Research Article

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Effectiveness of Gold Extraction with Thiourea Solution from Gold Rocks in Mount Tumpang Pitu Pasanggaran Banyuwangi

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Abstract: This research aims to determine the effect of adding an oxidizing solution in the gold extraction process using thiourea solution. The oxidizing agent used in thiourea leaching solution is $FeCl_3$. Variations of additional volume of oxidizing solution are 0 mL, 10 mL, 20 mL, 30 mL, and 40 mL. Based on the results obtained, the addition of 30 mL oxidant $FeCl_3$ can get optimal results. The thiourea leaching solution can extract gold as much as 46.7%.

Keywords: Extraction, gold, leaching, thiourea.

INTRODUCTION

Recovery of gold and silver has been predominantly performed by cyanidation since it is a simple and cheap process. Its use for the obtention of minerals started at the beginning of the 20th century, so it is a mature technology. However, cyanidation has several disadvantages, such as slow leaching kinetics and the high toxicity of cyanide [1]. Gold processing carried out by various industrial sectors including small-scale gold mining generally uses mercury with amalgamation techniques. The use of mercury in the process of separating gold ore is because mercury has properties and characteristics that can be used to bind gold by forming amalgam compounds (Au_2Hg_3) [2,3]. This method is commonly used in industry because of its effective and simple isolation process. However, behind the simplicity of the isolation process, this method has great dangers, especially in the field of environment and health, so gold separation techniques are needed with other methods that are safer and more environmentally friendly.

Another method that can be used in gold isolation is the leaching technique with safer solvents [4]. One of the safer solvents used for the gold isolation process is thiourea. The use of this solvent in the gold separation process is being developed. This is related to their ability to form complexes with gold metal. The advantages of this solvent leaching technique include a smaller environmental damage impact compared to commonly used methods and a faster gold dissolution process compared to cyanide solutions [5].

The gold leaching process by this solvent can be assisted by an oxidizing agent. The chemical oxidants used included iron (III), hydrogen peroxide, oxygen, and formamidine disulfide; the latter reagent was formed in situ by the action of both hydrogen peroxide and dissolved oxygen on thiourea [6]. Yanti *et al* (2023) observed that gold extraction from the rock used solution thiourea with $FeCl_3$ as the addition of oxidating agent**.** The study showed that Gold extraction at 0.2 M thiourea reached 58% for 3 hours [2]. Deschenes and Ghaali (1988) have observed the effect of concentration and addition of oxidizing agents on gold extraction results. The base metals concentration in the leach liquor parallels the gold recovery showing that thiourea leaching liberates gold attached to minerals [7].

This study aims to obtain the best leaching solution composition so that the gold extraction process can obtain optimum results. To achieve this goal, other factors such as thiourea concentration, oxidizing agent concentration, rock diameter size, leaching time, pH, temperature, and thiourea volume are kept constant while the volume of the oxidizing agent is varied.

METHODS

Materials and Equipment

Materials used are gold rock samples from the Gunung Tumpang Pitu mine, Pesanggaran-Banyuwangi, HCl (Merck 37%), HNO_3 (Merck 65%), H_2SO_4 (Merck 98%), gold standard solution, Fe standard solution, $CS(NH_2)_2$(Merck), $FeCl_3.6H_2O$ (Merck), distilled water, fine filter paper, aluminum foil.

The equipment used in this study were beakers, pipettes, glass funnels, spatulas, iron mortars and pestles, watch glasses, thermometers, measuring cups, stirrers, spray bottles, Buchner funnels, 100 mesh sieves, stirrers, analytical balances (Ohaus Analytical Plus), magnetic stirrers and electric heaters (Lab. Companion HP-3000), ovens (Memmert), pH meters (Jenway 3505), Atomic Absorption Spectrophotometers (Buck Scientific 205).

Preparation and pre-treatment

Natural rocks are ground and then sieved with a 100 mesh sieve. 100 grams of rocks passing 100 mesh are weighed and then put into a 250 mL beaker glass. Aquades is poured into the beaker until all the rocks are submerged and then stirred. The solution is filtered with a Buchner funnel and then washed again with aquades until the filtrate becomes colorless. The residue obtained is then heated in an oven until dry.

Other rock samples that have been prepared are then taken as much as 30 grams and put into a 400 mL beaker glass. 0.5 M H_2SO_4 solution is added with a solid/liquid volume ratio of 1:2. The mixture is stirred for 2 hours and then filtered with a Buchner funnel. The residue obtained is then washed again with distilled water until neutral. The residue is taken and then dried in an oven.

Analysis of gold (Au) content in samples

Rock samples before and after the pretreatment process were taken as much as 10 grams each and put into a 250 mL beaker glass that had been labeled A and B, then 40 mL of aquaregia

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concentrated HCl and concentrated HNO_3 with a volume solution was added to each beaker glass (made by mixing ratio of 3: 1) and left to stand until all the metals in the rock sample were dissolved. The solution obtained from each beaker glass was separated using filter paper and the filtrate was put into a 250 mL measuring flask then distilled water was added to the boundary mark. The solutions that had been made were then each diluted up to 100 times and their absorbance was measured using AAS.

Rock Leaching with Thiourea Solution

The pretreated rock sample was weighed as much as 10 grams then put into a 250 mL beaker glass and added with the previously prepared leaching solution. The mixture was then stirred for 6 hours at room temperature. After 6 hours, the mixture was separated with filter paper. The filtrate obtained was taken and then diluted up to 100 times. The amount of gold extracted in the solution was then analyzed using AAS.

The effectiveness of the leaching solvent is obtained by comparing the mass of gold in the leaching solution and the mass of gold in the rock when dissolved in aquaregia. The percentage of effectiveness is obtained by the following formula:

$$\% \text{ effectiveness} = \frac{mass\ of\ gold\ in\ leaching\ solution}{mass\ of\ gold\ in\ rock\ sample} x\ 100\%$$

RESULT AND DISCUSSION

Gold Analysis Results in Rock Samples

Pretreatment of rock samples to remove interfering metals such as iron (Fe), zinc (Zn), magnesium (Mg), and other metals is intended so that they do not react and consume thiourea solvents. A comparison of rocks before and after the pretreatment process can be observed in Figure 1. Based on the image, it can be seen that the rocks before pretreatment are darker in color than after going through the pretreatment process. In addition, the rocks that have been pretreated look slightly more shiny than the rocks before the pretreatment process [8].

(a) (b)

Figure 1. Results of washing with 0.5 M H_2SO_4 (a) before pretreatment and (b) after pretreatment

The amount of metals in rock samples before and after the pretreatment process can be known quantitatively using AAS. The sample destruction process is carried out by dissolving the rock sample in aquaregia. The reaction that occurs between gold in the rock and the aquaregia solution is as follows:

$$Au\ (s) + 4HCl\ (aq) + HNO_3\ (aq) \rightarrow HAuCl_4\ (aq) + NO_2\ (g) + 2H_2O\ (l) \quad (1)$$

The rock dissolution process produces brown gas which is NO_2 gas and a clear yellow destruction solution. Quantitatively, the amount of Iron (Fe), Copper (Cu), Zinc (Zn), and Gold (Au) metals before and after the pretreatment process can be seen in Figure 2. The results show that by washing using 0.5 M H_2SO_4, the amount of Iron (Fe) and Zinc (Zn) decreased while the amount of Copper (Cu) and Gold (Au) remained the same. This is related to the standard cell potential of each metal. The standard potential of Cu metal is quite positive so Cu will be more easily reduced and difficult to oxidize.

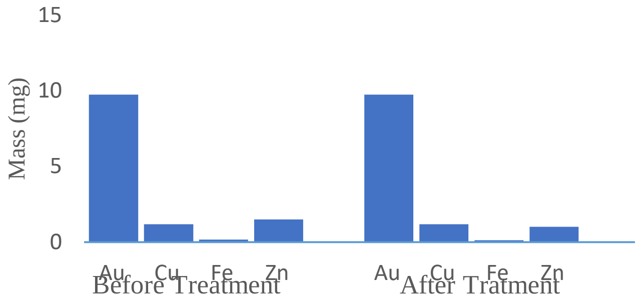

Figure 2. Amount of Cu, Fe, Zn, and Au metals before and after pretreatment in 10 grams of rock sample

Based on the results of the analysis, it can be seen that the average amount of gold in the rock sample is 39 ppm. The mass of gold in the sample is 9.75 mg. The gold content in the rock can be calculated by comparing the amount of gold in the rock and the amount of rock that is destroyed and shows that the gold content in the rock sample is 0.0975%.

Gold extraction in rock samples

Thiourea is an organic compound that is soluble in water and relatively stable. Thiourea is an organic compound that is soluble in water and relatively stable in acidic solutions (pH = 1-2). A more effective acid solution used in the thiourea leaching process is sulfuric acid [9[. Thiourea in an acidic medium forms a single cationic species with gold according to the following reaction (Groenewald, 1976).

$$Au + 2CS(NH_2)_2 \rightarrow Au[SC(NH_2)_2]^{2+} + e \quad (2)$$

The formation of the complex can occur due to the presence of an oxidant that can oxidize thiourea solvent into formamidine disulfide (FDS). FDS has a higher potential value than the reduction potential value of the gold-thiourea complex, which is 0.420 V so this allows the gold metal oxidation process to take place [10]. The formation of FDS requires a strong oxidizer so that the gold extraction process takes place quickly. Groenewald (1977) stated that gold can be extracted quickly in thiourea solution if the potential is above 0.4 V, this condition can be achieved if an oxidizer such as ferric ion or hydrogen peroxide is used. This formamidine disulfide will then react with excess thiourea and gold metal to form a cation complex [11]. The reactions that occur are as follows:

$$2CS(NH_2)_{2(aq)} + 2Fe^{3+}_{(aq)} \rightarrow H_2NCNHSSCNHNH_2(FDS)_{(aq)} + 2Fe^{2+}_{(aq)} + 2H^{+}_{(aq)}$$

$$H_2NCNHSSCNHNH_2\ (FDS)_{(aq)} + 2CS(NH_2)_{2(aq)} + 2Au_{(s)} + 2H^{+}_{(aq)} \rightarrow 2[Au(SC(NH_2)_2)_2]^{+}_{(aq)} \quad (3)$$

So the total reaction results from the two stages above are as follows:

$$Au_{(s)} + 2CS(NH_2)_{2(aq)} + Fe^{3+}_{(aq)} \rightarrow [Au(SC(NH_2)_2)_2]^{+}_{(aq)} + Fe^{2+}_{(aq)} \quad (4)$$

The leaching solution that will be contacted with the rock sample is a mixture of Fe^{3+} oxidizer solution and thiourea solution in various variations. The leaching process is carried out at room temperature to prevent degradation of the gold-thiourea complex and also to maintain the stability of thiourea [12]. The results of the AAS analysis on the filtrate can be observed in Figure 3.

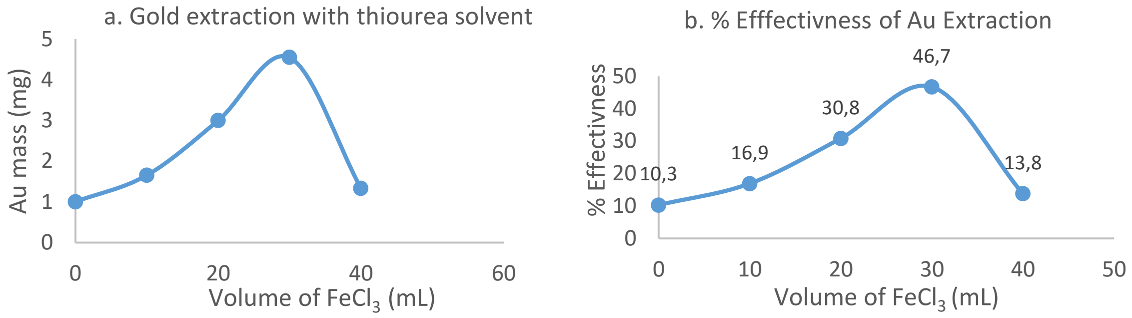

Figure 3. Results of gold extraction using thiourea leaching solution a. Weight of gold extracted b. Effectiveness of gold extraction

The results show that the leaching solution without the addition of Fe^{3+} oxidizer extracts gold in low amounts, namely only 10 ppm. The oxidizer that plays a role in the gold extraction process in the solution is oxygen. The presence of dissolved oxygen in the leaching system can oxidize the extracted gold, but the oxidation process using oxygen is slow, so the complex formation reaction also takes place slowly.

The addition of 10 to 30 mL of oxidizing agent solution in thiourea solution increases the amount of gold extracted. Increasing the amount of oxidizing agent in the leaching solution will increase the amount of formamidine disulfide. The role of formamidine disulfide in the leaching process is as an oxidizing agent that will oxidize gold to gold (I). The addition of 30 mL of Fe^{3+} oxidizing agent in the leaching solution can extract gold to a maximum of 35 ppm. The results show that thiourea solvent can extract gold up to 46.7% at a leaching solvent variation of 10:3.

The addition of 40 mL of Fe^{3+} oxidizer solution in thiourea solution causes the amount of gold extracted to decrease from 35 ppm to 9.5 ppm. Iron(III) as an oxidant causes the fastest initial rate of gold dissolution, but this rate immediately decreases due to the reaction between iron(III) and thiourea [6], so the addition of the oxidant agent $FeCl_3$ will reduce the effectiveness of gold extraction. The formamidine disulfide itself is a very active oxidant and is considered to proceed at a sufficient rate to achieve gold extraction within a practical time scale. Formamidine disulfide oxidizes to produce cyanamide, hydrogen sulfide, and elemental sulfur :

$$H_2NCNHSSCNHNH_2\ (FDS)_{(aq)} \rightarrow CS(NH_2)_{2(aq)} + H_2NCN_{(aq)} + S_{(s)} \quad (5)$$

This condition will cause increased consumption of thiourea and disrupt the reaction due to the formation of sulfur. The solution that can be applied to prevent this is to regulate the pH of the solution and the reduction potential value [13]

CONCLUSION

The volume of $FeCl_3$ oxidizer solution that must be added to the 10 ppm thiourea leaching solution so that the gold extraction process carried out at pH 2 for 6 hours is optimal is 30 mL. The effectiveness of the thiourea leaching solution is 46.7%.

REFERENCES

[1] Z. Gamiño-Arroyo, D. Pareau, A. Buch, F. I. Gomez-Castro, L. E. Sánchez-Cadena, M. Stambouli, J. El Bekri, and M. Avila-Rodriguez. "Design of multistage extraction system for simultaneous separation of silver and gold from thiourea solutions," *Chemical Engineering and Processing - Process Intensification*, vol. 164, no. 2021, p. 108391. https://doi.org/10.1016/j.cep.2021.108391.

[2] I. Yanti, T. Marliana, M. Anugrahwati, W. Wicaksono, and W. Winata, "The comparison of gold extraction methods from the rock using thiourea and thiosulfate," *Open Chemistry*, vol. 21, no. 1, p. 20230102, 2023. https://doi.org/10.1515/chem-2023-0102

[3] M. Hasab, F. Ghobeiti, Rashchi, and Sh Raygan, "Chloride–Hypochlorite leaching and hydrochloric acid washing in multi-stages for extraction of gold from a refractory concentrate," *Hydrometallurgy*, vol. 142, no. 2014, pp. 56-59. https://doi.org/10.1016/j.hydromet.2013.11.015.

[4] Li, Jinshan, and Jan Miller, "A review of gold leaching in acid thiourea solutions," *Mineral Processing and Extractive Metallurgy Review - MINER PROCESS EXTR METALL REV*, vol. 27, pp. 177-214, 2006. https://doi.org/10.1080/08827500500339315.

[5] S. Zheng, W. Yun-yan, and L. Chai. "Research status and prospect of gold leaching in alkaline thiourea solution." *Minerals Engineering*, vol. 19, pp. 1301-1306, 2006. https://doi.org/10.1016/j.mineng.2005.12.009.

[6] T. Groenewald, "The dissolution of gold in acidic solutions of thiourea," *Hydrometallurgy*, vol. 1, no. 3, pp. 277-290, 1976. https://doi.org/10.1016/0304-386X(76)90004-9.

[7] G. Deschênes and E. Ghali. "Leaching of gold from a chalcopyrite concentrate by thiourea," *Hydrometallurgy* 20, no. 2, pp. 179-202, 1988. https://doi.org/10.1016/0304-386X(88)90051-5

[8] P. Lacoste-Bouchet, G. Deschênes, and E. Ghali. "Thiourea leaching of a copper-gold ore using statistical design." *Hydrometallurgy*, vol. 47, no. 2, pp. 189-203, 1998. https://doi.org/10.1016/S0304-386X(97)00043-1.

[9] J. Li, and J. D. Miller. "Reaction kinetics for gold dissolution in acid thiourea solution using formamidine disulfide as oxidant," *Hydrometallurgy*, vol. 63, no. 3, pp.

215-223, 2022. https://doi.org/10.1016/S0304-386X(01)00212-2.

[10] M. J. Nicol, C. A. Flemin, and R. L. Paul, 1987. "The chemistry of the extraction of gold. *In: Stanley, G.C.(Ed), The extractive metallurgy of gold in south africa. South africa institute of mining and metallurgy*, vol. 15, pp. 831-905, 1987.

[11] L. Piga, C. Abbruzzese, P. Fornari, R. Massidda, and S. Ubaldini. "Thiourea leaching of a siliceous au-ag bearing ore using a four-factor composite design." society for mining," *Metallurgy & Exploration*, 1995.

[12] S. Örgül, and Ü Atalay. "Reaction chemistry of gold leaching in thiourea solution for a turkish gold ore," *Hydrometallurgy*, vol. 67, no. 1, pp. 71-77, 2002. https://doi.org/10.1016/S0304-386X(02)00136-6.

[13] N. Gönen, "Leaching of finely disseminated gold ore with cyanide and thiourea solutions," *Hydrometallurgy*, vol. 69, no. 1, pp. 169-176, 2003. https://doi.org/10.1016/S0304-386X(03)00005-7.