromet.2013.11.004.
- [64] Lapidus GT, González I, Nava JL, Benavides R y, Lara-Valenzuela C. In: Young CA, Taylor PR, Anderson y CG, Choi Y, editors. Integrated process for precious metal extraction and recovery based on electro-oxidized thiourea", hydrometallurgy 2008. Littleton, Colorado, U.S.A.: Society for Mining, Metallurgy and Exploration, Inc. (SME); 2008, ISBN 978-0-87335-266-6. p. 837–42.
- [65] Rochlin J. Informal gold miners, security and development in Colombia: charting the way forward. Extr Ind Soc 2018;5(3): 330–9. https://doi.org/10.1016/j.exis.2018.03.008.
- [66] Lopera González MA. Mining formalization in Bajo Cauca Antioquia through special reserve areas. An approach to institutional design from the framework of institutional analysis and development. Estud Políticos 2020;58:141–66. https://doi.org/10.17533/udea.espo.n58a07.
- [67] Rochlin James. Obstacles to mining formalization in Colombia. Resour Pol 2021;73:102135. https://doi.org/10. 1016/j.resourpol.2021.102135.
- [68] UNODC & Gobierno de Colombia. Explotación de oro de aluvión. Evidencias a partir de percepción remota 2018. 2019.
- [69] UNODC & Gobierno de Colombia. Monitoreo de territorios afectados por cultivos ilícitos 2018. 2019.
- [70] Rettberg Å, Cárdenas JC, y Ortíz-Riomalo JF. Mismo recurso, diferentes conflictos: un análisis de la relación entre oro, conflicto y criminalidad en seis departamentos colombianos. In: En Rettberg A, Nasi LC, Leiteritz R, Prieto Sanabria J, editors. ¿Diferentes recursos, conflictos distintos? : La economía política regional del conflicto armado y la criminalidad en Colombia. Bogotá: facultad de Ciencias Sociales, Editorial Uniandes; 2018.
- [71] UNODC & Gobierno de Colombia. Explotación de oro de aluvión. Evidencias a partir de percepción remota 2016. 2018.
- [72] UNODC & Gobierno de Colombia. Monitoreo de territorios afectados por cultivos ilícitos 2018. 2018.
- [73] Rubiano MJ, Vélez MA, Rueda X. Minería de oro artesanal y de pequeña escala. Estrategias para su formalización y diferenciación de la minería ilegal. 2020. Centro de Estudios sobre seguridad y drogas (CESED).
- [74] Bansah KJ, Dumakor-Dupey NK, Kansake BA, Assan E, Bekui P. Socioeconomic and environmental assessment of informal artisanal and small-scale mining in Ghana. J Clean Prod 2018;202:465–75. https://doi.org/10.1016/j.jclepro.2018. 08.150.

- [75] Machácek J. Typology of environmental impacts of artisanal and small-scale mining in African Great Lakes Region. Sustainability 2019;11(11). https://doi.org/10.3390/su11113027.
 [76] Calla-Choque D, Nava-Alonso F, Fuentes-Aceituno JC. Acid
- [76] Calla-Choque D, Nava-Alonso F, Fuentes-Aceituno JC. Acid decomposition and thiourea leaching of silver from hazardous jarosite residues: effect of some cations on the stability of
- the thiourea system. J Hazard Mater 2016;317:440—8. https://doi.org/10.1016/j.jhazmat.2016.05.085.
- [77] Calla-Choque D, Lapidus GT. Acid decomposition and silver leaching with thiourea and oxalate from an industrial jarosite sample. Hydrometallurgy 2020:105289. https://doi.org/10. 1016/j.hydromet.2020.10528.