

## AMMONIUM THIOSULFATE LEACHING OF AN OXIDE GOLD-COPPER ORE

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Mining of many secondary gold deposits is restrained by the occurrence of copper minerals soluble in cyanide that increases cyanide consumption to uneconomical levels. Among the available alternatives, ammonium thiosulfate leaching is highlighted, since in this process soluble copper is an essential reagent for gold oxidation. However,  $\text{Cu}^{2+}$  in excess, especially in the presence of oxygen, may cause thiosulfate oxidation.

In the present work the application of ammoniacal thiosulfate leaching to the processing of a Brazilian oxide gold-copper ore rich in cyanide soluble copper was investigated. The main objective was to establish the effect of the relative concentrations of the main reagents – ammonia,  $\text{Cu}^{2+}$ , oxygen, and thiosulfate – on gold extraction and thiosulfate consumption. The maximum gold extraction obtained was compatible with that obtained with cyanide leaching, indicating the possibility of use of thiosulfate. Lowering copper grade prior to thiosulfate leaching through sulphuric acid leaching had a negative effect on gold extraction, while injecting  $\text{N}_2$  in order to reduce aeration increased Au and Cu extraction without significant losses of thiosulfate.

**Key words:** thiosulfate, leaching, refractory ores, gold.

**Field:** Hydrometallurgy

## INTRODUCTION

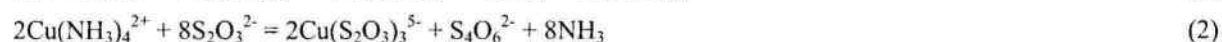
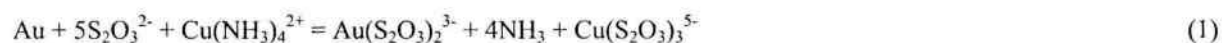
Too high levels of cyanide soluble copper in gold -copper ores may lead to significantly high cyanide consumption. Among many alternatives, ammonium thiosulfate (ATS) leaching is one of the most promising process routes, as in this system cupric ions, provided by soluble copper minerals present in the ore, act as gold oxidant. Additionally, ATS is regarded as a non-toxic compound (it is employed in agriculture as a fertilizer) making this reagent an attractive alternative to cyanide in those regions where environmental legislation banned cyanide.

Thiosulfate leaching of precious metals is known since the XIX century, when the von Patara process was developed (Aylmore and Muir, 2001). However, this technique was almost forgotten as cyanidation settled as the dominant process. The gold-thiosulfate complex has a high stability, second only to the gold-cyanide complex (Table 1).

**Table 1** – Stability constants of gold complexes (Aylmore and Muir, 2001)

Specie	Stability (log $K_{298K}$ )	Reference
$\text{Au}(\text{CN})_2^-$	38.30	Smith and Martell, 1989
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	28.00	Sullivan and Kohl, 1997
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	26.50	IUPAC, 1993
$\text{Au}(\text{NH}_3)_2^+$	26.00	Wang, 1992
$\text{AuCl}_4^-$	25.60	Wang, 1992
$\text{Au}(\text{SCN})_2^-$	16.98	Smith and Martell, 1989
$\text{Au}(\text{NH}_3)_2^+$	13.00	Hancock <i>et al.</i> , 1974
$\text{Au}(\text{SCN})_4^-$	10.00	Smith and Martell, 1989

Gold dissolution in this system depends on the presence of  $\text{Cu}^{2+}$  ions in solution, which in turn are stabilized by ammonia. Cupric ion oxidizes gold and thiosulfate complexes gold and copper ions, keeping them stable in solution (reaction 1). At the same time,  $\text{Cu}^{2+}$  also oxidizes thiosulfate ions, increasing reagent consumption (reaction 2). As cuprous ions are not able to oxidize gold, oxygen oxidizes them back to cupric. However, oxygen associated with cupric may speed up thiosulfate oxidation and can also generate species, such as disulfite, that hinder gold dissolution (Jeffrey *et al.*, 2003).



Freitas *et al.* (2001) investigated the application of this process to the treatment of Brazilian oxide gold-copper ores and concluded that it is possible to apply ATS leaching without addition of  $\text{Cu}^{2+}$  ions, since the ore provides enough cupric ions to render Au leaching possible. In that work relatively high reagent concentrations were employed and no attempts were made to optimize thiosulfate consumption. It was also verified that extending leaching times above 24 h did not increase gold extraction.

In the present work the use of ammoniacal thiosulfate leaching of a similar gold-copper ore was studied. The effect of the following variables on both gold extraction and thiosulfate concentration in solution were investigated: ammonia/thiosulfate ratio, use of nitrogen injection during leaching in order to reduce thiosulfate oxidation and removal of copper in the starting ore by leaching with sulphuric acid prior to ATS leaching.

## EXPERIMENTAL

Chemical analysis of the oxide gold-copper ore used is shown in Table 2. Mineralogical analysis of this ore (Table 3) indicates that copper is mainly associated with iron and manganese oxides, as well as copper carbonates (Fujikawa, 2001).

Thiosulfate leaching experiments were carried out in 2000 mL glass beakers under mechanical agitation for 24 h, room temperature and 33% solids. Copper removal prior to ATS leaching was done by contacting the ore with  $H_2SO_4$  in a similar procedure to that described before, under the following conditions: pulp density = 40 wt.%, reaction temperatures = 25°C and 60°C, leaching time = 15 minutes and amount of acid = 98.5 kg  $H_2SO_4$ /t ore. Tests in which nitrogen injection in the slurry was performed were done in a closed vessel with a rate of 50mL  $N_2$ /minute. In those experiments, the slurry was conditioned with  $N_2$  for 1h prior to ATS addition.

Only analytical grade reagents and distilled water were used in all leaching experiments. Gold and copper in solution were assayed by Atomic Absorption Spectroscopy (AAS). Solid residues were assayed for gold (fire-assay) and copper (ICP spectrometry). High Performance Liquid Chromatography (HPLC) was employed in order to establish thiosulfate concentration in solution.

**Table 2** – Chemical composition of the ore sample (Fujikawa, 2001)

Element	Grade (%)
Fe	39.4
Si	9.40
Al	4.50
Mn	1.61
PF	8.0
Ti	0.44
Cu	0.54
Cu <sub>sol</sub>	0.095
Au (g/t)	3.88
Ag (g/t)	20

**Table 3** – Copper distribution by minerals (Fujikawa, 2001)

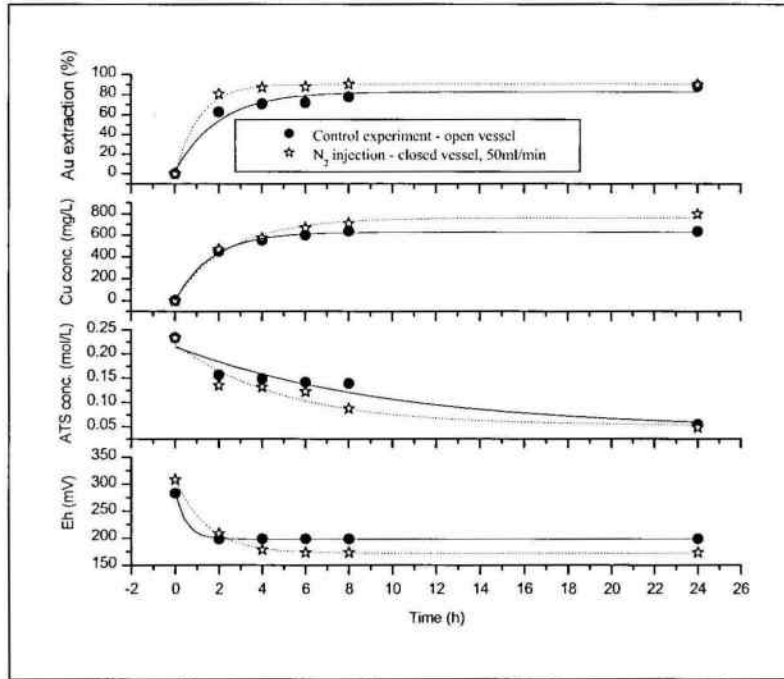
Minerals	Grade (%)
Goethite ( $FeO \cdot \alpha OH$ )	43
Malaquite ( $Cu_2CO_3(OH)_2$ )	27
Mn oxides	17
Cuprite ( $Cu_2O$ )	7
Hematite ( $Fe_2O_3$ )	2
Chlorite ( $(Mg, Al, Fe)_{12}(Si, Al)_8O_{20}(OH)_{16}$ )	2
Tenorite ( $CuO$ )	1
Native copper (Cu)	Trace
Digenite ( $Cu_{1.8}S$ )	Trace
Calcopirite ( $CuFeS_2$ )	Trace
Bornite ( $Cu_5FeS_4$ )	Trace

## RESULTS AND DISCUSSION

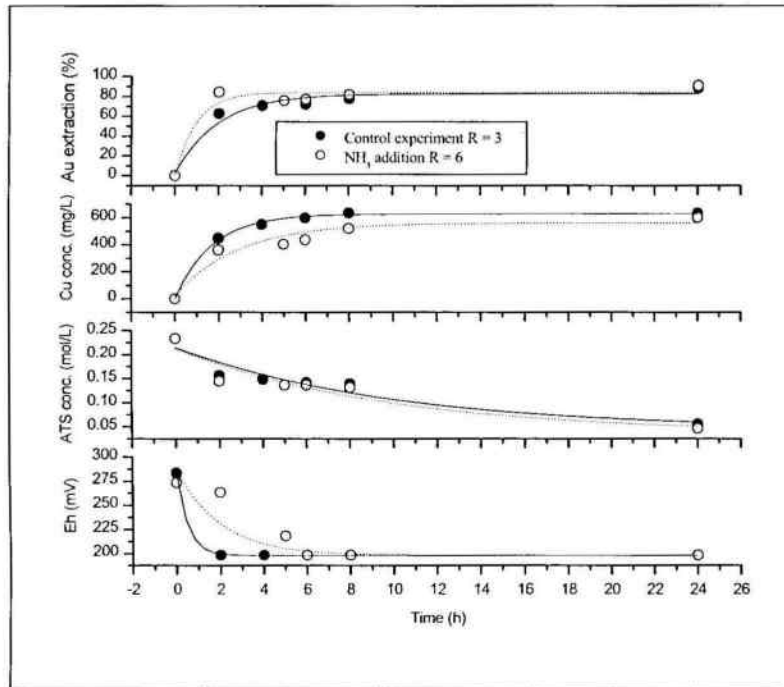
Initially, it was decided to employ experimental conditions resulting in a compromise between low consumption of thiosulfate and reasonable gold extraction. Thus, a first experiment - which will be referred as control experiment in the remaining of this paper - was done with 0.23 mol/L of ammonium thiosulfate and 0.67 mol/L of ammonium hydroxide. Results of this experiment are summarized in Figure 1. It can be seen that an extraction of gold up to 87% was achieved and that copper concentration in solution showed a sharp increase in the beginning of the test, levelling off at about 600 mg/L after 8 hours of leaching, with practically no increase in the remaining of reaction. Thiosulfate consumption of the control experiment was 52.9 kg ATS/t ore.

Copper is regarded as a catalyzing agent for gold dissolution in the ammonia-thiosulfate system, and, therefore, gold extraction is a function of cupric ions concentration in solution. However, an excess of cupric ions associated with oxygen may reduce thiosulfate concentration in solution (Jeffrey *et al.*, 2003), lowering gold extraction. Considering the ore sample used in the present study, which is rich in soluble copper, the effect of thiosulfate oxidation would be expected to have little effect on the decrease of cupric ion concentration. Thus, it seems reasonable to rule out the need of oxygen for regeneration of cupric ions. In order to investigate the effect of oxygen on Au and Cu extraction and ATS consumption, an experiment was carried out with nitrogen injection to the slurry. The results shown in Figure 2 clearly indicate that injection of nitrogen did improve gold leaching kinetics, and, surprisingly, copper extraction, but at the expense of a slightly higher thiosulfate consumption. This may be explained by the higher copper and gold concentration achieved in comparison to the control experiment. As expected, nitrogen injection reduced slurry's Eh.

In a further set of experiments the effect of varying the ratio of ammonia to thiosulfate -  $R = [\text{NH}_3]/[\text{S}_2\text{O}_3^{2-}]$  - in solution was evaluated. This was done by keeping thiosulfate concentration constant and adding enough ammonia to rise R from 2.9 (control experiment) up to 6. According to a previous study (O'Malley, 2002), an increase in ammonia/thiosulfate ratio provides the following benefits: stabilizes  $\text{Cu}^{2+}$ ; avoids excessive thiosulfate oxidation; improves gold and copper extractions. However, the results of the present study show that an increase in R (Figure 3) did provide a higher ratio of  $\text{Cu}^{2+}/\text{Cu}^+$  in solution as indicated by the higher Eh values (Dai *et al.*, 2003) as compared to the control experiment, with the total copper concentration showing a small decrease. Furthermore, these conditions resulted in a higher consumption of thiosulfate in comparison to the control experiment. Whether or not this conclusion is valid for all types of ores is a matter opened for discussion. At all events, the results of the present work, in which an oxide gold-copper ore was employed, clearly indicate that there is no advantage in increasing ammonia concentration in solution.



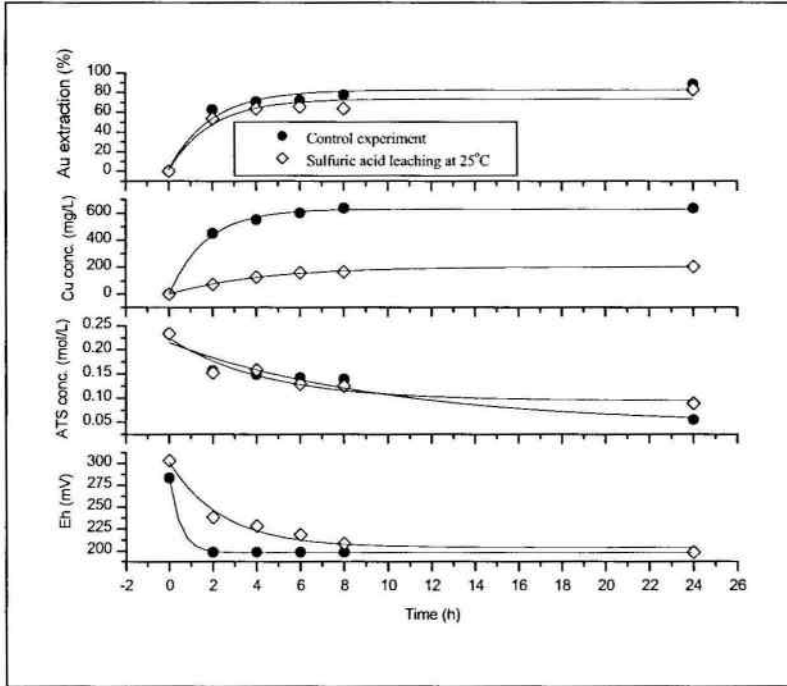
**Figure 1** – Gold extraction and thiosulfate and copper concentrations obtained at conditions of control experiment (open vessel, room temperature, 33% solids,  $[\text{NH}_3] = 0.67\text{mol/L}$ , and  $[\text{S}_2\text{O}_3^{2-}] = 0.23\text{mol/L}$ ), and effect of  $\text{N}_2$  injection (closed vessel, room temperature,  $\text{N}_2$  flow rate = 50mL/min, 33% solids,  $[\text{NH}_3] = 0.67\text{mol/L}$ , and  $[\text{S}_2\text{O}_3^{2-}] = 0.23\text{mol/L}$ )



**Figure 2** – Effect of increasing ammonia/ATS ratio on metals extraction and ATS concentration decrease (open vessel, room temperature, 33% solids, and  $[\text{S}_2\text{O}_3^{2-}] = 0.23\text{mol/L}$ )

Lowering copper grade prior to ATS leaching was investigated in order to verify if with a lower copper grade in the ore, both copper concentration in solution and thiosulfate consumption would be decreased without reducing gold extraction. The results shown in Figures 3 and 4 indicate that reducing copper content of the starting ore was not advantageous, as it resulted in little gain in thiosulfate consumption. In addition, not only

gold extraction was lower (around 82% extraction for pre-treated samples against 88% extraction obtained in the control experiment), but also reaction kinetics was slower than in the control experiment. Taken values from the literature (Molleman and Dreisinger, 2002) into account, one concludes that copper concentrations achieved in the present work were yet quite high. Therefore, there is no advantage in lowering copper concentration in order to reduce thiosulfate consumption, since this condition results in a slower kinetics and poorer final gold extraction (Figures 3 and 4). The higher values of Eh observed during pre-treated samples ATS leaching indicate the pre-treatment with sulphuric acid leaching can increase the ratio  $\text{Cu}^{2+}/\text{Cu}^{+}$  (Dai *et al.*, 2003).



**Figure 3** – Effect of sulphuric acid leaching pre-treatment at 25°C (open vessel, room temperature, 33% solids,  $[\text{NH}_3] = 0.67\text{mol/L}$ , and  $[\text{S}_2\text{O}_3^{2-}] = 0.23\text{mol/L}$ )

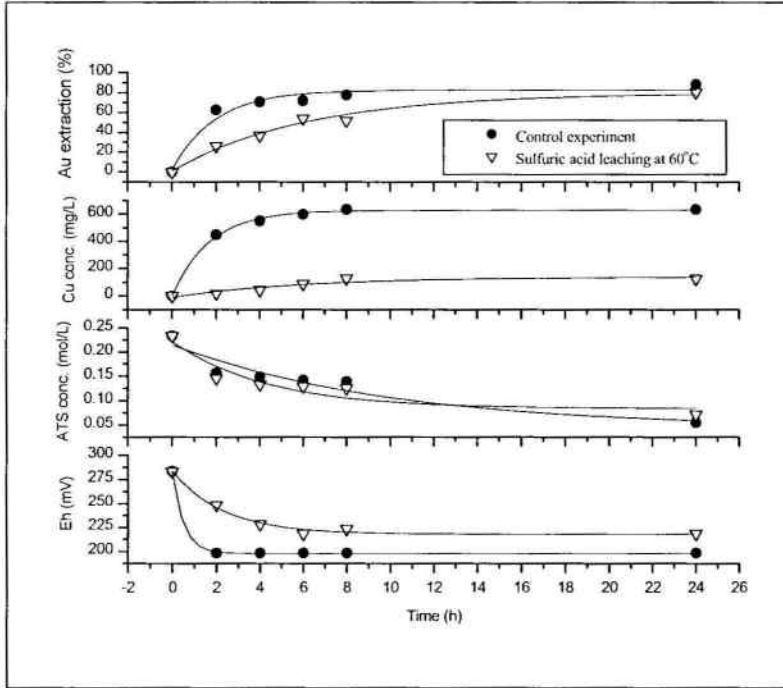


Figure 4 – Effect of sulphuric acid leaching pre-treatment at 60°C (open vessel, room temperature, 33% solids,  $[\text{NH}_3] = 0.67\text{mol/L}$ , and  $[\text{S}_2\text{O}_3^{2-}] = 0.23\text{mol/L}$ )

## CONCLUSIONS

Copper concentration in solution and the presence of oxygen in the slurry are critical parameters for the kinetics of gold dissolution in ammoniacal thiosulfate leaching and for the stability of thiosulfate in solution. In the present study, in which an oxide gold-copper ore rich in soluble copper was utilized, gold extractions after 24h of leaching were satisfactory for all tested conditions. In addition, the fast leaching kinetics of the thiosulfate-ammonia-copper system reported in literature was also confirmed. The use of nitrogen injection during leaching provided an increase in gold and copper extractions, with little influence upon thiosulfate concentration in solution at the end of leaching. This means that, for this kind of ore, reducing oxygen concentration in slurry does result in higher and faster gold extraction, with no significant increase in reagent consumption, even at high copper concentrations. Increasing ammonia concentration resulted in little gain in terms of gold extraction or thiosulfate consumption. Removal of copper by attacking the ore with sulphuric acid prior to ATS leaching resulted in lower gold and copper extractions, with little thiosulfate consumption. It was observed that is possible to increase Eh – and thus  $\text{Cu}^{2+}/\text{Cu}^+$  ratio – through sulphuric acid leaching pre-treatment or increasing  $\text{NH}_3/\text{S}_2\text{O}_3$  ratio.

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