# A NOVEL TREATMENT APPROACH FOR COPPER ORES BASED ON GLUTAMATE LEACHING

By

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## ABSTRACT

Currently, copper mining faces challenges, such as depleting high-grade ore deposits that contain easily extractable copper. Therefore, mining occurs in transitional and secondary sulfide enrichment zones, where oxide and sulfide minerals are mixed, causing difficulties in conventional processing. This paper presents a new alkaline process for extracting copper from copper oxide and sulfide minerals using monosodium glutamate coupled with copper sulfide precipitation. The leaching of tenorite in solutions containing 0.5 M glutamate was conducted at different temperatures (30, 45, and 60°C) in a 250 mL leach reactor with an agitated slurry and pH 9.4, achieving 97.7% copper dissolution within 2 hours at 60°C. Glutamate can also dissolve copper from sulfide mineral concentrated (composed mainly of covellite, lyonsite, bonattite, brochantite, and antlerite) with controlled dissolved oxygen (DO) levels at different temperatures. The copper extraction from sulfide concentrates in 0.5 M glutamate at 0.5 M, a temperature of 60°C and DO range of 10-15 ppm, was almost 100% after 2 h. The recovery of copper as pure copper sulfide was 99.2% at a Cu:NaHS molar ratio of 1:1.2 by sulfide precipitation. This work proposes a sustainable hydrometallurgy process to recover copper from a mixture of oxides and sulfides minerals using a non-toxic amino acid. The procedure involves two main stages: (i) leaching with aqueous alkaline monosodium glutamate solutions at pH 9.4 with varied temperature, glutamate concentration, and dissolved oxygen concentration, and (ii) PLS treatment by sulfide precipitation of copper, using NaHS addition. As a result, overall copper extraction of over 90% in the integrated process has been obtained.

*Keywords: mineral processing, copper dissolution, metal sulfide precipitation, amino acids, and monosodium glutamate.*

# INTRODUCTION

In the Earth's crust layer, copper is present at a low level of 0.0027 wt.% (27 mg/kg), but it is found in considerable quantity in ore deposits formed by hydrothermal processes. Copper deposits are classified into ten categories: porphyry, sediment-hosted, volcanic massive sulfide (VMS), red-bed copper, magmatic sulfide, epithermal, sedimentary exhalative (SEDEX), skarn, veins, and supergenes. Porphyry copper deposits are among the most economically important due to their large ore volumes and broad distributions (often >1000 Mt of ore at a copper content >0.5%). According to estimates, 60 % of all copper globally is produced from these deposits(1). In addition, as this kind of deposit grows deeper, the weathering and supergene enrichment, on many occasions, can lead to the formation of an oxidized zone, a transitional supergene zone, and a hypogene sulfide zone(2).

Currently, copper ore mining faces several challenges, such as the depletion of high-grade ore deposits containing easily extractable copper, as with ores in the oxide zone(2)(3). In many mining operations, copper mining occurs progressively more in the transition zone and the secondary sulfide enrichment zone. In the transition zone, it is possible to find a mixture of oxide and sulfide minerals, which generates difficulties using conventional treatment. Although flotation is the preferred process route for copper sulfide (such as chalcocite and covellite), recovery is not equally effective in oxidized overburden and transition zones due to poor floatability(2). There are two types of flotation treatments for oxides and mixed ores: direct flotation and sulfating flotation. Direct flotation for the oxide ores is impractical because collectors are typically expensive, have low selectivity, and have low efficiency. On the other hand, sulfidation flotation requires reagents such as $Na_2S$, $H_2S$, and NaHS, which can modify the surface chemistry of copper oxides by forming a kind of "synthetic covellite." This is the most effective flotation method for copper oxides. Nevertheless, it presents the condition that must be strictly controlled for pulp potential and reagent concentration because sub-optimal amounts lead to low copper recovery. At the same time, overdoses result in over-sulfuration, which causes a depression of the valuable mineral(4).

Due to the above, the recovery of copper from low-grade ores through hydrometallurgical routes has gained importance. In addition, it also presents some advantages such as short construction time, low cost, operational simplicity, good performance, and it is friendly to the environment(5)(6). These ores are generally leached with acid media such as sulphuric acid, nitric acid, and hydrochloric acid. However, it is possible to find these copper minerals associated with other oxide minerals and carbonates with high calcium and magnesium content as gangue materials, which, when interacting with acid, can solubilize a variety of metallic cations, resulting in an excessive increase in acid consumption and potentially cause severe operational problems in the solvent extraction stage(2)(7)(8). Additionally, in the case of some sulfides, low-leaching kinetics are observed(9). For these reasons, multiple investigations have been carried out on the leaching of copper from low-grade ores using alternative reagents such as organic acids(10)(11)(12)(13) or reagents in an alkaline medium such as cyanide(14)(15), ammonia(3)(7)(16)(17), and organic reagents. In particular, the latter presents some advantages over the acid medium, such as high selectivity in many cases, low corrosivity, and low reagent consumption(8)(9). However, challenges implementing conventional alkaline leaching agents, such as cyanide and ammonia, on an industrial scale are significant due to problems of toxicity, volatility, recovery difficulties, and environmental impact(2)(4)(9)(18)(19). Alkaline glycine has also been reported to selectively leach copper from different sources, such as oxides(2)(20), sulfides(8)(9)(19)(21), and metals(18)(22).

Recent studies by the authors of the present paper have reported the leaching of Au from pure foils and e-waste(23)(24), as well as preliminary results of Cu leaching(25)(26), using monosodium glutamate and an oxidant (such as $H_2O_2$ or $KMnO_4$). Monosodium glutamate, an environmentally benign salt derived from glutamic acid, can bind in a tridentate fashion with metal ions and leaches copper by forming a stable copper (II) glutamate complex(26). According to Perea et al. (2022), alkaline glycine solution leaches copper from tenorite efficiently, obtaining 90% recovery at 30°C for 24 hours and nearly 100% at 60°C in 2 hours(27). The authors have also observed that copper can be recovered from alkaline glutamate solutions through metal sulfide precipitation. It is a method of metal removal used in industry with some advantages, such as a lower solubility of metal sulfide precipitates, the ability to remove metal selectively, the ability to react rapidly, better-settling properties, and the ability to re-use sulfide precipitates by smelting(28). This study proposes two stages of a conceptual process: (i) leaching copper from tenorite and copper sulfide concentrate in alkaline glutamate solutions at room or elevated temperatures using oxygen as an oxidant for sulfide ores, and (ii) PLS treatment by sulfide precipitation of copper by addition of NaHS.

# EXPERIMENTAL

## Samples preparation and characterization

The experiments were carried out using samples of synthetic tenorite ($CuO$) and copper sulfide concentrate obtained from Merck and a Chinese supplier. These synthetic ores were characterized with a Malvern Mastersizer instrument to determine the particle size distribution. The results showed that these samples comprised a fine powder with 90 % particle sizes below 39 µm for the tenorite and 38 µm for copper sulfide concentrate composed mainly of covellite ($CuS$), lyonsite ($Cu_3Fe_4(VO_4)_6$), bonattite ($CuSO_4 \cdot 3H_2O$), brochantite ($Cu_4SO_4(OH)_6$), and antlerite ($Cu_3(SO_4)(OH)_4$). X-ray diffraction (XRD) analysis to determine the mineralogy of the samples indicated that copper oxide is almost 100% composed of tenorite, for the case of copper sulfide concentrates, in addition to the mentioned copper sulfide, contain hendersonite ($Ca_2V_9O_{24} \cdot 8H_2O$) and ferroactinolite ($(Ca, Na, K)_2Fe_5Si_8O_{22}(OH)_2$). Also, the chemical compositions of the samples were determined by X-ray fluorescence spectrometry, as shown in Table 1.

**Table 1: Percentage of the elemental composition of the synthetic copper samples determined by XRF.**

| Sample | Al | Si | P | S | Cl | Ca | Cu | Zn | As | Th | LE |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Tenorite | 0.59 | 0.7 | 0.27 | 0.0 | 1.93 | 0.17 | 73.88 | <LOD | <LOD | 0.76 | 21.52 |
| Sulfide concentrate | 0.33 | 0.41 | 0.18 | 7.4 | 1.6 | 0.33 | 42.9 | 0.05 | 0.04 | 0.36 | 46.4 |

LE: Light elements, which cannot be detected, include O, Na, C, and N.
LOD: Limit of detection

## Copper oxide leaching

All experiments were conducted using solutions prepared from analytical grade reagents and deionized water in a 250 mL glass reactor. The leaching tests were carried out using 1 gram of tenorite (0.5% w/v) in 200 mL of 0.5 M glutamate solutions at 30, 45, and 60°C through water-bath heating at atmospheric pressure and employing magnetic stirring at 300 rpm. At different times, ten samples of 3mL leach solution were collected using a syringe-membrane filter with a pore size of 0.45 um. The copper concentrations in the filtrates were determined using atomic absorption spectrophotometry (AAS).

## Copper sulfide leaching

For the leach test with dissolved oxygen (DO) control, the DO level in the leach pulp remained between a range of 10 to 15 ppm. Leaching tests were carried out at 30, 45, and 60°C in a 2 L glass reactor with slurry agitated at 300 rpm with an overhead stirrer. The tests were done using 10 grams of copper sulfide concentrate, added in 2 L alkaline monosodium glutamate solutions. Sodium hydroxide was used to adjust the solution's initial pH to 9.4. The DO level of the leach solution was measured and controlled over the whole leaching time using a RH-8301 DO controller and solenoid valve, as shown in Figure 1.

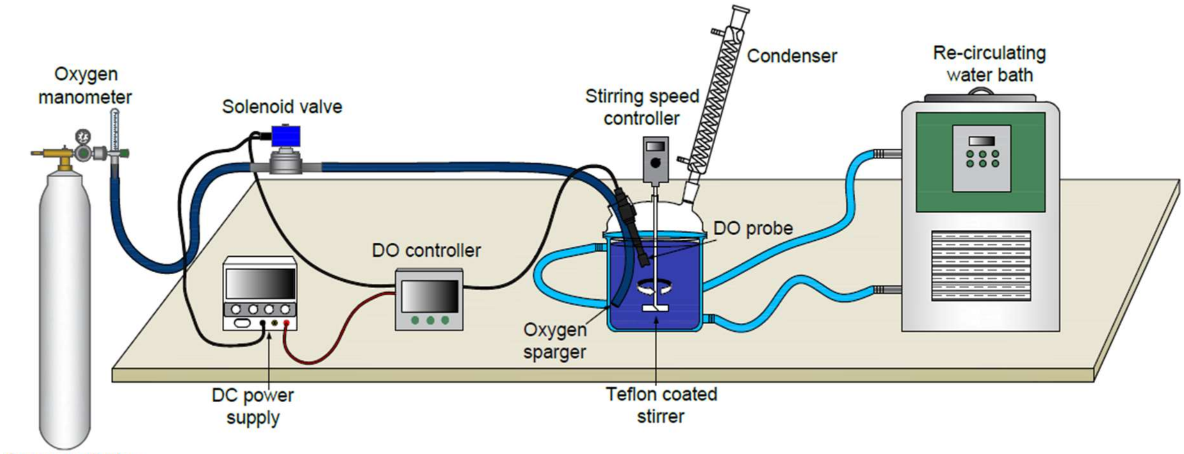

**Figure 1. Diagram of copper sulfide leaching apparatus setup.**

## Copper recovery

Precipitation tests were carried out using synthetic pregnant solutions (PLS) prepared with a concentration of 2.5 g Cu/L and 0.5 M glutamate using pentahydrate copper sulfate ($CuSO_4 \cdot 5H_2O$) and sodium L-glutamate hydrate ($C_5H_{10}NNaO_5$). Sodium hydrosulfide hydrate ($NaHS \cdot 1.5H_2O$) was added in different [Cu]:[NaHS] molar ratios in a 200 mL copper glutamate solution agitated at 300 rpm, pH 9.4, and room temperature. Samples of 10 mL copper glutamate solution were obtained using a syringe-membrane filter after 10 minutes. These samples were analyzed through AAS to determine copper recovery from the glutamate solution. An optical microscope (Leica DM 750 microscope connected to a digital camera HD 5 MGPXL WI-FI, Leica ICC50W) was used to analyze the copper sulfide precipitates after NaHS precipitation to obtain images that can then be analyzed and processed digitally to determine particle size and shape semi-quantitatively(29).

# RESULTS AND DISCUSSION

## Tenorite leaching

Figure 2 shows that the glutamate solution is effective in leaching copper oxides. It can be seen that copper extraction increases as temperature increases. In 2 hours at 30°C, 52,5% of the copper dissolves, while at 60°C, around 97.7% of the copper dissolves over the same time. After 10 hours, the complete copper dissolution was obtained at 60°C, while at 30 and 45°C, 89% and 92% were obtained, respectively. Similar copper concentrations were obtained after 24 hours at these temperatures, which indicates copper dissolution stopped after 10 hours of leaching. That can be attributed to surface passivation generated by the chemical interaction of the surface with intermediate products generated at these temperatures, such as copper hydroxide(27).

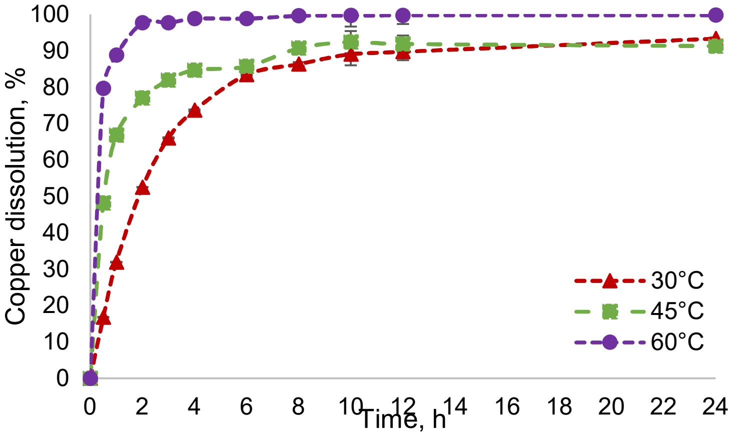

**Figure 2. Tenorite leaching at different temperatures. Working conditions: pH = 9.4, glutamate concentration = 0.5 M, and solids content = 5% w/v(27).**

## Glutamate-controlled oxygen system

The relationship between temperature and copper dissolution rate from copper sulfide concentrate is shown in Figure 3. Like tenorite, the results indicate that temperature affects the copper dissolution rate. Although in the first 30 minutes, the three temperatures had a similar extraction, after 2 hours at 30, 45, and 60°C, the copper dissolution was 83.6%, 89%, and 97.4%, respectively. Achieving the complete dissolution of copper at 45 and 60°C in 6 hours and at 30°C after 12 hours.

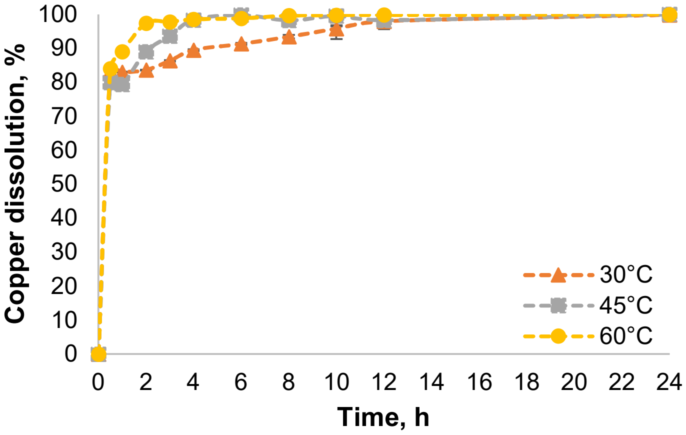

**Figure 3. Copper sulfides concentrate leaching at different temperatures. Working conditions: pH = 9.4, glutamate concentration = 0.5 M, solids content = 5% w/v, and DO = 10 – 15 ppm.**

## Copper sulfide (NaHS) precipitation

In a typical SART process to achieve copper recovery levels greater than 85%, stoichiometric sulfide dosage values vary between 95 and 120%(30)(31). Therefore, for recovery by precipitation, NaHS was added to the synthetic pregnant liquor at [$Cu_T$]:[NaHS] molar ratios of 1:0.8, 1:1, and 1:1.2 to study the effect that this variable has on the copper recovery from the glutamate solution and the results are shown in Table 2. In this table, it can be seen that the copper removals increase with the increasing [$Cu_T$]:[NaHS] molar ratio. Obtaining a 99.2% of the copper was recovered from the solution at a [$Cu_T$]:[NaHS] molar ratio of 1:1.2 in 10 minutes of residence time.

**Table 2: Copper extraction from copper glutamate aqueous solution using NaSH at room temperature and pH 9.4.**

| Sample | Cu Extraction, (%) |
|---|---|
| Cu:NaHS 1:0.8 | 71.26 |
| Cu:NaHS 1:1 | 90.6 |
| Cu:NaHS 1:1.2 | 99.2 |

The particle size of the sulfide precipitate was observed for each molar ratio by optical microscopy and image analysis. Figure 4 shows micrographs of suspension samples obtained for each test. As shown by these photos, copper sulfide precipitates formed with [$Cu_T$]:[NaHS] molar ratios of 1:0.8 and 1:1 have a high aggregation capacity, reaching a size of over 100 µm. While the particle size and aggregation capacity decrease with the increasing of [$Cu_T$]:[NaHS] molar ratio to 1:1.2. The optical micrographs in Figure 4 are supplemented with semi-quantitative cumulative aggregate size distribution curves derived from image analysis and processing (Figure 5). Ratifying that 90% of particles reached aggregation sizes over 100 µm with [CuT]:[NaHS] molar ratios of 1:0.8 and 1:1. On the other hand, the [CuT]:[NaHS] molar ratio of 1:1.2 showed a maximum aggregation size of 9.1 µm. According to this study, the higher the concentration of NaHS, the faster nucleation occurs, forming very fine particles, which can aggregate before Ostwald ripening dissolves fine particles and redeposits them on larger ones. While at lower concentrations, this happens much slower and more systematically, forming larger primary particles and often subsequently aggregates, which is in accordance with previous research(32).

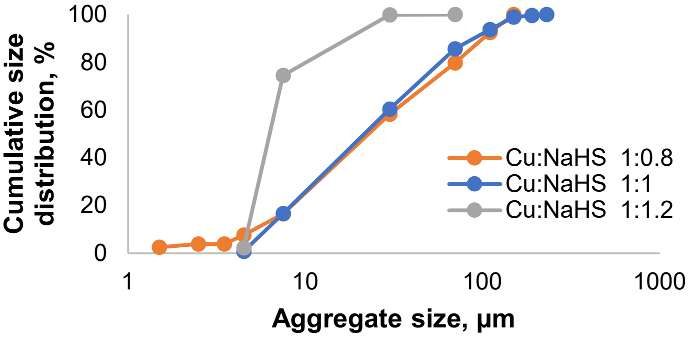

**Figure 4. Semi-quantitative cumulative aggregate size distribution curves.**

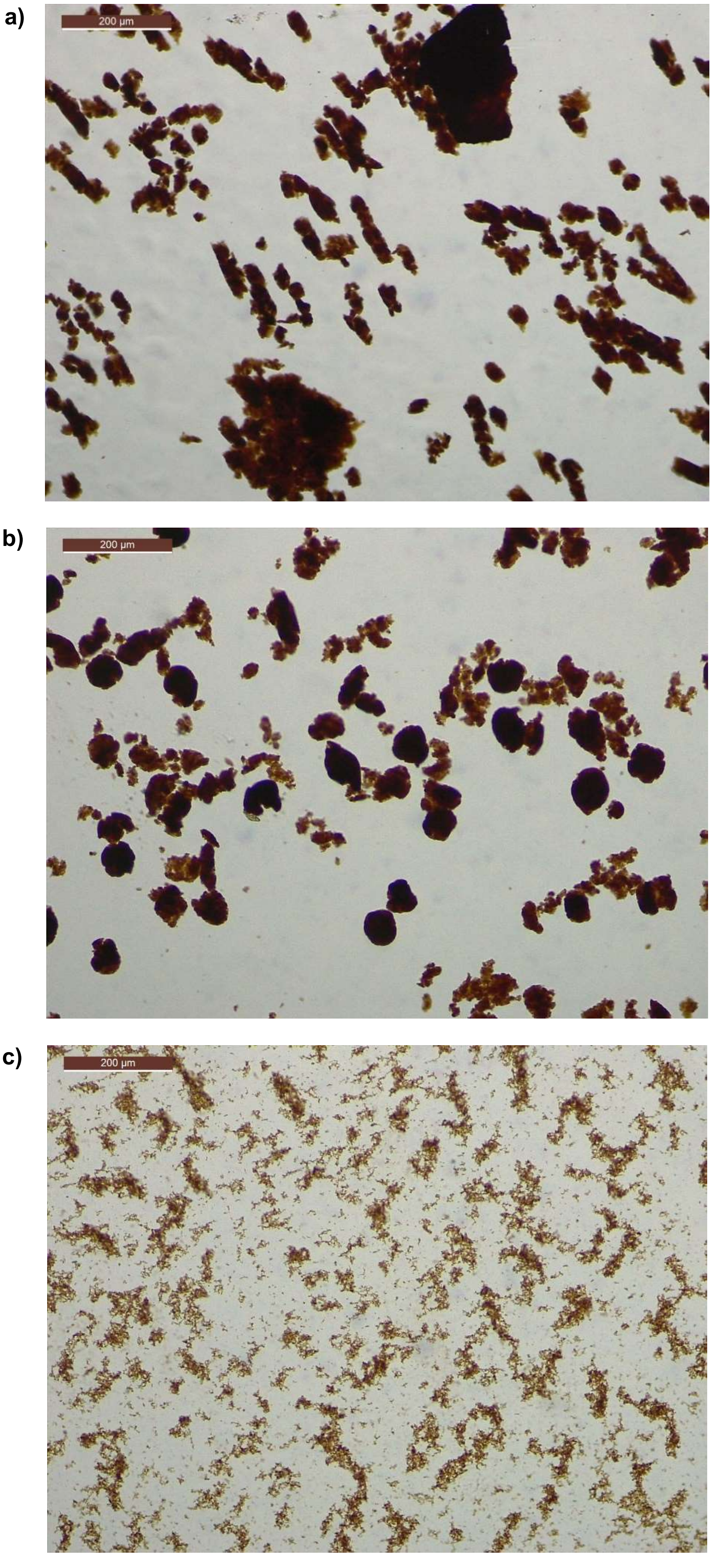

**Figure 5. Optical micrographs of copper sulfide precipitates. a) Cu:NaHS 1:0.8, b) Cu:NaHS 1:1, c) Cu:NaHS 1:1.2**

## Process flowsheet for alkaline glutamate leaching

An integrated copper leaching process can therefore be formed in alkaline glutamate systems by combining copper oxide and sulfide minerals, followed by a stage of copper precipitation and solid-liquid separation to recover copper from the solution and restore glutamate pH 9.4. Figure 6 shows the schematic diagram of the copper recovery. The first stage is the copper leaching in glutamate solutions at pH 9.4, followed by counter-current decantation (CCD) to recover pregnant leach solution (PLS) and eliminate tailings of the leaching process. Copper is recovered from the solution as copper sulfide precipitate using $NaHS$ addition and is separated from the solution by solid-liquid separation using flocculants in a thickening stage and filtration. The allow recovery of the glutamate solution to be used again in the leaching process. However,  it is necessary first to adjust the pH and add glutamate makeup, which is proportional to the loss of solution in the filtrate (% moisture in the filter cake) and the leach residue.

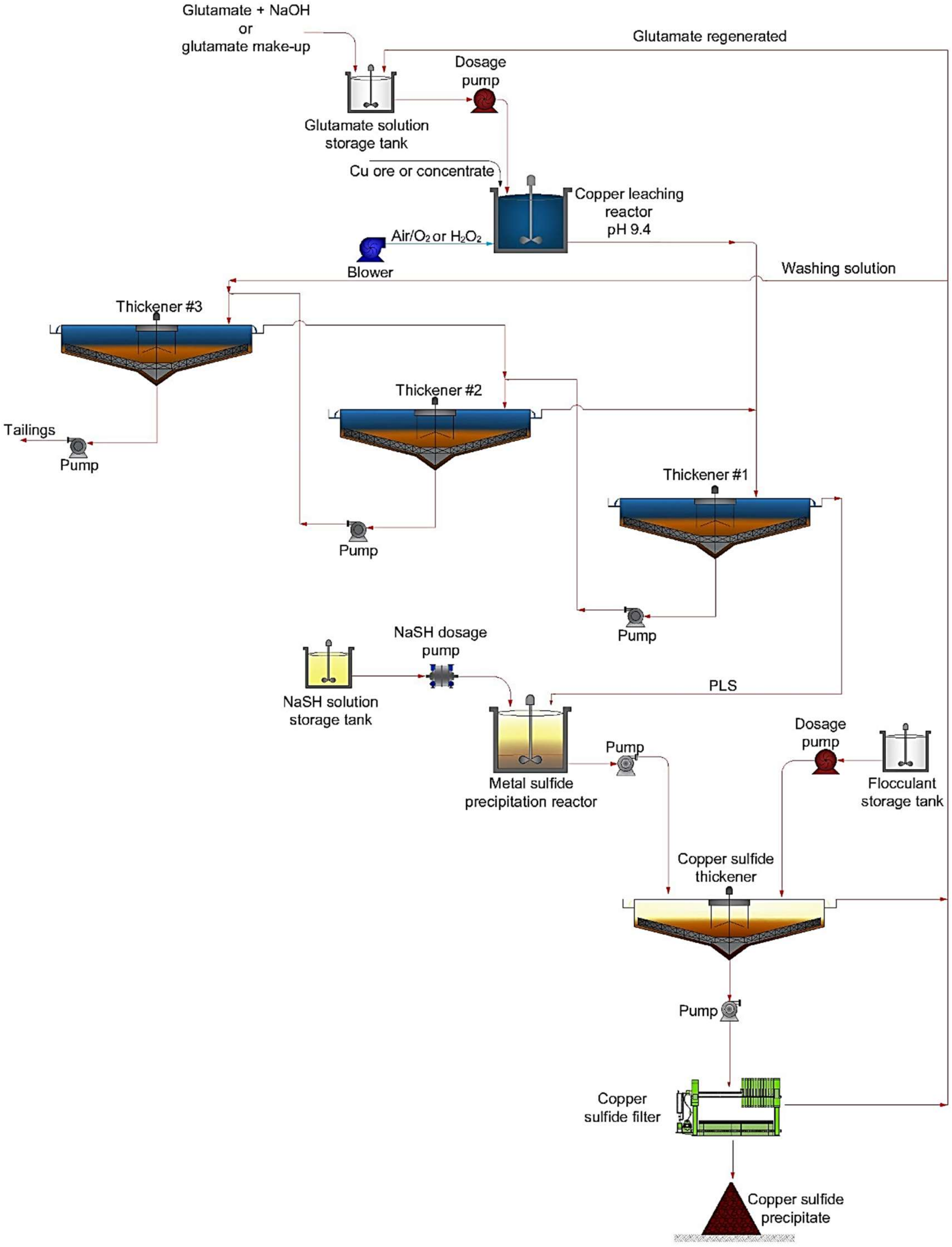

**Figure 6. Flowsheet for alkaline glutamate copper leaching and recovery by sulfide precipitation.**

## CONCLUSIONS

An alkaline process for extracting copper from copper oxides and sulfides has been proposed, as well as the chemistry involved in the main steps of the process, including reagent recirculation. Achieving copper recoveries over 90% at 30°C converts this process into a potential option for the heap leaching of copper oxide and sulfide. However,  the temperature significantly influences the kinetics leaching noted, obtaining an almost complete dissolution of copper from tenorite and sulfide concentrate in just 2 hours at 60°C, suggesting mild heating of the leach pulp could improve process efficiency. In addition, the results show that copper can be selectively recovered from glutamate solutions by sulfide precipitation, obtaining a higher grade and smeltable concentrate. Finally, to extract copper from oxides and sulfides, a conceptual flowsheet has been devised, which is technically feasible and can be an alternative for complex copper mineralization treatment that cannot be leached by acid media due to the content of gangue and oxidized minerals that consume acid.

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