www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems of Mineral Processing ISSN 1643-1049 (print) ISSN 2084-4735 (online)

Received July 11, 2016; reviewed; accepted April 26, 2017

Thiosulfate-copper-ammonia leaching of pure gold and pressure oxidized concentrate

Antti Porvali*, Lotta Rintala*, Jari Aromaa*, Tommi Kaartinen**, Olof Forsen*, Mari Lundstrom*

Abstract: In this research cyanide-free leaching of pure gold and pressure oxidized refractory gold concentrate by thiosulfate-copper-ammonia solutions were examined. A quartz crystal microbalance (QCM) was used to study gold leaching as a factorial series where the best gold leaching rate (2.987 mg/(cm²·h)) was achieved with a solution consisting of 0.2 M (NH₄)₂S₂O₃, 1.2 M NH₃, 0.01 M CuSO₄ and 0.4 M Na₂SO₄. Temperature had the greatest effect on the gold leaching rate. An increase in thiosulfate concentration (0.1-0.2 M) increased gold dissolution. The combined effect of temperature and ammonia concentration had a statistically significant effect on the gold leaching rate at 0.1 M M₂S₂O₃. Combination of applied potential and NH3:S2O3 ratio had a statistically significant effect on the gold leaching rate at 0.2 M M₂S₂O₃. An increase in applied potential decreased the gold dissolution rate at low ammonia concentrations but increased it at high concentrations. A pressure oxidized gold concentrate was leached for 6 hours in the batch reactor leaching experiments. The effect of rotative velocity (1.26-1.56 m/s) and slurry density (10-30 wt%) was investigated at the following leaching parameters: 0.2 M Na₂S₂O₃, 0.6 M NH₃, 0.01 M CuSO₄, 0.4 M Na₂SO₄. Lower slurry density (10 wt%) resulted in a higher Au leaching efficiency. An increase in the rotation rate did not have an effect on the final Au leaching recovery. The best Au leaching efficiency (89%) was achieved with 590 rpm mixing, 1.56 m/s rotative velocity and 10 wt% slurry density.

Keywords: gold leaching, thiosulfate, quartz crystal microbalance

Introduction

The industrially applied leaching method for gold ores and concentrates involves the use of cyanide as a ligand for dissolution of gold. Cyanide is technically and economically a viable method for gold processing, and therefore it is hard to bring a cyanide-free method into the market. However, a few accidents have been reported involving facilities using cyanide in gold leaching (Macklin et al., 2003). Therefore,

^{*}Department of Materials Science and Engineering, Aalto University, PO Box 16200, 00076 Aalto, Finland. Corresponding author: antti.porvali@alumni.aalto.fi (Antti Porvali)

^{**}VTT Technical Research Centre of Finland, Biologinkuja 7, 02150 Espoo, Finland: tommi.kaartinen@vtt.fi

there is an increasing interest towards cyanide-free leaching agents, such as chloride, thiourea and thiosulfate (Marsden and House, 2006; Choi et al., 2013).

In thiosulfate gold leaching, Cu^{2+} ions are commonly used as oxidizing agents, while the thiosulfate ion acts as a ligand forming a soluble gold thiosulfate-ammonia complex (Aylmore and Muir, 2001). It was suggested that gold leaching in the absence of Cu^{2+} ions, with an external current acting as a oxidizer, is not possible (Breuer and Jeffrey, 2002). Ammonia is commonly used to increase pH of solution up to 10-12 where thiosulfate and $Cu(NH_3)_4^{2+}$ complexes are thermodynamically stable (Aylmore and Muir, 2001). A typical redox potential for ammoniacal thiosulfate leaching ranges between 200 and 300 mV vs. SHE. In the absence of ammonia, or with excess copper, Cu^{2+} ions react with thiosulfate forming $CuS_2O_3^-$ and $S_4O_6^{2-}$ ions (Byerley et al., 1973; Rabai and Epstein, 1992; Zhang and Nicol, 2003).

The chemistry of thiosulfate leaching is complex (Aylmore and Muir, 2001) and the leaching mechanism is not fully understood but has been widely investigated (Senanayake, 2003, 2004, 2005a, 2005b, 2005c; Senanayake and Zhang, 2012a, 2012b). Lixiviant oxidation, degradation and the impact of oxidation products on gold dissolution were investigated with SO₄²⁻ ion addition reducing thiosulfate oxidation (Breuer and Jeffrey, 2003; Chu et al., 2003). One of the advantages claimed for thiosulfate is its ability to resist preg-robbing (Marsden and House, 2006). This is different to chloride leaching (Ahtiainen and Lundstrom, 2016) which is another cyanide-free lixiviant close to penetrating the market on industrial scale (Marsden and House, 2006; Intec Ltd., 2009; Controls, 2012; Ferron, 2012; Robinson et al., 2012; Dundee Sustainable Technologies, 2015; Lalancette et al., 2015). However, thiosulfate leaching of waste electrical and electronic equipment (WEEE) has also indicated pregrobbing type behaviour (Ha et al., 2010).

It is not clear how different parameters and their ranges affect pure gold and gold mineral leaching in the thiosulfate media. In the current research, gold dissolution in the thiosulfate solution was investigated both electrochemically (quartz crystal microbalance, QCM) and using batch leaching experiments for gold concentrate. The design of experiments was carried out with full factorial design by MODDE (MKS Data Analytics Solutions) software in order to build up a model reflecting the leaching rate of gold as a function of temperature (*T*), applied potential (*E*), ammonia-to-thiosulfate (NH₃:S₂O₃) ratio and their combined effects. In addition, leaching of the refractory gold concentrate was examined in batch reactor experiments.

Materials and methods

Electrochemical experiments

The gold dissolution rate was investigated using a pure gold crystal attached to a Stanford Research Systems Quartz Crystal Microbalance (SRS QCM200) as a working electrode. Mass change on the crystal was determined by the Sauerbrey equation (Buttry and Ward, 1992):

$$\Delta f = -C_f \cdot \Delta m,\tag{1}$$

where C_f is the sensitivity factor for the crystal used (56.6 Hz cm²/ μ g), f is the frequency (Hz) and Δm is mass change (μ g).

A saturated silver-calomel electrode (Radiometer 401) SCE \pm 0.241 V vs. SHE was used as a reference electrode and a platinum sheet as a counter electrode. The applied potential was controlled via a GillAC potentiostat (ACM Instruments). The volume of the reactor vessel was 1 dm³, and temperature was controlled via a vessel jacket and thermostat.

Sodium thiosulfate pentahydrate, ammonium thiosulfate (99% analytical grade), ammonia (25%), sodium sulfate (Baker grade), copper sulfate pentahydrate (technical grade) and distilled water (Millipore) were used in the experiments. The electrolyte was cooled/heated to the desired temperature for 30 minutes. Pure nitrogen was used in order to prevent thiosulfate degradation and formation of disulfite ions (Chu et al., 2003). Feng and Van Deventer (2007) suggested that nitrogen purging should be used with minerals having high sulfide concentrations.

In order to see whether there was consistency in the parameter ratios investigated, NH₃:S₂O₃, S₂O₃:Cu and NH₃:Cu ratios used in the published data were calculated (Table 1). It was shown that the ammonia-to-thiosulfate ratio ranged from 1 to 10, with 4–5 being the commonly used magnitude.

Table 1. Literature data of concentrations of copper, thiosulfate and ammonia and their NH₃:S₂O₃, S₂O₃:Cu²⁺ and NH₃:Cu²⁺ ratios based on the table in Aylmore and Muir (2001), with additional data treatment to reveal molar ratios regarding ammonia, thiosulfate and copper

Source	S_2O_3	NH ₃	Cu ²⁺	NH ·S O	S O :Cu ²⁺	NH ·Cu ²⁺
Source	(M)	(M)	(M)	NH ₃ :S ₂ O ₃ S ₂ O ₃ :Cu ²⁺		Nn ₃ .Cu
Feng and Van Deventer (2007)	0.1	0.5	0.006	5	16.7	83.3
Feng and Van Deventer (2006)	0.5	2.5	0.12	5	4.2	20.8
Xia and Yen (2003)	0.3	3.0	0.03	10	10	100
Breuer and Jeffrey (2002)	0.1	0.4	0.01	4	10	40
Feng and Van Deventer (2002)	0.5	2.0	0.012	4	41.7	166.7
Breuer and Jeffrey (2000)	0.1	0.4	0.01	4	10	40
Abbruzzese et al. (1995)	2.0	4.0	0.1	2	20	40
Yen et al. (1996)	0.4	0.2	0.03	0.5	13.3	6.7
Jeffrey (2001)	0.4	0.6	0.01	1.5	40	60
Tozawa et al. (1981)	0.5	1.0	0.04	2	12.5	25
Jeffrey et al. (2008)	0.1	0.8	0.01	8	10	80
Senanayake (2007)	0.25	1.0	0.06	4	4.2	16.7
Hemmati et al. (1989)	0.71	3.0	0.15	4.23	4.7	20
Hu and Gong (1992)	10.	2.0	0.16	2	6.3	12.5
Cao et al. (1992)	0.2	2.0	0.047	10	4.3	42.6
Cao et al. (1992)	0.3	2.0	0.047	6.66	6.4	42.6
Langhans et al. (1992)	0.2	0.09	0.001	0.45	200	90
Yen et al. (1998)	0.5	6.0	0.1	12	5	60
Wan and Brierley (1997)	0.1	0.1	0.005	1	20	20

Exp.	T (°C)	E (mV vs. SHE)	NH ₃ :S ₂ O ₃ Ratio
1	30	300	4
2	30	300	4
3	20	250	2
4	20	350	2
5	40	250	2
6	40	350	2
7	20	250	6
8	20	350	6
9	40	250	6
10	40	350	6

Table 2. The parameters for three electrochemical leaching experiment series by QCM (series 1-3). In series 1 and 2 Na₂S₂O₃ was used as thiosulfate salt and in series 3 the thiosulfate source was (NH₄)₂S₂O₃

Electrochemical gold leaching experiments were performed in three series that consisted of 10 measurements (Table 2). The first two series were carried out using sodium thiosulfate and the third using ammonium thiosulfate. Three variables were chosen for factorial analysis: temperature (20, 30, 40 °C), applied potential of the QCM electrode (250, 300, 350 mV vs. SHE) and initial ammonia concentration. The NH₃:S₂O₃ ratio investigated varied from 2 to 6 (Table 1) (Breuer and Jeffrey, 2000, 2002; Feng and Van Deventer, 2002, 2006, 2007). Concentrations in the series were as follows: series $1 - [Na_2S_2O_3] = 0.1$ M and $[NH_3] = 0.2 - 0.6$ M, series $2 - [Na_2S_2O_3] = 0.2$ M and $[NH_3] = 0.4 - 1.2$ M and series $3 - [(NH_4)_2S_2O_3] = 0.2$ M and $[NH_3] = 0.4 - 1.2$ M. Other reagents used were CuSO₄ (0.01 M) and Na₂SO₄ (0.4 M). Table 2 presents the NH₃:S₂O₃ ratio investigated in each series. The upper temperature was limited to 40 °C due to accelerated thiosulfate degradation at high temperatures.

During the experiment, the mass change was recorded by QCM. Each experiment lasted a maximum 20 minutes, the time depended on the gold dissolution rate from the QCM crystal.

Batch reactor experiments

The raw material used in the batch reactor leaching experiments was the refractory pyritic and arsenopyritic concentrate that was subjected to pressure leaching at industrial scale and provided as such for thiosulfate leaching. The raw material contained 47 ppm Au, 8 ppm Ag, 14% Fe, 11% Si and 4% S. A solid analysis was carried out by total leaching (HCl, HF and HNO₃) with the elemental analysis (ICP-MS) and fire assay (FA) for Au and Ag (Labtium Oy). The gold concentration was determined by using ICP-OES after fire assay enrichment.

In batch leaching, a 3 dm³ glass reactor vessel with integrated water jacket (LENZ LF 150) was used, with a solution volume of 2.4 dm³ before the concentrate was added. Temperature (30 °C) of the solution was controlled via a thermostat (Julabo ED-5 heating circulator with open bath). The nitrogen flow rate was controlled via a rotameter (Environics series 2000 computerized multi-component gas mixer) and set

to a constant 500 cm³/min. The redox was monitored. The particle size distribution was determined using the laser diffraction method (Malvern Instruments Mastersizer 2000). The solution used in the batch leaching experiments contained [Na₂S₂O₃] = 0.2 M, [NH₃] = 0.6 M, [CuSO₄] = 0.01 M and [Na₂SO₄] = 0.4 M. It was observed that at an NH₃:S₂O₃ ratio of \geq 4, the redox potential of the solution decreased with increasing ammonia concentration to values <180 mV vs. SHE, not favourable to gold dissolution. Ratios of NH₃:S₂O₃ = 3 resulted in an initial redox potential of 260 – 280 mV vs. SHE, which were suitable for batch reactor leaching.

In the batch reactor experiments, sodium thiosulfate pentahydrate (99%), ammonia (32%), distilled water, sodium sulfate (analytical grade), copper sulfate pentahydrate (technical grade) and pure nitrogen were used. The batch leaching series consisted of seven experiments with two variables investigated: mass transfer and slurry density (Table 3).

Batch leaching was conducted for 6 hours, with sampling at t = 15, 30, 60, 120, 240 and 360 minutes. Filtered solutions were frozen and sent for analysis (ICP-MS). The filtered leach residue was dried and analysed.

Exp.	RPM	Rotational velocity	Slurry density	Concentrate mass
		(m/s)	(wt%)	(g)
I	490	1.54	20	480
II	490	1.54	20	480
III	400	1.26	10	240
IV	400	1.26	30	720
V	590	1.85	10	240
VI	590	1.85	30	720

Table 3. Design of experiments for pressure oxidized gold concentrate batch leaching

Results

Electrochemical gold leaching results by quartz crystal microbalance

Quartz crystal microbalance (QCM) experiments showed that low temperature (20 °C) resulted in very low leaching rates in all experiments (Fig. 1). The best gold leaching rates were achieved at T = 40 °C in all series. This supports the earlier findings that thiosulfate leaching is chemically controlled (Jeffrey, 2001). It can be seen that the NH₃:S₂O₃ ratio of 2 resulted in the best leaching rates when the electrode was polarized to 250 mV vs. SHE (series 2 and 3). In contrast, the NH₃:S₂O₃ ratio of 6 resulted in the best leaching rates at higher potential (350 mV vs. SHE, series 1-3). Ammonium thiosulfate (series 3) was shown to result in higher gold leaching rates compared to sodium thiosulfate (series 1 and 2) at equal molarities, which supported the earlier studies (Jeffrey et al., 2008; Feng and Van Deventer, 2010).

Black precipitates caused by the instability of thiosulfate and copper sulfide precipitation were seen at the bottom of the reactor in the following experiments:

series 1, exp. 3-6 ([Na₂S₂O₃] = 0.1 M, [NH₃] = 0.2 M, both at 20 and 40 °C) and series 3, exp. 3 ([S₂O₃] = 0.2 M, [NH₃] = 0.4 M, T = 20 °C). This suggests that low ammonia concentration and low NH₃:S₂O₃ ratio decreased thiosulfate stability.

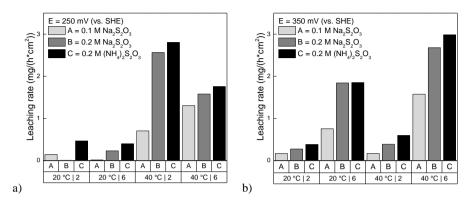


Fig. 1. Gold leaching rate during thiosulfate leaching a) at 250 mV and b) at 350 mV vs. SHE. The values of T (20 and 40 °C) and NH₃:S₂O₃ ratio (2 or 6) are presented on the x axis

Using factorial analysis in MODDE, it was possible to determine which parameters, if any, had statistically significant correlation with the gold leaching rate. Series 1 and 3 were found to be statistically valid and repeatable and temperature was found to have the most significant effect on the gold dissolution rate in both series. Leaching rates were shown to improve at higher temperatures. For the series 1 it was also found that the combined effect of temperature and ammonia concentration, and hence, the NH₃:S₂O₃ ratio, had a statistically significant effect, with a greater ratio improving the gold leaching rate at a thiosulfate concentration of 0.1 M. In the series 3, (thiosulfate concentration of 0.2 M) a combined effect of applied potential and ammonia concentration, and hence the NH₃:S₂O₃ ratio, was found to have a positive effect on gold leaching, suggesting that with an increasing potential the importance of excess ammonium increases.

By a factorial analysis, an equation describing gold dissolution in thiosulfate solution could be formed for the statistically valid series 1 and 3 (Eq. 2 and 3, respectively):

$$Y = 0.037598T + 0.00165E - 2.91911c - 7.59 \cdot 10^{-5}TE + 0.053975Tc + 0.004762Ec - 0.29129$$
 (2)

$$\log_{10} Y = 0.041067T - 0.00273E - 1.10292c - 9.49 \cdot 10^{-6} \cdot TE -0.00385Tc + 0.0042Ec - 0.36552$$
(3)

with Y describing the gold leaching rate (mg/(cm 2 ·h)), T temperature (°C), E applied potential (mV vs. SHE) and c NH₃ concentration (M).

In Equations (2) and (3) the effects of potential and NH₃ concentration were included, although these parameters were not statistically significant. The statistically significant parameters in Eq. (1) were T and T·c and in Eq. (3) T and E·c. Both models had $R^2 > 0.97$. The Q^2 estimated the goodness of fit and was usually between 0 and 1, and for very poor models negative. For the series 1 $Q^2 = 0.59$, model validity was 0.45, p = 0.006 and reproducibility 0.998. For the series 3 $Q^2 = 0.82$, model validity was 0.63, p = 0.004 and reproducibility 0.995. It indicated the interaction between parameters that were found to be statistically significant but the models cannot be considered as ideal.

Figure 2 shows the contour surfaces calculated using Eqs. (2) and (3). It can be seen that higher temperature results in higher gold leaching rates according to both equations at lower and higher potentials (250 vs. 350 mV vs. SHE). Also, when comparing the modelled leaching rates a higher thiosulfate concentration (0.2 vs 0.1 M) shows the increased gold dissolution rate (Fig. 2a vs. 2b and Fig. 2c vs. 2d) at both lower and higher potentials. However, the effect of ammonia, and thus the NH₃:S₂O₃ ratio, is highly dependent on the electrode potential, and thus on the oxidative conditions. Under highly oxidative conditions (E = 350 mV vs. SHE) increasing ammonia supports gold dissolution in all the environments investigated. However, at lower potentials (E = 250 mV), which are more typical for thiosulfate concentrate leaching, increasing ammonia concentration, and thus the NH₃:S₂O₃ ratio, increases the gold dissolution rate only at lower thiosulfate concentration (0.1 M, equation 2), whereas at higher thiosulfate concentration (0.2 M, equation 3) it has a negative impact on the gold dissolution rate. This shows that the effect of the ammonia concentration, and thus the effect of the NH₃:S₂O₃ ratio, is highly dependent on the oxidative potential.

The intrinsic reason for the leaching efficiency behavior is most likely related to the speciation of complexes in the solution as the concentration of reagents and applied potential changes. It was determined by Senanayake (2004) that the gold dissolution is most efficiently facilitated by adsorption of mixed thiosulfate-ammonia-copper complex on the surface of gold, following its redox reaction. Other complexes of Cu²⁺ may be either insufficient or less efficient for the purpose. Additionally, it was shown elsewhere (Aylmore and Muir, 2001; Wan et al., 2003; Senanayake, 2004) that the speciation of copper species in thiosulfate solutions varied significantly depending on the solution conditions. It can be explained by variation in speciation of complexes with change in the potential applied in such a way that the conditions of efficient gold dissolution change.

Thiosulfate concentration of 0.2 M was chosen to be used in the batch leaching experiments based on the higher leaching rates achieved in the QCM tests, when compared to 0.1 M. Temperature of 30 °C was chosen instead of T=40 °C in order to avoid thiosulfate degradation and ammonia vaporization at a reasonable gold dissolution rate. Ammonia concentration of 0.6 M was chosen based on electrochemical experiments showing higher leaching rates (and higher redox

potentials) when a lower $NH_3:S_2O_3$ ratio was used at lower electrode potentials. However, the redox potentials of solution were additionally observed as a function of time and $NH_3:S_2O_3=3$ gave a higher redox potential than $NH_3:S_2O_3=4$, which was chosen for the batch test series.

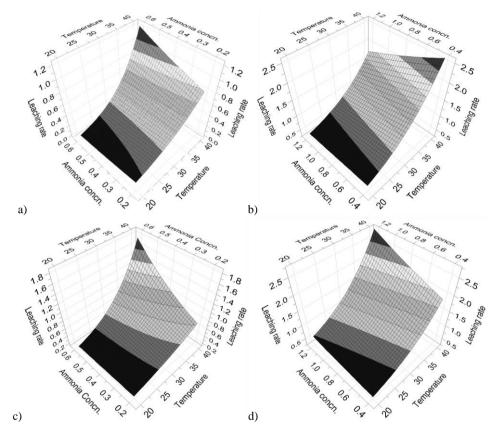


Fig. 2. Leaching rate of gold vs. SHE during thiosulfate leaching a) at E = 250 mV, demonstrated by a contour surface using equation (2), b) at E = 250 mV, demonstrated by a contour surface using equation (3), c) at E = 350 mV, demonstrated by a contour surface using equation (2), d) at E = 350 mV, demonstrated by a contour surface using equation (3). The units used were: leaching rate (mg/(cm²·h)), ammonia concentration (M) and temperature (°C)

Batch reactor gold leaching results

The particle size distribution was shown to be small: d(0.5) 5.3 μ m, d(0.8) 16.6 μ m and the weighed residual was 0.2%. Wet sieving was used to obtain another estimate of the validity of the laser diffraction method setup and it was shown that roughly 13% of the particles remained on a 32 μ m sieve.

The redox potential of the solution was recorded during batch leaching tests for the refractory pyritic and arsenopyritic concentrate (Fig. 3). This potential decreased along

with increasing slurry density due to faster reduction of oxidized species to reduced species (cupric reduction to cuprous) and the absence of oxygen feed regenerating the oxidant. Experiments I and II were conducted with identical parameters (490 rpm and slurry density of 20 wt%), the redox behaviour being quite identical. Experiments IV and VI had a slurry density of 10 wt% and a rotation rate of 400 vs. 590, respectively. It can be seen that the lower rotation rate also resulted in less oxidized species (cupric) reduction. However, improved mass transport (VI) increased the reaction rate and finally reduced the redox potential to a similar level as that measured with a 20 wt% slurry density at t = 360 min. In addition, it was clearly shown that at a higher solid concentration (30 wt%), the redox potential decreased faster than at lower slurry densities. However, with sufficiently high long leaching time, $t \ge 240$ min, the degree of reactions (cupric reduction) was identical at 20 and 30 wt% slurry density.

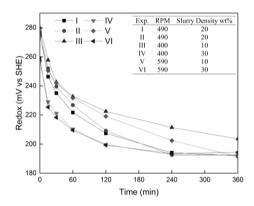


Fig. 3. Redox potential (mV vs. SHE) as a function of time during thiosulfate batch leaching for pressure oxidized gold concentrate

The pH was measured during the gold concentrate thiosulfate leaching experiments. The pH was shown to decrease by approx. 0.2 pH units during all of the batch leaching experiments.

Although the redox potentials (Fig. 3) suggest that the concentrate dissolution continued throughout the entire six-hour leaching with 10 wt% and for four hours with 20-30 wt%, Figure 4 shows that the maximum gold dissolution was already reached after 1-2 hours in most of the experiments. This indicates that there were other elements than gold present in the concentrate that dissolved slightly or, possibly, the thiosulfate was being degraded, decreasing the redox potential over time. Figure 4 also suggests that higher mass transfer (higher rotation rate) did slightly favour higher gold recoveries into the solution.

A fire assay analysis (FA) for a leach residue is known to be a more accurate analysis for gold recovery compared to solution analysis from frozen thiosulfate solution samples. For that reason the final gold recovery was determined by FA and the results are presented in Table 4. It was shown that the gold recovery to the solution

varied between 81 – 89%. It can be clearly seen that at 10 wt% and 20 wt% slurry density (Exp. I, II, III and V), higher gold recoveries were achieved compared to experiments with high solid density (30 wt% in Exp. IV and VI). In the studied environment, the effect of mass transfer rate (mixing speed) was not shown to have an effect on the final gold recovery based on solid analysis. However, the redox potentials in Fig. 3 and the solution analysis in Fig. 4 suggest that the effect of mass transfer (mixing speed) may have an effect on gold recovery at lower leaching times. The gold recovery cannot be directly interpreted from the solution analysis, since the amount of concentrate, and thus the amount of gold exposed to leaching varied in experiments I-VI.

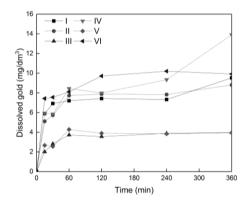


Fig. 4. Concentration of dissolved gold in solution as a function of leaching time during thiosulfate batch leaching for pressure oxidized gold concentrate

Table 4. Measured Au leaching efficiency
based on the solid analysis of pressure oxidized gold concentrate

Exp.	Au yield	
	%	
I	88	
II	88	
III	88	
IV	88 82 89	
V	89	
VI	81	

Conclusions

Temperature was shown to have the most significant effect on the gold leaching rate in the quartz crystal microbalance experiments. Also, the increase in thiosulfate concentration resulted in a higher gold leaching rate at the investigated concentration range $(0.1-0.2\ M)$. $(NH_4)_2S_2O_3$ was shown to result in a slightly higher gold dissolution rate compared to $Na_2S_2O_3$.

It was observed that at low $NH_3:S_2O_3$ ratio equal to 2, the oxidative power had a negative impact on the gold dissolution rate, suggesting that an increase in potential can either enhance degradation of thiosulfate at lower NH_3 concentration or unfavorably alter speciation of copper complexes, decreasing the gold dissolution rate. Conversely, at high $NH_3:S_2O_3$ ratio equal to 6, positive impact of oxidative power was observed. An increase in the oxidative power may change the speciation of copper complexes favorably or decrease thiosulfate degradation, increasing the gold dissolution rate.

At 0.1 M thiosulfate concentration, the combined effect of temperature and ammonia was a statistically significant parameter, and the gold dissolution rate improved with increasing these parameters. At a higher thiosulfate concentration (0.2 M), the combined effect of the potential applied and ammonia concentration was shown to be significant.

The batch reactor leaching series was conducted for pressure oxidized gold concentrate. The analysis of a redox potential showed that leaching was nearly completed after six hours of leaching experiments, with the redox potential decreasing faster in the presence of higher solid mass or higher mass transfer. However, the solution analysis indicated that gold dissolution was already complete in most of the experiments after 1-2 hours of leaching.

The final gold leaching efficiency based on the analysis of solids amounted to 81–89%, with a lower solids concentration favoring higher gold extraction. The rotation rate was shown to have no effect on the gold leaching efficiency.

Acknowledgement

The authors would like to thank the funder of the research, K.H. Renlunds Stiftelse (K.H. Renlund's Foundation), for their generous contribution. The authors would like to also thank ARVI project for additional funding. RawMatTERS Finland Infrastructure (RAMI) supported by Academy of Finland is greatly acknowledged.

References

- ABBRUZZESE, C., FORNARI, P., MASSIDDA, R., VEGLIÒ, UBALDINI, S., 1995, *Thiosulfate leaching for gold hydrometallurgy*, Hydrometallurgy 39, 265-276.
- AHTIAINEN, R., LUNDSTROM, M., 2016, *Preg-robbing of gold in chloride-bromide solution*, Physicochem. Probl. Miner. Process 52, 1, 244-251.
- AYLMORE, M.G., MUIR, D.M., 2001, Thiosulfate leaching of gold a review, Miner. Eng. 14, 135-174
- BREUER, P.L., JEFFREY, M.I., 2000, Thiosulfate leaching kinetics of gold in the presence of copper and ammonia, Miner. Eng. 13(10-11), 1071-1081.
- BREUER, P.L., JEFFREY, M.I., 2002, An electrochemical study of gold leaching in thiosulfate solutions containing copper and ammonia, Hydrometallurgy 65, 145-157.
- BREUER, P.L., JEFFREY, M.I., 2003, The reduction of copper(II) and the oxidation of thiosulfate and oxysulfur anions in gold leaching solutions, Hydrometallurgy 70, 163-173.
- BUTTRY, D.A., WARD, M.D., 1992, Measurement of interfacial processes at electrode surfaces with the electrochemical quartz crystal microbalance, Chem. Rev. 92, 1355-1379.

- BYERLEY, J., FOUDA, S.A., REMPEL, G.L., 1973, Kinetics and mechanism of the oxidation of thiosulphate ions by copper(II) ions in aqueous ammonia solution, Dalton Trans. 7, 889-893.
- CAO, C., HU, J., GONG, Q., 1992. *Leaching of gold by low concentration thiosulfate solution*, Randol Gold Forum, Vancouver, Randol International, Colorado, USA, 293-298.
- CHOI, Y., BARON, J.Y., WANG, Q., LANGHANS, J., KONDOS, P., 2013. *Thiosulfate processing from lab curiosity to commercial application*, in: Proceedings of the World Gold Conference 2013, The Australian Institute of Mining and Metallurgy Publication Series 9, 45-50.
- CHU, C.K., BREUER, P.L., JEFFREY, M.I., 2003, The impact of thiosulfate oxidation products on the oxidation of gold in ammonia thiosulfate solutions, Miner. Eng. 16, 265-271.
- CONTROLS, S., 2015. Nippon N-CHLO PILOT Plant, retrieved from http://www.sgcontrols.com.au/case-studies/nippon-n-chlo-pilot-plant, 2015.
- DUNDEE SUSTAINABLE TECHNOLOGIES, 2015. *Dundee sustainable technologies: cyanide free gold extraction process*. Retrieved from: www.dundeetechnologies.com/en/technology, 2015.
- DUNDEE, TECHNOLOGIES DURABLES INC., 2015, Method and a system for gold extraction with halogens, US 9051626 B2.
- FENG, D., VAN DEVENTER, J.S.J., 2002, Leaching behaviour of sulphides in ammoniacal thiosulphate systems, Hydrometallurgy 63, 189-200.
- FENG, D., VAN DEVENTER, J.S.J., 2006, Ammoniacal thiosulfate leaching of gold in presence of pyrite, Hydrometallurgy 82, 126-132.
- FENG, D., VAN DEVENTER, J.S.J., 2007, The effect of sulphur species on thiosulfate leaching of gold, Miner. Eng. 20, 273-281.
- FENG, D., VAN DEVENTER, J.S.J., 2010, Effect of thiosulphate salts on ammoniacal thiosulphate leaching of gold, Hydrometallurgy 105, 120-126.
- FERRON, J., 2012. Silver recovery from complex concentrates a mineralogical approach, T.T. Chen Honorary Symposium on Hydrometallurgy, Electrometallurgy and Materials Characterization, Orlando, Florida, USA, 371-382.
- HA, V.H., LEE, J-C., JEONG, J., HAI, H.T., JHA, M.K., 2010, Thiosulfate leaching of gold from waste mobile phones, J. Hazard. Mater. 178, 1115-1119.
- HEMMATI, M., HENDRIX, J.L., NELSON, J.H., MILOSAVLJEVIC, E.B., 1989. Study of the thiosulphate leaching of gold from carbonaceous ore and the quantitative determination of thiosulphate in the leached solution, Extraction Metallurgy '89 Symposium, Institute of Mining and Metallurgy, London, UK, 665-678.
- HU, J., GONG Q., 1992, *Recovery of gold from thiosulfate solution*, Huagong Yejin (Eng. Chem. Metall.) 10, 45-50.
- INTEC LTD. (2009). Intec Gold Process. Australia: © Intec Ltd.
- JEFFREY, M.I., 2001, Kinetics aspects of gold and silver leaching in ammonia-thiosulfate solutions, Hydrometallurgy 60, 7-16.
- JEFFREY, M.I., WATLING, K., HOPE, G.A., WOODS, R., 2008, *Identification of surface species that inhibit and passivate thiosulfate leaching of gold*, Miner. Eng. 21, 443-452.
- LALANCETTE, J-M., DUBREUIL, B., LEMIEUX, D., 2015, Method and a system for gold extraction with halogens, US 9051626 B2.
- LANGHANS, J.W., LEI, K.P.V., CARNAHAN, T.G., 1992, Copper-catalysed thiosulfate leaching of low grade gold ores, Hydrometallurgy 29, 191-203.
- MACKLIN, M. G., BREWER, P. A., BALTEANU, D., COULTHARD, T. J., DRIGA, B., HOWARD, A. J & ZAHARIA, S., 2003, The long term fate and environmental significance of contaminant

- metals released by the January and March 2000 mining tailings dam failure in Maramures County, upper Tisa basin, Romania, Appl. Geochem. 18(2), 241-257.
- MARSDEN, J.O., HOUSE, C.I., 2006. *The chemistry of gold extraction*, 2nd Edition, Society of Mining, Metallurgy and Exploration (SME), Littleton (CO), USA, 651.
- MKS DATA ANALYTICS SOLUTIONS, Modde 8.0 / 9.1, http://umetrics.com/
- MOYES, H., HOULLIS, F., 2010, Recovering metals from sulfidic materials, US7858056 B2.
- MOYES, J., HOULLIS, F, 2010, Recovering metals from sulfidic materials, US 7858056 B2.
- MUIR, D.M., AYLMORE, M.G., 2004. Thiosulfate as an alternative to cyanide for gold processing issues and impediments, Trans. Inst. Min. Metall., Sect. C, 113(1), 2-11.
- RABAI, G., EPSTEIN, I.R., 1992, Equilibria and kinetics of the fast interaction between copper(II) and thiosulfate ions in aqueous solution, Inorg. Chem. 31, 3239-3242.
- ROBINSON, T., LEE, F., HEIDEL, A. (2012). Demonstration of the CESL Gold Process. CESL Limited.
- SENANAYAKE, G., 2004, Analysis of reaction kinetics, speciation and mechanism of gold leaching in and thiosulfate oxidation by ammoniacal copper(II) solutions, Hydrometallurgy 75, 55-75.
- SENANAYAKE, G., 2005a, Gold leaching by thiosulfate solutions: critical review on copper(II)—thiosulfate—oxygen interactions, Miner. Eng. 18, 995-1009.
- SENANAYAKE, G., 2005b, The role of ligands in thiosulfate leaching of gold, Gold Bull. 38/4, 170-180.
- SENANAYAKE, G., 2005c, Kinetic model for anodic oxidation of gold in thiosulfate media based on adsorption of MS2O32-ion-pair, Hydrometallurgy 76, 233-238.
- SENANAYAKE, G., 2007, Review of rate constants for thiosulphate leaching of gold from ores, concentrates and flat surfaces: Effect of host minerals and pH, Miner. Eng. 20, 1-15.
- SENANAYAKE, G., PERERA, W.N., NICOL, M.J., 2003. *Thermodynamic studies of the gold* (III)/(I)/(0) redox system in ammonia-thiosulphate solutions at 25 C, in: Hydrometallurgy 2003, Proceedings of the 5th International Symposium, 155-168.
- SENANAYAKE, G., ZHANG, X.M., 2012a, Gold leaching by copper(II) in ammoniacal thiosulphate solutions in the presence of additives. Part I: A review of the effect of hard—soft and Lewis acid-base properties and interactions of ions, Hydrometallurgy 115-116, 1-20.
- SENANAYAKE, G., ZHANG, X.M., 2012b, Gold leaching by copper(II) in ammoniacal thiosulphate 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, 21-29.
- TOZAWA, K., INUI, Y., UMETSU, Y., 1981, Dissolution of gold in ammoniacal thiosulfate solution, 110th Annual Meeting of AIME, A81-25: 1-12.
- WAN, R.Y., BRIERLEY, J.A., 1997, Thiosulfate leaching following biooxidation pretreatment for gold recovery from refractory carbonaceous-sulfidic ore, Min. Eng. 76, 76-80.
- WAN, R.Y., LEVIER, K.M., 2003, Solution chemistry factors for gold thiosulfate heap leaching, Int. J. Miner. Process. 72, 311-322.
- XIA, X., YEN, W.T., 2003, Improvement of thiosulfate stability in gold leaching, Miner. Metall. Proc. 20(2), 68-72.
- YEN, W.T., AGHAMIRIAN, M., DESCHENES, G., THEBEN, S., 1998, *Gold extraction from mild refractory ore using ammonium thiosulfate*, in: Proceedings of the International Symposium on Gold Recovery, 15.
- YEN, W.T., STOGRAN, K., FUJITA, T., 1996, Gold extraction from a copper bearing ore by thiosulfate leaching, Resources Treatment Technology 43(2), 83-87.
- ZHANG, S., NICOL, M.J., 2003, An electrochemical study of the dissolution of gold in thiosulfate solutions Part I: Alkaline solutions, J. Appl. Electrochem. 33, 767-775.