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Gold recovery from pressure oxide residues using thiosulfate

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Gold recovery from pressure oxide residues using thiosulfate

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Abstract. Considering the toxicity and environmental problems created using cyanide in industrial applications of gold extraction, intensive research has been developed during the decades for identifying new effective reagents able to replace cyanide in gold extraction operations. The high thermodynamic stability of gold complexes with certain compounds is the first prerequisite for the selection of a promising extractant. The stability of gold-thiosulphate complex, though considerably lower than that of cyanide, is the highest amongst other alternative ligands, and for this reason it has been thoroughly investigated with laboratory and pilot scale tests. Ca-thiosulphate salt was selected for evaluation in the framework of the present work, as a promising cyanide-free alternative for obtaining the recovery of gold from the pressure oxidation (POX) residue of gold bearing sulfide concentrates. Thiosulfate leaching experiments were carried out, examining variables including initial thiosulfate concentration, initial pH, temperature, and solid-liquid mixing ratio (S/L). Findings reveal promising gold recovery rates with potential optimization through parameter adjustments. The objective of this research is to offer valuable insights into the feasibility of employing thiosulfate as a gold recovery agent, advocating environmentally conscious practices in the metallurgical industry and addressing challenges linked to pressure oxidation residues.

Keywords: calcium thiosulfate; gold extraction; pressure oxidation residues; gold bearing sulfide concentrates, cyanide free gold recovery.

1   Introduction

Cyanide was the ultimate gold extractant for many years until the environmental concerns surrounding its use, particularly its toxicity to humans and aquatic life, came to light. As a result of these risks, many countries have banned the use of cyanide in gold mining. In the United States, for example, the Environmental Protection Agency (EPA) has banned the use of cyanide in new gold mining operations by 1979[1,2]. The search for cyanide-free lixiviants for gold recovery has gained significant momentum in recent years due to the environmental concerns associated with cyanide usage [3-5]. A plethora of alternative lixiviants have emerged as promising replacements for cyanide, offering potential advantages in terms of environmental friendliness, safety, and
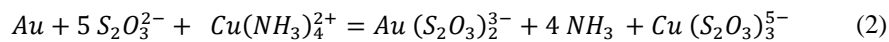
applicability to a wider range of ores. Thiosulfate, thiourea, ammonia, thiocyanate, citric and ascorbic acid have been evaluated as alternative agents [6,7].

Among these alternative lixiviants, thiosulfate stands out as a prominent candidate. Thiosulfate exhibits low toxicity, biodegradability, and the ability to leach gold from various ore types, including refractory sulfide ores that are challenging to treat with cyanide [3-5]. Additionally, thiosulfate-based processes have demonstrated promising economic viability. Thiosulfate is already being used in some gold mining operations, and it is likely to become more common in the future. Barrick Gold's (Goldstrike mine in Nevada, USA) developed a commercial scale, thiosulfate-based process for gold extraction, in 2015 [8]. Compared to cyanide leaching, the thiosulfate system exhibits increased complexity in its underlying chemistry. However, through meticulous control of key parameters such as redox potential (Eh), pH, and the concentrations of thiosulfate, oxidant, and oxygen within the leaching solution, it is possible to achieve high levels of gold extraction with comparatively low reagent consumption for certain types of ore [9].
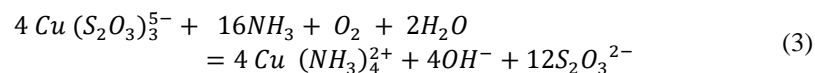
The investigation of the thiosulfate system for gold extraction has encompassed a diverse array of oxidants. These potential oxidizing agents include molecular oxygen, copper(II) ammine complexes, cobalt(III) ammine complexes, and various iron(III) complexes [5]. In solutions with alkaline or neutral pH values, containing thiosulfate, gold exhibits gradual dissolution in the presence of an oxidizing agent [5,10]. This dissolution of gold is an electrochemical phenomenon, characterized by the involvement of oxygen as the oxidant and thiosulfate as the ligand [5,11]:

$$4Au + 8\,S_2O_3^{2-} + O_2 + 2H_2O = 4Au\,(S_2O_3)_2^{3-} + 4\,OH^- \qquad (1)$$
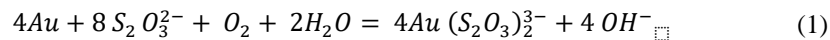
The oxidation of metallic gold to the aurous Au^+ ion in 0.10 M ammoniacal thiosulfate in the presence of Cu(II) occurs at Eh of 0 V and can be simply represented by the following reactions:

$$Au + 5\,S_2O_3^{2-} + Cu(NH_3)_4^{2+} = Au\,(S_2O_3)_2^{3-} + 4\,NH_3 + Cu\,(S_2O_3)_3^{5-} \qquad (2)$$

and

$$\begin{aligned} 4\,Cu\,(S_2O_3)_3^{5-} + 16NH_3 + O_2 + 2H_2O \\ = 4\,Cu\,(NH_3)_4^{2+} + 4OH^- + 12S_2O_3^{2-} \end{aligned} \qquad (3)$$

The mechanism involves the formation and absorption of mixed Cu(II) ammonia thiosulfate complexes on the gold surface with simultaneous oxidation of gold [12-16]. Cu(II) is used as a catalyst for this reaction at concentrations 10^{-3} to 10^{-4} M (60-6 ppm) [17], with oxygen acting to reoxidize Cu(I) to Cu(II). Nevertheless, the dissolution of gold by thiosulfate is subject to passivation, influenced by the presence of various cations (e.g. Fe and Ag) and chemical species such as humic acid or ammonia in the leaching solution. This passivation occurs mainly due to the accumulation of sulfur coatings resulting from the decomposition of thiosulfate on the gold surface [5, 18-20]. The use of CaS_2O_3 salt instead of NaS_2O_3 or $(NH_4)_2S_2O_3$ salt in the leaching has beneficial effects on gold extraction, where calcium appears to prevent the formation of thiosulfate degradation products on the gold surface and assists in the maintenance of a constant and high leaching rate during prolonged leaching [21]. The use of calcium thiosulfate

and copper as catalyst without any ammonia is the basis of Barrick Gold's commercial-scale thiosulfate plant for treating carbonaceous ores [22, 23].

The dissolution rates of gold using calcium thiosulfate surpass those achieved with sodium thiosulfate, exhibiting considerable acceleration under all comparable conditions, particularly in the presence of Cu(II) and/or sulfide minerals. This can be explained by the stronger affinity between thiosulfate ions and the divalent cation Ca^{2+}, resulting in the formation of ion pairs, which appears to be more robust compared to the interaction between thiosulfate ions and monovalent cations. Divalent cation-thiosulfate complexes exhibit higher equilibrium constants compared to their monovalent counterparts [13,14,24]. In the study by Feng and van Deventer (2010), enhanced gold recoveries were noticed when treating sulfide and pyrite concentrate using calcium thiosulfate salt [21]. Their experimental work involved the use of ammonium and Cu(II) at a pH of approximately 11.5. It should be mentioned that without ammonia, copper exists solely as Cu(I)-thiosulfate, lacking oxidizing properties. Consequently, the role of copper differs in the thiosulfate-oxygen system compared to the copper-ammoniacal thiosulfate system. In the latter, calcium interacts with anionic $Cu(I)-S_2O_3$ complexes in the solution, maintaining a higher solution potential. Calcium can also act as stabilizer before the formation of $Au(S_2O_3)_2^{3-}$ [16]. In another study, leaching tests were implemented by mixing pressure-oxidized carbonaceous ore residues (supplied by Goldstrike ore in Nevada, USA) with calcium thiosulfate and in presence of Cu(II) at a pH value of 8 and a temperature of 50°C [23]. The gold recovery was around 80% with addition of resin in leach. Conducting leaching tests for gold recovery in lower pH prevents gypsum formation and precipitation on ore particles in the presence of calcium. The evaluation of oxygen-calcium thiosulfate system using the electrochemical rotating disc technique to an oxide ore was investigated by Zhang et al. (2014) [25]. Results from this study indicated that a combination of Cu(II), high temperature, and the use of CaS_2O_3 over sodium enhanced the gold dissolution rate.

The chemistry of the thiosulfate system is relatively complicated. However, by properly maintaining and controlling the leaching parameters, high gold extractions can be achieved with low reagent consumption for some auriferous ores. Various additives have been suggested for inclusion in the thiosulfate leaching system to enhance gold recovery and decrease reagent consumption, but their success varies [5]. The use of CaS_2O_3 salt in the leaching stage has beneficial effects on gold extraction during the treatment of a sulfide and pyrite concentrate, as calcium appears to prevent the formation of thiosulfate degradation products on the gold surface and assists in the maintenance of a constant and high leaching rate during prolonged leaching. The effectiveness of applying thiosulfate to different ore types will vary, and the leaching conditions must be customized to accommodate each specific application [5].

Calcium thiosulfate was evaluated in the framework of the present study, as a promising non-cyanide reagent for the recovery of gold from the pressure oxidation (POX) residue of gold bearing sulfide concentrates. The investigated parameters included CaTS concentration, 0.05-0.15 M, initial pH of the slurry, 7- 10, temperature, 30-50ºC, and solid to liquid ratio, 10-30%. All the experiments were carried out using a constant Cu(II) concentration, 0.8 mM. The effect of treatment duration was also examined for

all the above operating conditions, conducting tests with a total duration of 2, 6 and 24 hours.

2   Materials and Methods

2.1   Materials

Pressure oxidation residue (POX)

The gold recovery by CaTS was evaluated at a sample of the pressure oxidation residue from Olympias mixed concentrate produced by Metso-Outotec under the following conditions S/L=14%, T=200ºC, pO_2=400 kPa, t=3 h. The pressure oxidation residue and the mixed concentrate were characterized by X-ray diffraction (XRD) analysis and XRF analysis. The XRD analysis was performed using a Rigaku MiniFlex benchtop XRD and at a scan speed of 1° min $^{-1}$. XRF analysis was conducted using SPECTRO XEPOS energy dispersive X-ray fluorescence (ED-XRF) spectrometer.

Chemicals

The following chemicals were used during the tests: calcium thiosulphate, pure 30-50% solution in water (Thermoscientific, Belgium), copper sulphate pentahydrate (ChemLab, Belgium), calcium hydroxide, >95% (ChemLab, Belgium). The reagents used for the determination of calcium thiosulphate (CaTS) concentration included the following chemicals: sodium thiosulphate pentahydrate >99% (Alfa Aesar, Germany), starch (ChemLab, Belgium), potassium iodate for analysis, (Sigma Aldrich, Canada), potassium iodide for analysis (Merck, Germnay). Some leaching experiments were carried out in the presence of resin (resin in leach tests). The type of resin used was Puromet MTA5011 and was kindly provided for free by Purolite Company.

2.2   Experimental conditions

The central operating conditions used during the experimental work were as follows: solid-liquid ratio, S/L=20% w/v, pH=7.0, initial concentration of calcium thiosulphate, CaTS, equal to 0.1 M, Cu(II) concentration 0.8 mM, temperature T=40ºC.

The investigated parameters included the initial concentration of CaTS, 0.05, 0.10 and 0.15 M, the initial pH 7, 8.5 and 10, the solid to liquid ratio, 10, 20 and 30 % w/v and the operating temperature 30, 40 and 50ºC. A resin in leach (RIL) test was also implemented at central experimental conditions by adding the anionic resin Purogold MTA5011 in the pulp (100 g/L), during the leaching of POX-mixed with CaTS.

All the experiments were carried out using a constant concentration of Cu(II)= 0.8 mM (50 mg/L). The effect of treatment duration was also investigated under all the examined conditions, by conducting tests with a total duration of 2, 6 and 24 hours. The experimental conditions are summarized in Table 1.

Table 1. Experimental conditions of leaching tests (Cu(II)= 0.8 mM, t=2, 6 and 24 hours)

No	S/L, %	T, ºC	pH	CaTS, M	Other
1	20	40	7	0.1	
2	20	40	8.5	0.1	
3	20	40	10	0.1	
4	20	40	7	0.05	
5	20	40	7	0.15	
6	20	30	7	0.1	
7	20	50	7	0.1	
8	10	40	7	0.1	
9	30	40	7	0.1	
10	20	40	7	0.1	Resin in leach*

* Addition of Purogold MTA5011 (100 g/L)

2.3 Experimental procedure

The experiments were carried out in shaking flasks of 250 mL capacity. For the preparation of experimental slurries 20 g of POX were mixed with 50 mL of deionized water (DW). The pH of the slurry was raised to the target pH value, 7, 8.5 or 10, by adding dropwise a Ca(OH)$_2$ solution (the supernatant of 1% w/v lime suspension). After that step, 10 mL of concentrated CaTS (0.5, 1 or 1.5 M) and 1 mL of 80 mM CuSO$_4$ were added in the slurry. Deionized water (DW) was added until the final volume of leaching solution was equal to 100 mL. The conical flasks were placed into an incubator, maintaining constant temperature conditions, and applying an agitation of 250 rpm. After the end of predetermined leaching duration (2h, 6h and 24h), the shaking flasks were removed from the incubator and the solids were separated from the leachate by vacuum filtration. Some batch experiments were conducted in duplicates to evaluate the repeatability of leaching tests.

2.4 Sampling and Analyses

The leachate solution was analyzed for pH, oxidation reduction potential (ORP) and dissolved oxygen (DO). The pH of leachate solution was measured using the pH meter Metrohm 827 pH Lab, the dissolved oxygen was analyzed by Microprocessor oximeter (OXI 196, WTW) and the ORP was determined using Hach multipolymeter HQ40d. A part of the solution was kept for metal analysis (Au, Cu, Fe, As, Zn, Pb and Si) by using atomic absorption spectrometer, Perkin Elmer PinAAcle 900T. The calcium thiosulphate concentration in the leachate solution was analyzed by iodometric titration. Solid residues were washed with distilled water and were kept in the oven for 24 h, at 100ºC, to be completely dried. The dried solid residues were analyzed for their Au content.

The Au at solid residues was determined by wet acid digestion method with aqua regia combined with solvent extraction with MIBK.

3   Results

Characterization of the Olympias concentr1ate and pressure oxidation residue

The composition of the Olympias mixed concentrate and of the POX residue is shown in Table 2. The gold content in the sulphide concentrate was close to 20 mg/t. A higher gold content in POX equal to 45.4g/t was determined.

Table 2. Chemical composition of Olympias concentrated and of the POX-residue.

	Olympias concentrate	POX-residue
Element (%)		
Fe	33.9	20.5
As	11.1	14.9
S	33.3	
S(SO$_4$)		4.36
Ca	2.21	3.38
Pb	0.62	1.50
Au (g/t)	**19.9**	**45.4**

The crystalline phases identified in the sulphides were pyrite, arsenopyrite, calcite, dolomite and quartz (Table 3). The approximate content was calculated based on the chemical composition of the samples. In the pressure oxidation residues, the only arsenic containing phase detected in the XRD patterns was a compound reported as Basic Ferric Arsenate-Sulfate (BFAS, $Fe(AsO_4)_{(1-x)}(SO_4)_x(OH)_x$) in the relevant literature.

Table 3. Crystalline phases identified by XRD and approximate modal composition of the feed material (Olympias concentrate) and pressure oxidized residue (POX).

Crystalline phases	Name	Pdf**		
Sulphides			**Olympias concentrate**	
FeS_2	Pyrite	71-1680	54.2	
FeAsS	Arsenopyrite	42-1320	22.3	
$CaCO_3$	Calcite	72-1652	3.77	
$CaMg(CO_3)_2$	Dolomite	75-1656	2.91	
SiO_2	Quartz	46-1045	11.1	
Oxidized residue				**POX**
$Fe(AsO_4)_{(1-x)}(SO_4)x(OH)x$	BFAS*	na		51.1
$H_3OFe_3(SO_4)_2(OH)_6$	H_3O-jarosite	36-0427		5.0
$Fe(OH)_3$	Bernalite	46-1436		9.79
$CaSO_4.2H_2O$	Gypsum	76-1746		14.5
$CaSO_4$	Anhydrite	37-1496		
SiO_2	Quartz	46-1045		19.6

*   BFAS: Basic Ferric Arsenate Sulfate, XRD data from relevant publications (Papassiopi et al., 1994, Dutrizac & Jambor, 2007)

**   Powder Diffraction File, produced by the International Centre for Diffraction Data (ICDD), in Crystallographica Search-Match (*CSM*) database

Effect of pH

Variation of pH as a function of time
The tests were carried out adjusting the initial pH at three different values, namely 7, 8.5 and 10. However, the pH was not maintained constant during the experiments. As shown in Fig. 3, the trend of pH evolution was augmentative in the case of initial pH 7.0 and after 24 hours reached the value 8.0. The tests carried out with initial pH 8.5 presented a relatively small fluctuation as a function of time and after 24 hours the pH was equal to 8.3. The most important variation was observed in the case of initial pH 10, where pH dropped to 8.5 after 24 hours.
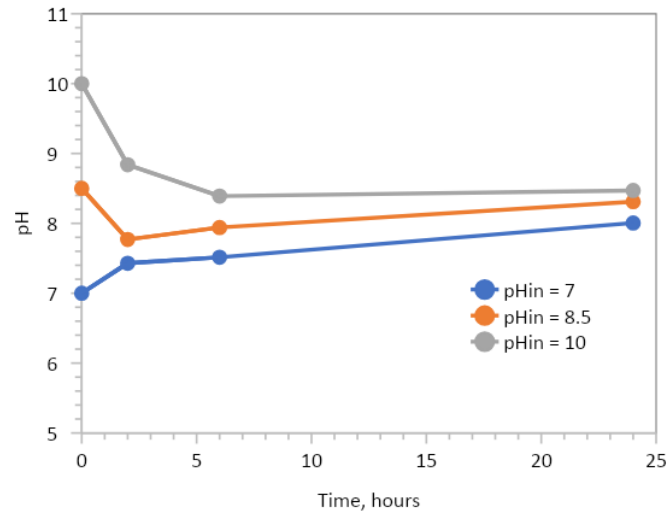
Figure 3. Time evolution of pH in the tests carried out with different initial pH values (0.1M CaTS, 40°C, S/L = 20%)

Effect of initial pH on gold leaching

The extraction of gold as a function of time during the tests carried out with different initial pHs is shown in Figure 4. The highest extraction achieved was equal to 40.6% and was observed in the tests with initial pH 7.0 at 6 hours. When the duration of treatment extended from 6 to 24 hours, gold leaching decreased from 40.5% to 34.8%. When the initial pH was adjusted to higher values, i.e., 8.5 and 10, the kinetics of gold extraction was clearly slower.
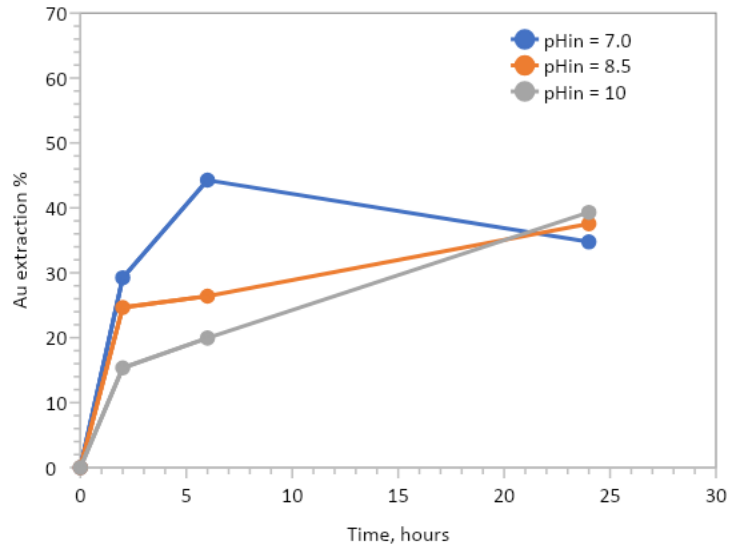
Figure 4. Effect of initial pH on gold leaching (0.1M CaTS, 40°C, S/L = 20%)

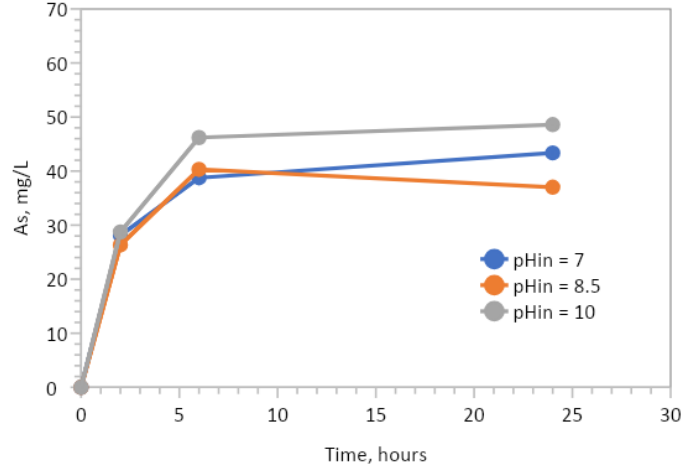*Evolution of CaTS concentration*

The evolution of thiosulphate concentration is shown in Fig. 5. The observed fluctuations are partially due to the instability of titrations reagent. The results of 24 hours suggest a relative decrease of thiosulphate concentration, when the pH decreased from 10 to 7. Namely the concentration of thiosulphate remained constant in the test with initial pH 10, decreased by 10% in the test with initial pH 8.5 and by 20% in initial pH 7.
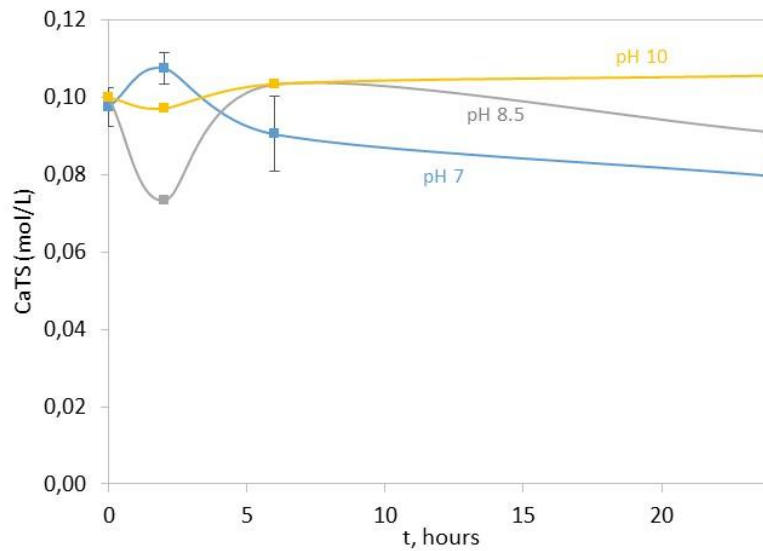
Figure 5. Concentration of thiosulphates in the experiments with different initial pH (0.1M CaTS, 40°C, S/L = 20%)

Effect of initial pH on the release of arsenic

The concentrations of As in the tests carried out with different initial pHs are shown in Figure 6. After 6 hours, arsenic concentration ranged between 46 and 49 mg/L in the tests with initial pH 10, while in the tests with initial pH 7 and 8.5 ranged between 37 and 43 mg/L. Taking into consideration that POX-mixed contains 15% As and that the experiments were carried out with 20% pulp density it is calculated that As release is in the order of 0.12-0.16%.
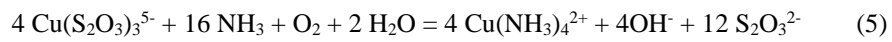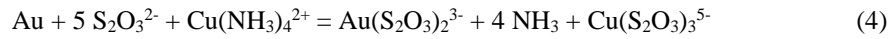
Figure 6. Effect of initial pH on the release of As (0.1M CaTS, 40°C, S/L = 20%)
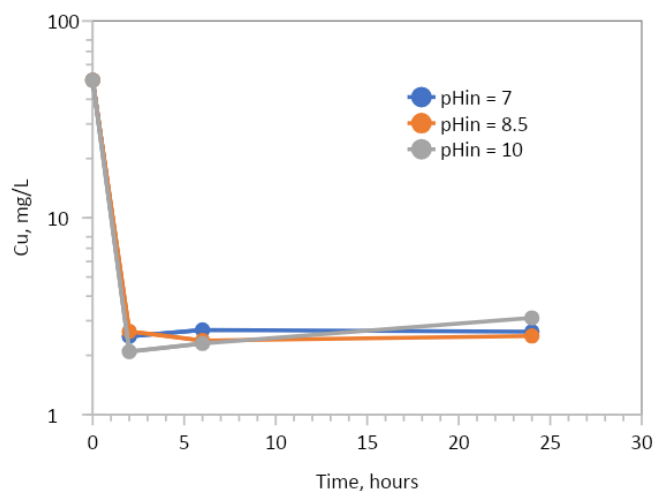
Concentration of Cu

All the tests were carried out with addition of 0.8 mM Cu(II), i.e. 50 mg/L. The concentrations measured in the leaching solutions at all treatment times and all initial pH values ranged between 2.1 and 3.1 mg/L (Figure 7). The results suggest that copper is not maintained in solution in this specific system.

The catalytic role of Cu(II) during the leaching of gold with thiosulphate has been extensively studied [15,16,21]. In most studies, leaching was carried out in the presence of free ammonia, NH_3, at levels varying from 0.4 up to 3 M. The catalytic role of Cu in the presence of NH_3 is represented in equations (4) and (5).

$$Au + 5\ S_2O_3^{2-} + Cu(NH_3)_4^{2+} = Au(S_2O_3)_2^{3-} + 4\ NH_3 + Cu(S_2O_3)_3^{5-} \tag{4}$$

$$4\ Cu(S_2O_3)_3^{5-} + 16\ NH_3 + O_2 + 2\ H_2O = 4\ Cu(NH_3)_4^{2+} + 4OH^- + 12\ S_2O_3^{2-} \tag{5}$$

In the above studies, copper was added to the solution at levels varying between 0.5 and 10 mM (32-636 mg/L) and was maintained in solution, even at strong alkaline pHs, due to the formation of strong aqueous complexes with ammonia, as Cu(II), or with thiosulphates, as Cu(I).

Figure 7. Copper concentration (at logarithmic scale) in the tests with different initial pHs
(0.1M CaTS, 40°C, S/L = 20%)

Thermodynamic calculations indicate that, at neutral and alkaline pHs and in the absence of ligands, such as ammonia or thiosulphates, divalent copper precipitates as $Cu(OH)_2$ and monovalent copper as Cu_2O (see Fig. 8). In the presence of free NH_3 both Cu(I) and Cu(II) can be maintained in the aqueous phase at levels as high as 400-8000 mg/L. In non-ammoniacal solutions containing thiosulphates, Cu(II) is maintained in solution at concentrations above 50 mg/L only at relatively low pH values (pH<7). Cu(I) forms much stronger complexes with thiosulphate and can be maintained in solution at levels between 790 and 3500 mg/L in the whole pH range between 6.5 and 10.5.

In the present work the experiments were carried out in ammonia free solutions. Based on the above thermodynamic considerations, the rapid decrease of copper concentration from the initial value of 50 mg/L to 2.1-3.1 mg/L (Fig. 8) is probably due to the precipitation of $Cu(OH)_2$. To maintain copper (II) in solution the pH should be regulated at values below 7. The residual copper 2-3 mg/L is probably monovalent copper. According to Zang et al. (2013), Cu(II) is reduced to Cu(I) after mixing with thiosulphate in non-ammoniacal solutions, and the measured copper in solution exists only as a Cu(I)-TS complex [26].
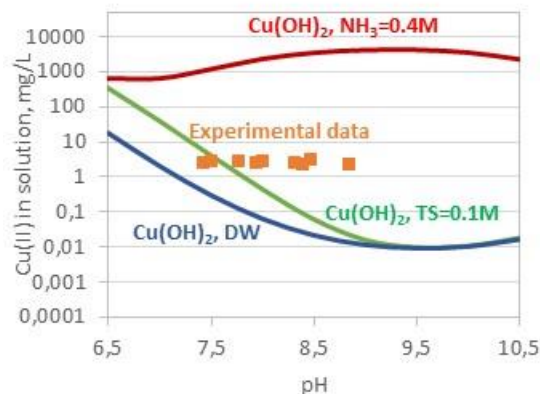
(a)   Cu(II)
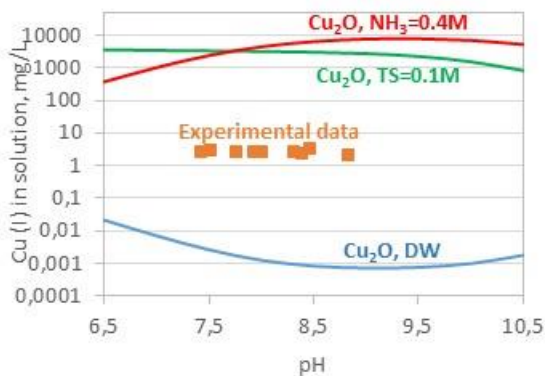
(b) Cu(I)

Figure 8. Solubilities of Cu(II) and Cu(I) vs pH in deionized water (DW), in a solution contain-
ing 0.1 M Ca-thiosulphate, and in a solution containing 0.4 M NH_3. Thermodynamic calcula-
tions carried out with Visual Minteq and assuming as possible solid phases $Cu(OH)_2$ for Cu(II)
and Cu_2O for Cu(I).

Redox potential and oxygen concentration

The values of redox potential in all the tests varied in the range 100-180 mV (refer-
ence electrode Ag/AgCl/KCl$_{sat}$) and the concentration of aqueous oxygen was between
6 and 9.5 mg/L.

Effect of CaTS concentration

Gold extraction

The effect of CaTS concentration on gold leaching is presented in Fig. 9. The max-
imum gold extraction, 65%, was obtained at 6 hours, using 0.15 M CaTS. At the same
time interval gold extraction was 25.5% with 0.05 M CaTS and 44.3% with 0.1 M
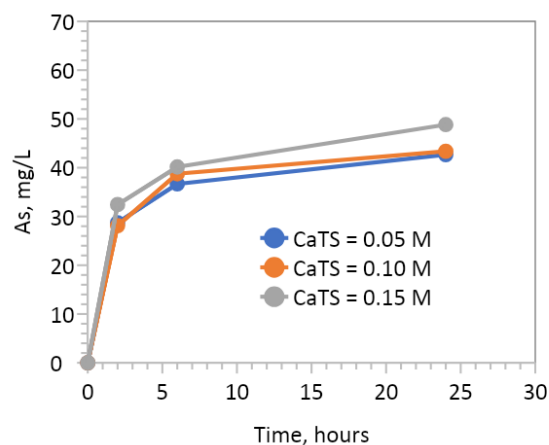CaTS.

The dissolution of gold was lower when the duration of treatment increased from 6 to 24 hours. This can be attributed to the reprecipitation or adsorption of dissolved gold, a phenomenon which has been often reported in the literature [26-30]. According to Daenzer et al. (2016) the stability of dissolved gold in CaTS solutions is negatively affected by the presence of pyrite, activated carbon or gypsum [30]. The pressure oxidized residue POX-mixed, used as feed material in this work, does not contain any pyrite or carbonaceous material, but the gypsum content is high, i.e. close to 15%, and may explain the observed decrease of gold extraction at longer treatment times.
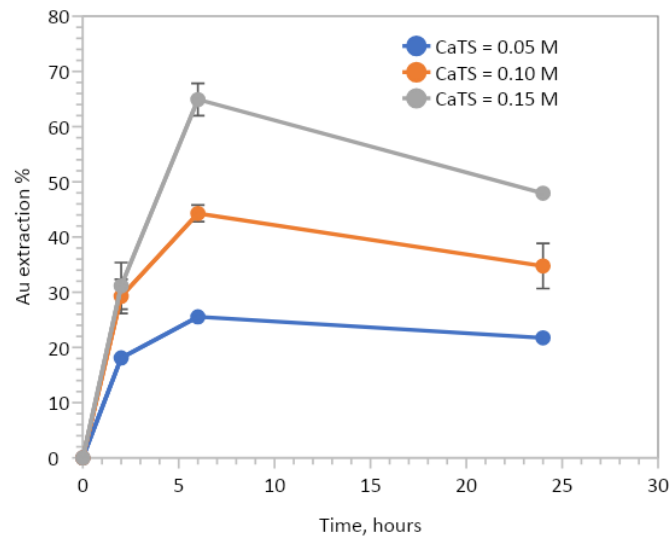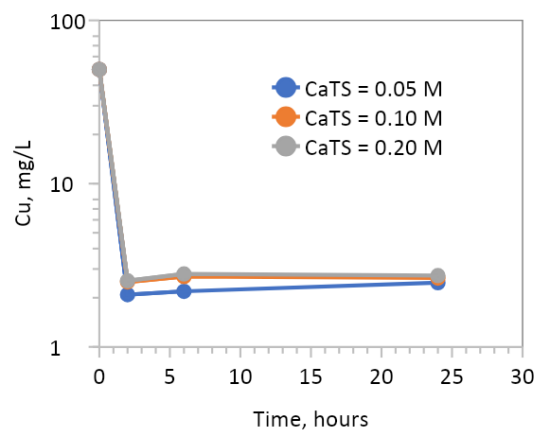

Figure 9. The effect of CaTS concentration on gold extraction (pH 7, 40ºC, S/L 20%).

Evolution of pH, As and Cu

All the experiments with different CaTS concentrations were conducted with initial pH 7. The evolution of pH followed a similar trend, regardless of the CaTS level. A similar trend was also observed for the evolution of As and Cu (Fig 10a and 10b).

(a)

(b)

Figure 10. Evolution of As (a) and Cu (b) in the tests carried out with different
CaTS concentrations.

Effect of solid to liquid ratio

As shown in Figure 11, the increase of solid to liquid ratio from 100 to 300 g/L has
limited effect on the percentage of gold extraction. The maximum extraction is ob-
served at 6 hours and the observed variation of values, 37%-44%, was not very different
from the variation between reproducibility experiments.

The trend of pH evolution, as well as the evolution of Cu concentration is similar in
all three S/L ratios, namely the pH was increased to around 8.2 and the concentration
of Cu was 3g/L after 24h. The concentration of As after 24 hours of treatment increased
from 36.6 to 58.9 mg/L, when the S/L ratio increased from 100 to 300 g/L.
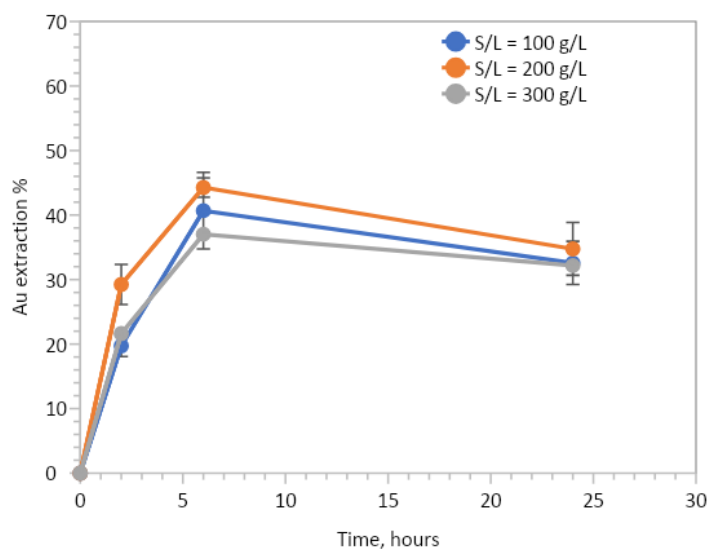
Figure 11. The effect of solid to liquid ratio on gold extraction (pH=7, CaTS=0.1 M, T=40oC)

Effect of temperature

The increase of operating temperature had a positive effect on the kinetics of gold extraction (Figure 12). Increasing the temperature from 30 to 40 and 50°C, gold extraction after 6 hours was equal to 31%, 44% and 50%, respectively. After 24 hours gold extraction was equal to 42% at 30°C (still at increasing trend), dropped from 44% to 35% at 40°C, and dropped from 50% to 47% at 50°C.

The operating temperature had no effect on the evolution of pH and on Cu concentration. Similarly, the dissolution of As after 24 hours of treatment was not affected by the operating temperature and ranged between 37 and 43 mg/L.
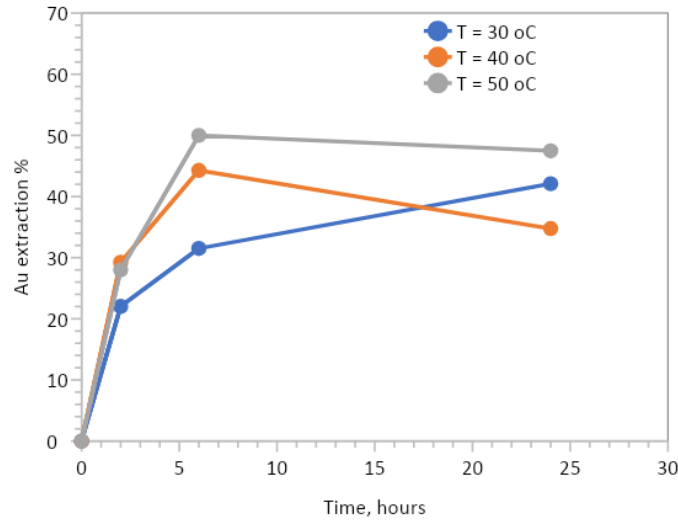
**Figure 12.** The effect of temperature on gold extraction (pHin=7, CaTS=0.1 M, S/L=20%)

Resin in Leach test

The resin in leach (RIL) test was carried out at central experimental conditions by adding the anionic resin Purogold MTA5011 in the pulp (100 g/L), during the leaching of POX-mixed with CaTS. The results regarding gold extraction are presented in Figure 13. The addition of resin was found to decelerate the process of gold extraction. At 6 hours the dissolution of gold was equal to 25% with the resin against 44% without resin. However, gold extraction at 24 hours was higher in the presence of the resin, 52% against 35% without resin.

The addition of the resin has caused an important decrease of thiosulphate concentration as shown in Figure 14(a). Namely, the concentration of CaTS dropped from 0.1 M to 0.05 M after 6 hours and 0.035 M after 24 hours. Moreover, the concentration of copper dropped below detection limit. It seems that the thiosulphate anions, either free or complexed with Ca or Cu(I), are strongly adsorbed by the resin and this may explain the slower kinetics of gold extraction.
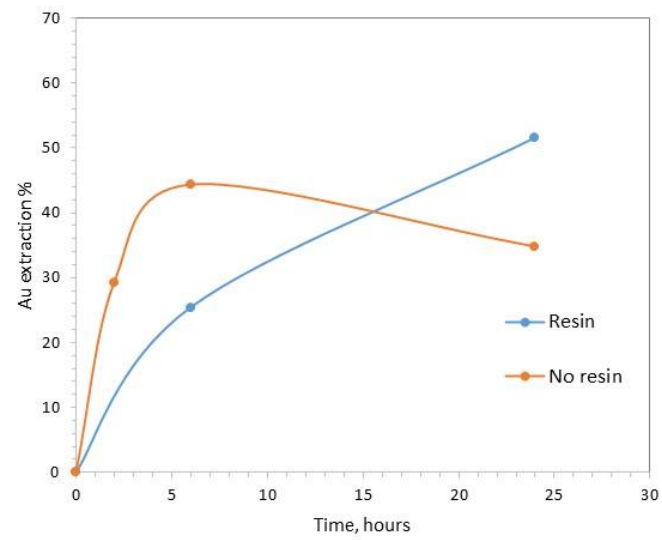
Figure 13. Comparison of gold extraction with and without resin (pHin=7, CaTS=0.1 M, S/L=20%, T=40ºC).

(a)

(b)
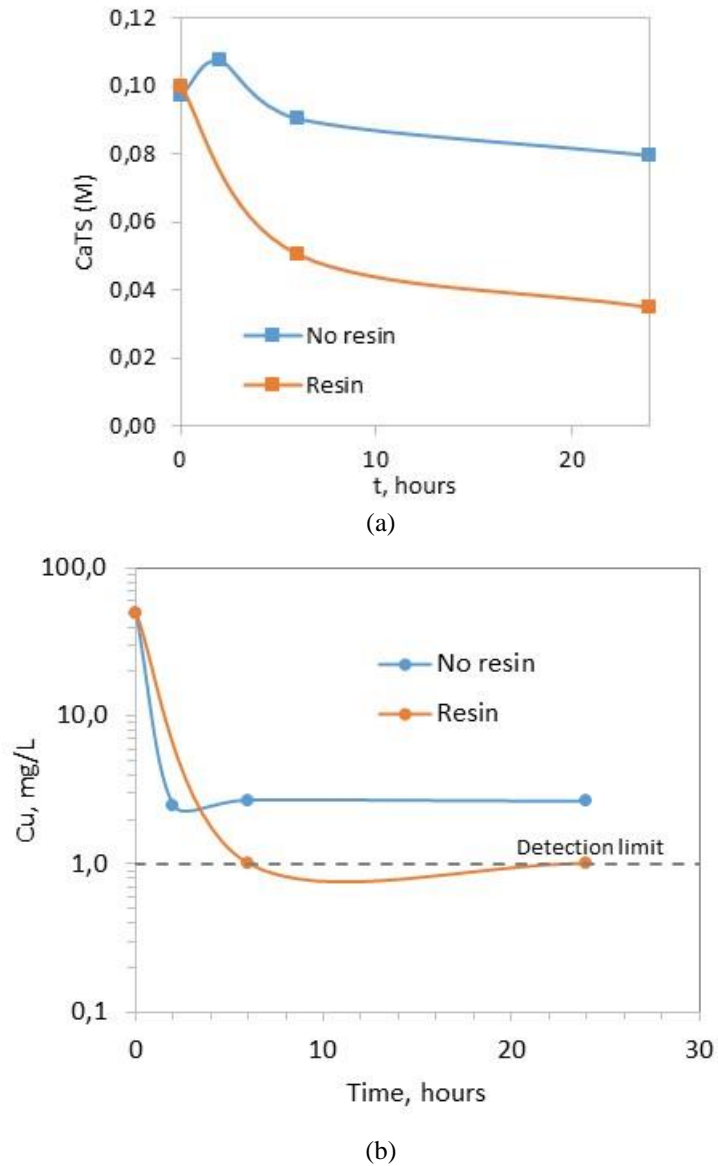
Figure 14. Effect of resin addition on the concentration of (a) thiosulphate and (b) copper in the leachate

4   Discussion

Comparison of CaTS performance with published data

Published data regarding gold extraction using CaTS in ammonia free solutions are summarized in Table 4.

Table 4. Published data regarding gold extraction using CaTS in ammonia free solutions.

Reference	Gold bearing material	Max Au extraction. Conditions	Extraction, t=6h	Comments
[26]	Oxidized ore, Au 4.4 g/t (NaCN leachable Au >95%)	35.1%, CaTS=0.3M, Cu=10 mM, O_2, pH=10, T=50°C, t=48h	8.2%	Only 9.2% Au extraction, with air instead of pure O_2.
[26]	Cu-Au conc. (S 28%), Au 7.7 g/t. (NaCN leachable Au 62%)	71.4%, CaTS=0.3M, Cu=2-10 mM, O_2, pH=10, T=50°C, t=48 h	38.9%	Dissolution of Cu from the conc. Decrease of TS from 0.3 to 0.067 M at 48 h
[26]	Cu-Au conc., Au 15 g/t (NaCN leachable Au 98%)	74.0%, CaTS=0.3M, Cu=2-36 mM, O_2, pH=10, T=50°C, 24 h	23.1%	Dissolution of Cu from the conc. Decrease of TS from 0.3 to 0.117 M
[26]	Pyrite conc., Au 45 g/t (NaCN leachable Au 90%)	52.4%, CaTS=0.3M, Cu=2 mM, O_2, pH=10, T=50°C, t=48h	21.8%	Decrease of TS from 0.3 to 0.147 at 48 h
[30]	Oxidized preg-robbing ore, Au 2.96 g/t	62.5% (45% in 6h) CaTS=0.1M, Cu=0.8 mM, air, pH=8.5, T=50°C, t=74h	~45%	
[31]	Alkaline POX, Au 2.3g/t. Quartz 59.3%, dolomite, 23.1%, calcite 4%, gypsum 2.5%, TCM 1.9%, Fe_2O_3 0.8%, FeS_2 0.8%	65.3%, CaTS=0.2M, air, pH=10, T=50°C, t=24h		Negligible TS consumption due to the presence of CO_3.Possible dissolution of Cu from POX 10% TS consumption in 24 hours
[31]	Acidic POX, Au 2.5 g/t. Quartz 88.8%, gypsum 7.5%, Fe_2O_3 1%, FeS_2 0.1%	75.5%, CaTS=0.2M, air, pH=10, T=50°C, t=24 h		
Present study, 2024	Acidic POX, Au 45.4% g/t. Quartz 20%, gypsum 14.5%, BFAS 52%	65%, CaTS=0.15M, Cu=0.8 mM, air, pH=7-8, T=40°C, t=6 h.	65%	

TCM: Total carbonaceous matter

Zhang et al. (2013) performed experiments with 4 different samples, one oxidized ore, two Cu-Au concentrates and one pyrite concentrate [26]. The gold content varied from 4.4 g/t in the oxidized ore up to 45 g/t in the pyrite concentrate and the percentage

of NaCN leachable gold varied in the range 62%-98%. The maximum gold extraction, 74%, was obtained from a Cu-Au concentrate under the following conditions: CaTS=0.3 M, initial Cu 2 mM, injection of pure O_2, pH=10, T=50°C, t=24h. The concentration of copper increased from 2 to 36 mM during the treatment due to dissolution from the concentrate. The use of pure oxygen, in combination with the presence of copper, caused the oxidation of thiosulphate and the decrease of TS concentration by almost 60% within 24 hours.

Daenzer et al. (2016) applied the treatment on a sample of oxidized preg-robbing ore with Au 2.96 g/t, provided by Barrick Gold. The treatment was carried out with CaTS=0.1 M, Cu=0.8 mM, supply of air, pH=8.5, T=50°C, t=74 h. The extraction of gold was equal to 62.5% [30].

Soleymani et al. (2021) performed experiments with the pressure oxidized residues, produced in the Barrick's acidic and alkaline POX units of the CaTS process [31]. The conditions used were as follows: CaTS=0.2M, air, pH=10, T=50°C, t=24 h. There was no reference to any external addition of Cu, but it was assumed that there was dissolution of copper at least from the alkaline POX. The obtained gold extraction was 65.3% from the alkaline POX and 75.5% from the acidic POX. The lower extraction from the alkaline POX was attributed to the fact that an important amount of gold was locked in iron oxides and hydroxides (14%) and in FeS_2 (13%), while in the acidic POX only 5% of gold was locked in these phases.

In the present study the maximum extraction of gold was 65%, obtained at conditions similar to the above studies (CaTS=0.15 M, Cu=0.8 mM, air, pH=7-8, T=40°C), within a relatively short treatment time, i.e. t=6 h. According to the available published data the extraction obtained at 6 hours was lower, ranging between 8.2% and 45%, but the increase of treatment time had in all cases a positive effect with final extraction rates up to 74% [26, 30]. In this study the extension of treatment duration from 6 to 24 hours caused reprecipitation of dissolved gold. The main drawback of the thiosulphate process in the system, seems to be the instability of gold-TS complexes, probably related with the high content of gypsum and oxidized Fe(III) phases.

5   Conclusions

This study investigated the feasibility of utilizing a thiosulfate (TS) system for gold extraction from pressure oxidation residue under controlled conditions. The maximum gold dissolution achieved was 65% at 0.15 M CaTS, 40°C, pH 7.5, and 6 hours of leaching. Increasing the concentration of CaTS from 0.05 to 0.15 M had a clear positive effect on Au extraction, while the increase of pH from 7 to 10 negatively impacted gold extraction. Increasing the solid to liquid ratio from 100 to 300 g/L has a minimal impact on the percentage of gold extraction, whereas raising the temperature from 30 to 50°C enhances gold extraction. The estimated release of arsenic ranged from 0.12% to 0.16%, for pH 7-10.

Purogold MTA5011SO4 resin successfully enhanced gold recovery to 52% within 24 hours while also adsorbing a significant amount of TS (60%). However, the absence

of NH$_3$ prevented Cu(II) from catalyzing gold extraction, and thermodynamic calculations suggest lower pH values are necessary for stabilizing Cu(II) in solution. While the process proved partially successful, the main limitation appears to be the instability of gold-TS complexes, potentially due to the high content of gypsum and oxidized Fe(III) phases in the studied system. Further research is needed to address these limitations and optimize the thiosulfate system for efficient gold extraction in such environments.

References

1. Environmental Protection Agency (EPA). (1979, August 16). Final rule for control of cyanide used in or near surface waters. Federal Register, 44(161), 47398-47411. https://www.epa.gov/smartsectors/mining-sector-information.
2. Environmental Protection Agency (EPA). (2006, December 13). Final rule for control of cyanide used in or near surface waters: Revisions to the cyanide rule. Federal Register, 71(244), 75619-76026. https://www.epa.gov/sites/default/files/2015-12/documents/9013a.pdf.
3. Hilson, G. and Monhemius A.J.: Alternatives to cyanide in the gold mining industry: what prospects for the future?, Journal of Cleaner Production 14 (12–13), 1158-1167 (2006).
4. Zhu, Y. Liang, X. & Zhang, M.: Thiosulfate leaching of gold: A review. Journal of Hazardous Materials, 336, 174-184 (2017).
5. Aylmore, G.M. Chapter 28: Thiosulfate as an Alternative Lixiviant to Cyanide for Gold Ores Adams, M.D. (Ed.), Gold Ore Processing, second ed., Elsevier, 2016, 485-523.
6. Senanayake, G. Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications. Minerals Engineering 17, 785-801 (2004).
7. Aylmore, M.G. Chapter: 21: alternative lixiviants to cyanide for leaching gold ores. In: Adams, M.D. (Ed.), Gold Ore Processing, first ed. Elsevier B.V., Amsterdam, Netherlands, 501-539 (2005).
8. Patent US11639540B2, Method for carbon-catalysed thiosulfate leaching of gold-bearing materials, Published 2 May 2023, Barrick Gold Corp (2023).
9. Wan, R.Y. Importance of solution chemistry for thiosulfate leaching of gold. In: Proceedings, World Gold '97. The Society for Mining, Metallurgy and Exploration, Inc., Littleton, CO, USA, 159- 162 (1997).
10. White, H.A. The solubility of gold in thiosulphate and thiocyanate. J. Chem. Metall. Min. Soc. S. Afr., 6, 109-111 (1905).
11. La Brooy, S.R., Fixing the cyanide issue – Alleviation or replacement? ALTA 2017, 2-27 (2017).
12. Senanayake, G. Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications. Minerals Engineering, 17, 785-801 (2004).
13. Senanayake, G. Kinetic model for anodic oxidation of gold in thiosulfate media based on the adsorption of MS2O3 -ion-pair. Hydrometallurgy 76, 233-238 (2005a).
14. Senanayake, G. The role of ligands and oxidants in thiosulfate leaching of gold. Gold Bull. 38 (4), 170-179 (2005b).
15. Senanayake, G. Catalytic role of ammonia in the oxidation of gold in copper free thiosulfate solutions. Hydrometallurgy 77, 287-293 (2005c).

16. Senanayake, G., Zhang, X.M. Gold leaching by Cu(II) in ammoniacal thiosulfate solutions in the presence of additives. Part II: effect of residual Cu(II), pH and redox potentials on reactivity of colloidal gold. Hydrometallurgy 115-116, 21-40 (2012).

17. Lam, A.E., Dreisinger, D.B. The importance of the Cu(II) catalyst in the thiosulfate leaching of gold. In: Young, C.A., Alfantazi, A.M., Anderson, C.G., Dreisinger, D.B., Harris, B., James, A. (Eds.), Hydrometallurgy, Leaching and Solution Purification, vol. 1. TMS, Warrendale, 195-211 (2003).

18. Chen, J., Deng, T., Zhu, G., Zhao, J. Leaching and recovery of gold in thiosulfate based system - a research summary at ICM. Trans. Indian Inst. Met. 49 (6), 841-849 (1996).

19. Zhang, S., Nicol, M.J. An electrochemical study of the dissolution of gold in thiosulfate solutions. Part I - Alkaline solutions. J. Appl. Electrochem 33, 767-775 (2003).

20. Baron, J.Y., Mirza, J., Nicol, E.A., Smith, S.R., Leitch, J.J., Choi, Y., Lipkowski, J. SERS and electrochemical studies of the gold-electrolyte interface under thiosulfate based leaching conditions. Electrochim. Acta 111, 390-399 (2013).

21. Feng, D., van Deventer, J.S.J., . Effect of thiosulfate salts on ammoniacal leaching of gold. Hydrometallurgy 105, 120-126 (2010).

22. Braul, P. Thiosulfate going commercial. CIM Mag. 8 (1), 42-45 (2013).

23. Choi, Y., Baron, J.Y., Wang, Q., Langhans, J., Kondos, P. Thiosulfate processing e from lab curiosity to commercial application. In: World Gold Conference Proceedings, Brisbane, Qld, 26-29th September 2013 45-50 (2013).

24. Smith, R.M., Martell, A.E., Motekaitis, R.J. Critically Selected Constants of Metal Complexes Database, Version 5.0 Software. National Institute of Standards and Technology (1998).

25. Zhang, H., Dai, X., Breuer, P. Factors affecting gold leaching in thiosulfate-O2 solutions. In: Proceedings of the ALTA Gold Conference Perth WA, 30-31st May 2014. ALTA Metallurgical Services, Melbourne, Australia, 9 (2014).

26. Zhang, H., Dai, X., Breuer, P. Factors affecting gold leaching in thiosulfate-O2 solutions. ALTA 2013 May 30-31st; Perth, Australia: ALTA Metallurgical Services Publications (2013).

27. Zhang, H. and Jeffrey M. A study of pyrite catalysed oxidation of thiosulfate. Hydrometallurgy Proceedings of the Sixth International Symposium 2008 Phoenix, AZ: Society for Mining, Metallurgy, and Exploration (SME) (2008).

28. Dai, S., Li, P., Wang, Q., Feng, D. Effect of additives on thiosulfate leaching of a gold ore. Bulgarian Chemical Communications, Volume 49, Special Edition K2, 48 – 53 (2017).

29. Zhang H, Jeffrey M, A study of pyrite catalysed oxidation of thiosulfate. Hydrometallurgy 2008 Proceedings of the Sixth International Symposium; 2008; Phoenix, AZ: Society for Mining, Metallurgy, and Exploration (SME) (2008).

30. Daenzer R.; Dreiseinger, D. and Choi Y. Role of polythionates on the stability gold in the leaching of double refractory ores in the calcium thiosulfate-air leaching system. ALTA 2016 Gold Pm Proceedings, pp. 282-298 (2016).

31. Soleymani M., Sadri F., Ghahreman A. Effect of mixing acidic and alkaline pressure oxidation discharges with different ratios on gold thiosulfate leaching efficiency. Hydrometallurgy 205, 105744 (2021).