

# Thiosulfate Leaching of the Auriferous Ore from Castromil Deposit: A Case Study

Rui Sousa, Aurora Futuro, António Fiúza

**Abstract**—The exploitation of gold ore deposits is highly dependent on efficient mineral processing methods, although actual perspectives based on life-cycle assessment introduce difficulties that were unforeseen in a very recent past. Cyanidation is the most applied gold processing method, but the potential environmental problems derived from the usage of cyanide as leaching reagent led to a demand for alternative methods. Ammoniacal thiosulfate leaching is one of the most important alternatives to cyanidation. In this article, some experimental studies carried out in order to assess the feasibility of thiosulfate as a leaching agent for the ore from the unexploited Portuguese gold mine of Castromil. It became clear that the process depends on the concentrations of ammonia, thiosulfate and copper. Based on this fact, a few leaching tests were performed in order to assess the best reagent prescription, and also the effects of different combination of these concentrations. Higher thiosulfate concentrations cause the decrease of gold dissolution. Lower concentrations of ammonia require higher thiosulfate concentrations, and higher ammonia concentrations require lower thiosulfate concentrations. The addition of copper increases the gold dissolution ratio. Subsequently, some alternative operatory conditions were tested such as variations in temperature and in the solid/liquid ratio as well as the application of a pre-treatment before the leaching stage. Finally, thiosulfate leaching was compared to cyanidation. Thiosulfate leaching showed to be an important alternative, although a pre-treatment is required to increase the yield of the gold dissolution.

**Keywords**—Gold, leaching, pre-treatment, thiosulfate.

## I. INTRODUCTION

THE concept of sustainable mining has progressively spread over the last fifteen years. One descendent concept is the “green gold”, which embraces diverse concerns for human welfare, community robustness, environmental integrity and overall social and corporative responsibility [1].

Cyanidation process has been supported by a long history of robust research, development and well successful industrial operations experience [2]-[4]. However, the low recoveries from carbonaceous ores are important concerns for the gold mining industry [1]. Thiosulfate leaching is a process that leaches gold from bearing ores without the usage of a toxic reagent offering a similar recovery for the leaching operation. The major concerns for thiosulfate leaching are the high reagent

consumption and the selection of the operating conditions that allow for a similar leaching yield [5].

The use of thiosulfate was reported for the first time in 1857 and 1905 to dissolve gold, but this process was forgotten due to the success of the cyanide process [6]. Thiosulfate anion is tetrahedral in shape and it is theoretically derived by replacing one of the oxygen atoms by a sulfur atom in a sulfate anion. The sulfur to sulfur distance indicates a single bond, implying that the sulfur bears a significant negative charge while the S-O interactions have double bond character [7].

The chemistry of thiosulfate process is complex, even in the absence of a gold ore containing host minerals, mainly due to the simultaneous reactions of copper(II) and oxygen with both, gold and thiosulfate. In addition to the various background reactions which involve copper(II), thiosulfate, oxygen and various degradation products of thiosulfate, the formation of mixed complex or ion-pairs such as  $\text{Cu}(\text{NH}_3)_3(\text{S}_2\text{O}_3)$  and  $\text{NaS}_2\text{O}_3^-$  have also contributed to the difficulties in quantitative analysis of results to rationalize the thermodynamics and kinetics of gold oxidation [8].

In the alkaline copper-ammonia-thiosulfate system the most common sulfide minerals that exist in refractory gold ores become unstable in the thiosulfate solution in the normal operatory conditions used for gold leaching. The presence of certain sulfide minerals accelerates the thiosulfate degradation and consumes, and retards the dissolution of gold. Leaching experimental results confirm that thiosulfate is much more stable in the leaching of oxide ores compared to its stability in the leaching of sulfide and/or carbonaceous ores [1].

Copper (II) can be maintained at high concentration, being a faster oxidant in thiosulfate medium. It acts as a redox mediator in ammoniacal thiosulfate solution for gold oxidation according to the anodic and cathodic reactions  $\text{Au} \rightarrow \text{Au(I)} + e^-$  and  $\text{Cu(II)} + e^- \rightarrow \text{Cu(I)}$ , respectively, where the Cu(I) produced is oxidized to Cu(II) by oxygen, thus completing the redox cycle [9].

The reaction between Cu(II) and  $\text{S}_2\text{O}_3^{2-}$  ions is one of the biggest concerns in thiosulfate leaching, as it can lead to a lower residual Cu(II) concentration and decrease the rate of the gold leaching [10].

Fig. 1 schematizes the gold leaching process by thiosulfate.

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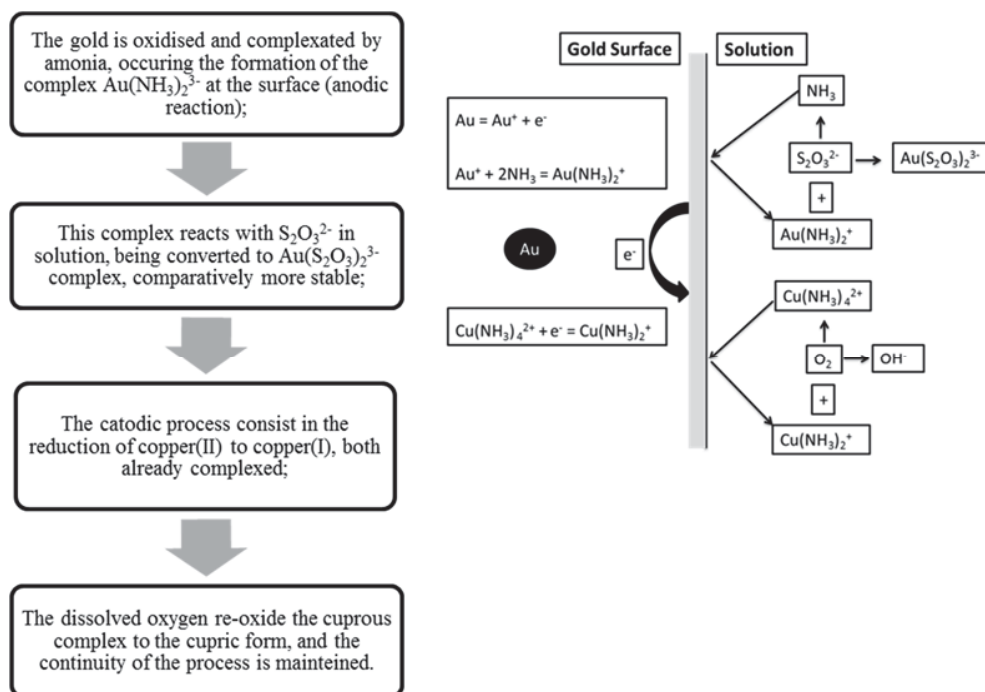
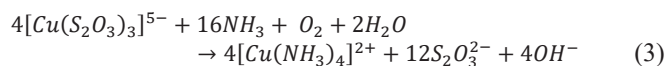
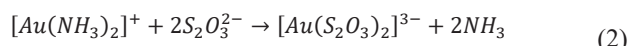
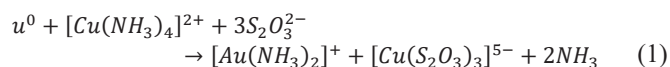
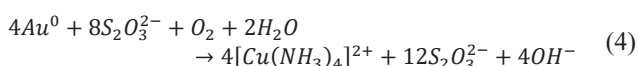


Fig. 1 Basic reaction on thiosulfate leaching

The reactions (1)-(4) describe the leaching behavior of gold in a thiosulfate system are [11]:



Net reaction:



Thiosulfate leaching studies should always consider the main effects that thiosulfate, ammonia and copper have on the leaching process (TABLE 1). Furthermore, the efficiency of thiosulfate leaching also depends on the pH and on the temperature. Thiosulfate leaching must be alkaline, with values between 8.5 and 12, to guarantee the stability of the reagents. Lower pH could lead to the thiosulfate decomposition preventing the gold dissolution process by coating the gold surface and rendering the copper species less effective [7]. Temperatures between 30°C and 40°C achieve higher gold dissolution and minimize ammonia losses and copper (II) reduction [7], although there are some other contradictory reports some supporting the fact that leaching yield increases with temperature [12]-[14] while others support the opposite [15], [16].

Finally, the ammoniacal-thiosulfate leaching presents some other components that could have impact on the leaching performance (TABLE II).

TABLE I  
PREDICTABLE EFFECT OF CHEMICAL REAGENTS ON LEACHING

Component	Predictable effect on leaching
Thiosulfate	Converts copper(II) to copper(I) for further gold leaching. In the absence of oxygen, copper(I) ions cannot return to the copper(II) state, originating the precipitation of copper sulfide from solution [7]. The decomposition of thiosulfate leads to the precipitation of copper sulfides, which is related to the availability of oxygen. Limited solubility results in a low gold dissolution, based on the slow catalytic reaction of copper [17]. Avoids the gold precipitation and the formation of free sulfide ion. Allows for the stabilization of thiosulfate, but it also contributes for a lower Eh and reduces the Cu(II) in solution.
Ammonia	Can be oxidized to sulfate by Cu(II) ion [4].
Copper	Can increase the gold extraction and reduce the thiosulfate consumption. Can buildup adverse effects to the system activity, being recommended the addition of lime [4].

## II. EXPERIMENTAL

### A. Materials

The ore used in this study, constituted by quartz, reduced and oxidized sulfides and iron oxides, was collected at the Castromil deposit, north of Portugal, located within Hercynian granite on the eastern portion of Valongo anticline, characterized by the occurrence of gold/antimony deposits [17]. Pyrite, chalcocopyrite, pyrrotite, goethite, gold, galena and quartz are the main minerals.

TABLE II  
PREDICTABLE EFFECT OF OTHER COMPONENTS ON LEACHING

Component	Predictable effect on leaching
Oxygen	Converts copper(II) to copper(I) for further gold leaching. In the absence of oxygen, copper(I) ions cannot return to the copper(II) state, originating the precipitation of copper sulfide from solution [7]. The decomposition of thiosulfate leads to the precipitation of copper sulfides, which is related to the availability of oxygen. Limited solubility results in a low gold dissolution, based on the slow catalytic reaction of copper [17].
Sulfite	Avoids the gold precipitation and the formation of free sulfide ion. Allows for the stabilization of thiosulfate, but it also contributes for a lower Eh and reduces the Cu(II) in solution. Can be oxidized to sulfate by Cu(II) ion [4].
Sulfate	Can increase the gold extraction and reduce the thiosulfate consumption. Can buildup adverse effects to the system activity, being recommended the addition of lime [4].
Manganese, sulfur, lead and zinc	Manganese dioxide improves both kinetics and gold extraction. Sulfur increases the gold dissolution and reduces the thiosulfate decomposition. Lead and zinc have no effect in the thiosulfate consumption, but the presence of these ions shows beneficial effects in the gold dissolution [7].
Hematite and pyrite	Hematite reduces the gold dissolution due to the coating that hematite forms in the gold surface and can also originate the oxidative decomposition of thiosulfate. Pyrite has a catalytic effect in the decomposition of thiosulfate [7].

#### B. Sample Preparation

This study aims to assess the feasibility of thiosulfate leaching of the Castromil gold ores. Some relevant aspects such as the liberation of gold produced by comminution were already known and available from other studies. Thus, comminution was programmed in order to obtain a particle size distribution suitable for the leaching tests.

A first stage of fragmentation was performed in a jaw crusher, followed by a second stage using a roll crusher. The ore was then grinded by an attrition mill in order to attain the final size reduction. The  $K_{80}$  after the roll crusher was 4.26 mm and after the mill was 0.48 mm (Fig. 2).

#### C. Leaching Solutions Preparation

The thiosulfate leaching tests developed for this study were carried out with the following commercial chemicals: Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), ammonia water ( $\text{NH}_3$ ) (28%) and cupric sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). Thiosulfate and cupric sulfate were dissolved in demineralized water. They were mixed and ammonia was added to obtain the final leaching solution. Finally, the solution and the ore were inserted into the leaching vessel. It is important to note that the referred concentrations for thiosulfate and copper are related to  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . To simplify, they will be respectively referred as thiosulfate and copper concentrations.

Cyanide leaching was carried out with addition of solid sodium cyanide (NaCN) directly to the reaction vessel.

#### D. Methods

Initially a few thiosulfate leaching experiments were carried out, in order to determine the best dosage for the chemicals referred above. Reactions were performed in a 1 L borosilicate cylindrical vessel with hemispherical bottom using an agitator Heidolph RZR 2021. The solid/liquid ratio was 40%, and the leaching was performed at room temperature during 7 hours.

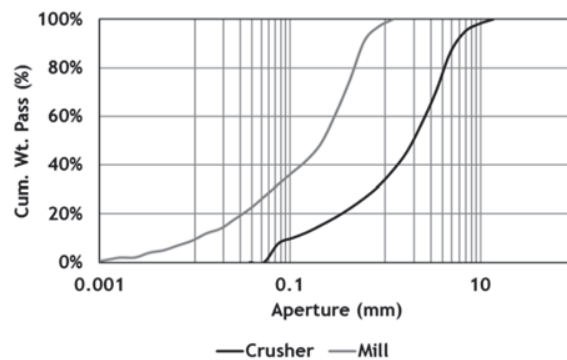


Fig. 2 Comparison between crushed ore and milled ore

Once determined the best reagent dosage, it was possible to study the variations caused on the leaching recovery by increasing the temperature and the solid/liquid ratio. Thus, in the first experiment the single change was the increase of the solid/liquid ratio to 60%. Afterwards, a second new experiment was performed changing the temperature to 50°C.

The test that achieved the best gold dissolution yield was repeated in order to obtain kinetic data. As next, the effect of a pre-treatment of the ore was assessed, by heating for 30 minutes at 500 °C. The best thiosulfate leaching conditions obtained were then applied to the pre-treated ore, for comparison purposes. Again, a kinetic experiment was performed.

Finally, a leaching experiment with cyanide was performed. This test was carried out with a solid/liquid ratio equal to 1. The pulp was added to the reactor and kept in suspension through a mechanical stirrer using a rotation speed that avoided death-areas. After 1 hour of agitation the sodium cyanide was added. The cyanide concentration in the liquid phase was analyzed during the test with a cyanide electrode. Liquid samples were taken at 6h, 12h and 24h.

### III. RESULTS AND DISCUSSION

#### A. Thiosulfate Leaching – Exploratory Tests

In order to achieve the best reagent dosage for the thiosulfate leaching of gold, a factorial plan was applied to the sample obtained from Castromil deposit (Test I – XII). Thiosulfate concentration was varied between 1 and 2 M, ammonia was tested with 0.2 M, 1 M and 2 M concentrations, and copper sulfate was varied between 0 and 0.01 M (Fig. 3).

The increase of thiosulfate concentration decreases the Au dissolution, except when the ammonia concentration was 0.2 M. Thiosulfate concentrations higher than 1 M caused the decrease of the gold dissolution, which probably is due to the difficult adsorption of ammonia onto gold, retarding the formation of  $\text{Au}(\text{NH}_3)_2^+$  complex, that is essentially to react with  $\text{S}_2\text{O}_3^{2-}$  to form  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ . Therefore, it appears that for higher thiosulfate concentrations, the ammonia concentration should be reduced. The increase of ammonia should be accomplished of a decrease in the thiosulfate concentration. For the studied ore, the best results were achieved with 1 M of thiosulfate and 2 M of ammonia.

Copper addition increased gold dissolution, except for very low ammonia concentrations, which could be due to the fastest formation of cupric-amine complex  $\text{Cu}(\text{NH}_3)_4^{2+}$ , that interacts with Au forming a gold-amine complex, ensuring the continuity of the gold dissolution process, and maintaining the concentration ratio of ammonia to thiosulfate within a certain range. With 1M of thiosulfate, the increase of ammonia maximizes the impact of the copper addition, i.e., that becomes higher for increased ammonia concentrations. In the tests carried out with thiosulfate 2 M, the increase of ammonia also improved the effect of the copper addition, while for the ammonia concentrations higher than 1 M this effect was no longer observed. Based on this critical analysis, the best reagents dosage is 1 M of thiosulfate, 2 M of ammonia and 0.01 M of copper sulfate (Test VI).

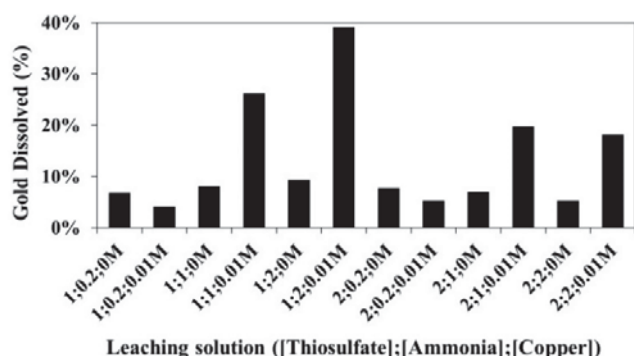


Fig. 3 Leaching performance with different reagent concentrations

After the evaluation of the best dosage of the leaching reagents, two new tests were performed. First, the solid/liquid ratio was changed to 60% (Test XIII). After, a new experiment was performed by increasing the temperature to approximately 50°C (Test XIV). In the first test 36% of gold was dissolved, while with the increase in temperature the quantity of dissolved gold was only 9%. Therefore, it is possible to affirm that the variation of solid/liquid ratio did not affect the yield of the leaching process, while the increase in temperature decreased the gold recovery. This might also have been caused by vaporization losses of the solution that could reduce the efficiency/equilibrium of the leaching solution.

#### B. Effect of Pre-Treatment on Thiosulfate Leaching

It has been reported by various researchers that refractory gold ores should be pre-treated before leaching due to the association between gold and sulfides [18]-[20] and based on the presence of certain sulfide minerals that accelerate the thiosulfate degradation, consuming thiosulfate and retarding the gold dissolution. Excessive thiosulfate consumption and leaching passivation could be caused by the presence of sulfide minerals due to the thiosulfate decomposition [21]. Based on the low gold recoveries achieved in the previous tests, a new experiment was performed after roasting the ore at 500°C during 30 minutes, in order to reduce the sulfur content of the ore. The leaching solution of Test VI was applied to Test XV and Test XVI, both kinetic tests. Test XV was performed with non-pre-treated ore and Test XVI was performed with pre-

treated ore. It is clear that the test performed with pre-treated ore achieved a higher gold recovery (85.5%) in the liquid solution, almost twice the recovery of non-pre-treated ore (44.7%) (Fig. 4). Furthermore, it appears that Test XVI could enhance higher gold dissolution ratio with longer leaching time, while for Test XV a slight decrease of gold recovery was verified after 7 hours. The leaching kinetics was similar for both tests in the early stages of leaching, but after 2 hours, the dissolution ratio decreased in Test XV. It could be due to the higher thiosulfate consumption motivated by the presence of a high quantity of sulfides.

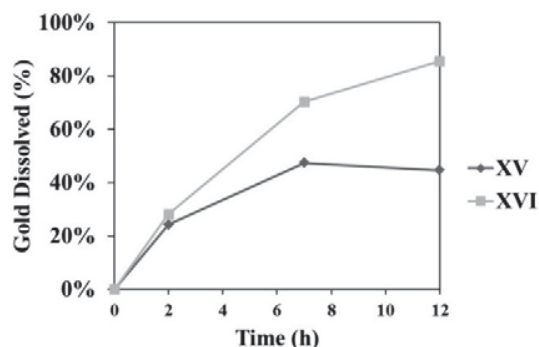


Fig. 4 Comparison between non-pre-treated ore (Test XV) and pre-treated ore (Test XVI) thiosulfate leaching

#### C. Comparison between Thiosulfate and Cyanide Leaching

As mentioned above, cyanide leaching is the most applied and efficient treatment for gold recovery. Therefore, it is mandatory that any other leaching method should be compared to cyanidation. With this purpose a cyanide leaching test was carried out using a residence time of 24 hours (Test XVII). During the test some samples were taken in order to perform a kinetic analysis. A cyanide electrode was used to verify the presence of cyanide on the reactor. After 18 hours, the cyanide concentration was too low, and a new addition of NaCN was necessary to ensure the continuation of the gold dissolution process. After 24 hours, it was possible to dissolve 83.5% of gold from the ore to the leaching solution (Fig. 5).

Now, it is possible to compare the leaching performance of cyanide and thiosulfate (Fig. 6). It is important to note that the cyanidation process was not optimized as the thiosulfate leaching process, but it is expected that the conditions that were applied were very close to the optimal ones. It is evident that for the first 12 hours, Test XVI achieved a better gold dissolution yield (85.5%) than the cyanide leaching (Test XVII) that achieved 70.4%. It can also be concluded that the thiosulfate leaching presents a faster kinetic. For these reasons, it is possible to affirm that thiosulfate leaching could represent an alternative to the cyanidation of Castromil gold ore, but a pre-treatment stage should be performed before the leaching process.

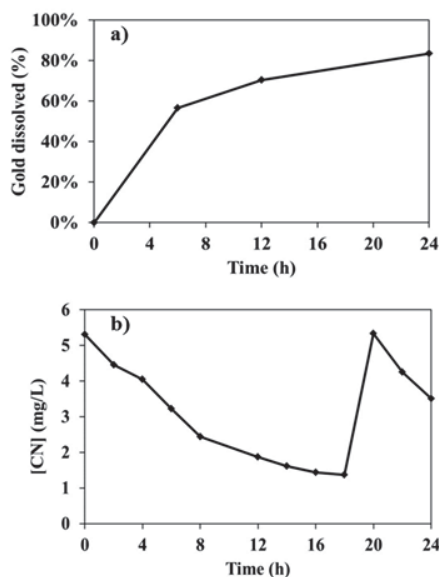


Fig. 5 Cyanide leaching (a) Gold dissolution vs Time; (b) cyanide concentration during the leaching.

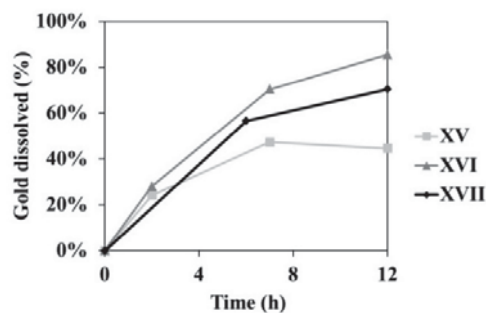


Fig. 6 Comparison between thiosulfate and cyanide leaching

#### IV. CONCLUSIONS

This study aims to contribute for the search of alternative leaching processes that could replace the use of cyanide and simultaneously study the leaching process of the Castromil gold ore deposit. It was experimentally performed a complete analysis of the most relevant operatory conditions that could affect the efficiency of the thiosulfate leaching process. The exploratory thiosulfate leaching tests showed that: a) the increase in thiosulfate concentration decreases the gold dissolution, b) higher ammonia concentrations are needed to improve the gold recovery, and c) the addition of copper increases the gold dissolution yield. After establishing the best composition for the leaching solution, other parameters such as temperature and solid/liquid ration were also changed. The optimal thiosulfate leaching operatory conditions were defined as follows: leaching solution composed by 1M of thiosulfate, 2M of ammonia and 0.01 of copper sulfate, at room temperature using a solid/liquid ratio of 0.4. With these conditions, 44.7% of gold was solubilized, which for an industrial process represents a poor result.

As it is known that a high presence of sulfides contributes to the inefficiency of thiosulfate leaching, a roasting pre-treatment was applied to the ore. The roasting allowed for the oxidation

of some sulfide minerals, rendered the leaching process easier, and decreased the additional thiosulfate consumption caused by the presence of sulfides, this increasing the quantity of leaching solution available for the reaction with gold.

Finally, it was necessary to compare the thiosulfate leaching with cyanidation. It was possible to conclude that cyanide leaching could enhance similar gold dissolution ratio (83.5%) that thiosulfate leaching of pre-treated ore (85.5%), but with longer residence time. In what concerns of thiosulfate leaching without pre-treatment the cyanide process showed clearly a better yield.

As main conclusion, the thiosulfate leaching could be an alternative to cyanidation for the Castromil ore, provided that a pre-treatment stage is performed.

#### ACKNOWLEDGMENT

This work is a part of a research project supported by the Portuguese National Funding Agency for Science, Research and Technology (FCT) within the project "Tools for sustainable gold mining in EU (SUSMIN)", a transnational cooperation project within the Network on the Industrial Handling of Raw Materials for European Industries.

#### REFERENCES

- [1] Hendrix J., Is there a green chemistry approach for leaching gold. *Papers in Sustainable Mining* 2005, 2.
- [2] Bas, A. D., Koc, E., Yazici, Y., Devenci, H., Treatment of copper-rich gold ore by cyanide leaching, ammonia pretreatment and ammoniacal cyanide leaching. *Transactions of Nonferrous Metals Society of China* 2014, 25, (2), 597-607.
- [3] Habashi, F., *Principles of Extractive Metallurgy*. Paris, Vol. 2.
- [4] Keskinen, S. Comparison of cyanide and thiosulfate leaching for gold production (A literature Review). Lappeenranta University of Technology, Lappeenranta, 2013.
- [5] Muir, D. M., Aylmore, M.G., Thiosulphate as an alternative to cyanide for gold processing - issues and impediments. *Mineral. Process. Extr. Metall* 2004, 38, 170-179.
- [6] Lidel, *Handbook of non-ferrous metallurgy - Recovery of metals*. New York, 1945.
- [7] Oraby, E. Gold leaching in thiosulfate solution and its environmental effects compared with cyanide. Curtin University of Technology, Curtin, 2009.
- [8] Senanayake, G., Gold leaching by thiosulphate solutions: a critical review on copper(II) - thiosulphate-oxygen interactions. *Minerals Engineering* 2005, 18, 995 - 1009.
- [9] Ritchie, I. M., Nicol, M.J., Staunton, W.P., Are there realistic alternatives to cyanide as a lixiviant for gold at the present time? *Cyanide: Social and Economic Aspects*; 2001, 427-440.
- [10] Senanayake, G., 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. *Elsevier, Hydrometallurgy* 2012.
- [11] Grosse, A. C., Dicoski, G.W., Shaw, M.J., Haddad, P.R., Leaching and recovery of gold using ammoniacal thiosulfate leach liquors (a review). *Hydrometallurgy* 2002, 69, 1-21.
- [12] Zipperian, D., Raghavan, S., Wilson, J., Gold and silver extraction by ammoniacal thiosulfate leaching from rhyolite ore. *Hydrometallurgy* 1988, 19, 361-375.
- [13] Hemmati, M., Hendrix, J.L., Nelson, J.H., Milosavljevic, E.B., Study of the thiosulfate leaching of gold from carbonaceous ore and the quantitative determination of thiosulfate in the leached solution. In *Extraction Metallurgy '89*, Metallurgy, I. M., Ed. London, UK, 1989; pp 665-678.
- [14] Zhou, G. H., Li, H.R., Rong, Q.X., Gold extraction by ammoniacal thiosulfate leaching from a gold ore containing copper at room temperature. *Multipurpose Utilisation of Mineral Resources* 1999, 5.

- [15] Fujita, T., Yen, W.T., Jeyadevan, B., Takano, S., Toyota, E., Kuzuno, E., In *Gold leaching from electric machine part scraps using thiosulfate or hypochlorite.*, East-Asian Resources Recycling Technology, Kunming, China, 1997; Kunming, China, 1997; pp 36-45.
- [16] Abbruzzese, C., Fornari, P., Massidda, R., Veglio, F., Ubaldini, S., Thiosulfate leaching for gold hydrometallurgy. *Hydrometallurgy* 1995, 39.
- [17] Valance, J. C., M., Bairon, M.C., Shepherd, T. J., Naden, J., Role of aplitic magmatism and C-rich rocks in the Castromil deposit (north Portugal). *European current research on fluid inclusions* 2001.
- [18] Robinson, J. J., The extraction of gold from sulphidic concentrates by roasting and cyanidation. *J.S. African Institute Mineral Metallurgy* 1988, 88, 117-130.
- [19] Nagy, I., Mrkusic, P.G., McCulloch, H.W., *Chemical treatment of refractory gold ores.*; National Institute for Metallurgy: Johannesburg, 1966.
- [20] Hansen, K. R. N., Laschinger, J. E., *The roasting of refractory gold ores and concentrates.*; National Institute for Metallurgy: Johannesburg, 1966.
- [21] Feng, D., van Deventer, J. S. J., Oxidative pre-treatment in thiosulphate leaching of sulphide ores. *International Journal of Mineral Processing* 2010, 94, 28-34.