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Recovery of Gold with AgNO₃ Pretreatment by Cyanidation at Heap Leaching Cijiwa Gold Ore Processing

Esthi Kusdarini^{1*}, Agus Budianto², and Flaminggo Gingga¹

- 1. Mining Engineering Department, Faculty of Mineral & Ocean Technology, Adhi Tama Surabaya Institute of Technology, Surabaya 60117, Indonesia
 - 2. Chemical Engineering Department, Faculty of Industrial Technology, Adhi Tama Surabaya Institute of Technology, Surabaya 60117, Indonesia

*E-mail: esti@itats.ac.id

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Abstract

This research was undertaken to study the effect of adding silver nitrate (AgNO₃) during leaching of gold ore for Au recovery. Its focus is to obtain the weight of Au in feed and concentrate, the effect of AgNO₃ on Au recovery, the concentration of AgNO₃ that led to optimum recovery, and the weight of bullion and Au content in bullion. This research was conducted using quantitative descriptive method with experimental technique and the research steps include the following: 1) rock and treatment plant preparation, 2) tests with variable AgNO₃ concentrations, 3) analysis feed and concentrate samples using atomic absorption spectroscopy (AAS), 4) measurement of concentrate density, 5) burning of activated carbon to get the bullion, and 6) weighing bullion and Au content. There was increase Au recovery from 12.57% to 36.15%. On addition of 0 to 4 gram of AgNO₃, whereby highest recovery was obtained on the addition of 4 g of AgNO₃ concentration to 150 kg of feed.

Abstrak

Perolehan Emas dari Proses Sianidasi dengan *Pretreatment* AgNO₃ pada *Heap Leaching* Bijih Emas Cijiwa. Penelitian ini dilakukan untuk mempelajari pengaruh penambahan perak nitrat (AgNO₃) selama pelindian bijih emas terhadap perolehan Au. Fokus penelitian adalah untuk mendapatkan berat Au dalam umpan dan konsentrat, pengaruh AgNO₃ pada perolehan Au, konsentrasi AgNO₃ yang menyebabkan perolehan optimal, dan berat bullion dan kandungan Au dalam bullion. Penelitian ini dilakukan dengan menggunakan metode deskriptif kuantitatif dengan teknik eksperimental dan langkah-langkah penelitian meliputi: 1) persiapan instalasi dan pengolahan batuan, 2) menguji dengan variabel konsentrasi AgNO₃, 3) menganalisa sampel umpan dan konsentrat menggunakan spektroskopi serapan atom (SSA), 4) mengukur densitas konsentrat, 5) membakar karbon aktif untuk mendapatkan *bullion*, dan 6) menimbang *bullion* dan kandungan Au. Hasil penelitian menunjukkan bahwa terjadi peningkatan perolehan Au dari 12,57% menjadi 36,15%. Pada penambahan 0 sampai 4 gram AgNO₃, perolehan tertinggi dicapai pada penambahan 4 g AgNO₃ ke dalam 150 kg umpan.

Keywords: AgNO3, ore, gold, recovery, cyanidation

Introduction

Cijiwa gold ore is located in Kertajaya village, Simpenan district, Sukabumi district, West Java, Indonesia. This gold ore comes from gold deposits associated with sulfide minerals, including pyrite (FeS $_2$), chalcopyrite (CuFeS $_2$), sphalerite (ZnS), arsenopyrite (FeAsS), covellite (CuS), and calcalk (Cu $_2$ S). Results of atomic absorption spectroscopy (AAS) analysis of samples taken at locations with

coordinates of 106° 35' 33.1'' E dan 07° 07' 0.84'' S at an elevation of 700-800 masl indicate that the ore contains Au 4.0570 ppm and Ag 3.5000 ppm.

Cyanidation is one process that can be used to extract gold (Au) from its ore and is safer for environmental health than amalgamation [1]. It can be performed via heap leaching, vat leaching, or agitated leaching [2, 3]; however, heap leaching is mostly adopted by local people because of its simple design, low operating costs,

and small investment [4]. Leaching can be done with cyanide solution or microorganisms (bioleaching) [5]. The Au recovery during cyanidation can be increased by optimizing operating conditions [6], increasing the amount of dissolved oxygen in the concentrate, and reducing mineral impurities. Oxygen in the concentrate can be increased by adding hydrogen peroxide (H_2O_2) [7]. The Au content of low ore and the presence of mineral impurities hinder the gold solubility, resulting in the need of more cyanide solution for processing. In gold deposits containing pyrite and arsenopyrite, the gold tends to be chemically bound to arsenic in pyrite and arsenopyrite, which would lead to a small Au recovery. This condition indicates that gold atoms replace arsenic or iron atoms in sulfide lattice [8].

Generally, in cyanidation, impurities of metallic minerals would dissolve in the cyanide solution, whereas quartz impurity is insoluble. Several studies have been conducted to remove mineral impurities from gold ores prior to processing using cyanidation methods; this would prevent the impurities from interfering with the dissolution of gold ions in the cyanide solution. There are different treatment methods for reducing different mineral impurities. For example, gold ore containing high manganese (Mn) can be pretreated by adding FeS₂ and H₂SO₄ during leaching to reduce Mn [9], while arsenic impurities can be reduced by adding Fe₃O₄ @ SiO₂ @ TiO₂ nanosorbent during leaching [10].

Research has shown that mineral impurities may interfere with the binding of Au with the cyanide solution [9,10]. If a gold ore contains sulfide minerals, Pb salts can be added, such as Pb (NO₃)₂ and Pb (CH₃COOH)₂; they would help oxidize the metals contained in rocks, and can increase the degree of liberation and the contact of granules with NaCN solution. In addition, Pb²⁺ ions can precipitate sulfide ions from mineral impurities. When added during leaching, Pb(NO₃)₂ has proven to adequtely increase Au recovery [11]. However, the Pb elements contained in the tailings and wastewater may be harmful to the environment since Pb is a non-biodegradable heavy metal. If Pb sinks into groundwater or is absorbed into plants around the tailings, it would potentially harm the health of humans and other living things that consume them because of its accumulation as it moves along the food cycle [12]. This accumulation can interfere with activity, growth, metabolism, or reproduction [13].

Several research on reducing mineral impurities has been widely conducted, and has led to reducing Mn and arsenic impurities [9, 10]. Cijiwa gold ore contains sulfur (S) as high as 5.18% and an Au content, of only 4.05 ppm; therefore, a research involves pretreatment of sulfur removal is of much interest. In such research, Pb salts were used to crush pyrite, oxidize the metal

contained therein, and precipitate the S²⁻ ions, which resulted in a favorable Au recovery of over 90% [11]. However, the Pb²⁺ ions from PbNO₃ would enlarge the content of minerals in the tailings, such as copper, lead, zinc, and sulfide [14].

This study refined previous research by using silver nitrate (AgNO₃) salt as oxidizing agents instead of Pb salts. The former can destroy pyrite, expand the contact surface of the ore with cyanide solution, oxidize metals contained in rocks, and precipitate sulfur ions to avoid the formation of thiocyanate. Moreover, Ag⁺ ions that may be included inwaste are non-toxic and do not endanger human health, and the salt oxidizing properties of Ag are stronger than those of Pb salts. The addition of AgNO₃ in the leaching process improved Au recovery.

Methods and Methods

Materials and Methods. The materials used are Cijiwa rocks at coordinates 106° 35' 33.1" E dan 07° 07' 0.84" S with elevation of 700-800 masl, technical NaCN (PT Insoclay Acidatama Indonesia, tohor lime (CaO), AgNO₃ pa (Merck), pH meter, water, activated carbon from coconut shell (Kyodo Yushi), HCl pa 37% (Merck), and HNO₃ pa (Merck), while the tools used are crusher, hammer, scale, pumps, sprinklers, buckets, gauze, stirrers, PVCpipes, waterproof tarps of high density polyethylene material, analytical balance, and picnometer.

Comminution. Rocks as much as 750 kg were smoothed with a jaw crusher to a size of about 0.5 cm. This study consists of five experiments, so the rocks were split into five parts, each weighing 150 kg, and the Au content in rocks was analyzed using AAS analysis. The comminution process is to loosen Au from the mineral impurities.

Leaching. The experiment was conducted five times with AgNO₃ concentrations of 0, 1, 2, 3, and 4 grams. Rocks containing gold were destroyed to a size of about 0.5 cm. Leaching at each experiment was done by mixing 150 kg of gold rocks/feed, AgNO₃, 400 grams of NaCN, 50 grams of chalk (CaO), and 70 liters of water into a heap leaching treatment tub, which had a waterproof material of high density polyethylene as its base. The bottom of the tub is sloped 3°-6° to facilitate the flow of the circulating concentrate.

The chalk was dissolved in water before it was introduced into the treatment basin. The pH of the Aurich solution was maintained around 10–11 to optimize Au recovery. After chalking, AgNO₃ was added to destroy sulfide compounds such as pyrite, chalcopyrite, and other impurities and oxidize the metals contained therein. Essentially, Au is expected to oxidize into Au⁺

ion and bind with CN ions. A solution of NaCN was then sprayed into the treatment basin using a sprinkler. The leaching solution prior to passing the activated carbon was a rich solution (concentrate).

During leaching, the metallic minerals would dissolve in the NaCN solution. The dissolution reaction of Au is shown in equation (1) [15], while those of mineral impurities are shown in (2), (3), and (4) [16].

4 Au
$$_{(s)}$$
 + 8 NaCN $_{(s)}$ + O_{2 $_{(g)}$} + 2 H₂O $_{(l)}$ \longrightarrow 4 NaAu(CN)_{2 $_{(aq)}$} + 4 NaOH $_{(aq)}$ (1)

$$\begin{array}{c} Cu_2S_{(s)} + 6CN^{-}_{(aq)} \\ 2[Cu(CN)_3]^{2^{-}}_{(aq)} + S^{2^{-}}_{(aq)} \end{array} \tag{2}$$

$$ZnS_{(s)} + 4CN^{-}_{(aq)}$$
 2[$Zn(CN)_4$]²⁻ (aq) + $S^{2-}_{(aq)}$ (3)

FeS
$$_{(s)} + 6CN^{-}_{(aq)} + 2O_{2(g)}$$
 [Fe(CN)₆]⁴⁻ $_{(aq)} + [SO_4]^{2-}_{(aq)}$ (4)

The S^2 ions formed in equations (2) and (3) would react with the oxygen shown in (5). In addition, sulfide ions can also react with cyanide ions and oxygen to form thiocyanates, as shown in equation (6).

$$2 S^{2-}_{(aq)} + 2 O_{2(g)} + H_2O_{(I)}$$

$$[S_2O_3]^{2-}_{(aq)} + 2 OH_{(aq)}$$
(5)

$$S^{2^{-}}_{(aq)} + CN^{-}_{(aq)} + 0,5 O_{2(g)} + H_{2}O_{(l)} \longrightarrow CNS^{-}_{(aq)} + 2 OH^{-}_{(aq)}$$
 (6)

Heap Leaching Processing. After leaching for about 30 minutes, the rich solution was passed through activated carbon in a column (Carbon in Column / CIC), and the process of circulation lasted for 24 hours for each test. The image of the concentrated circulation is shown in Figure 1.

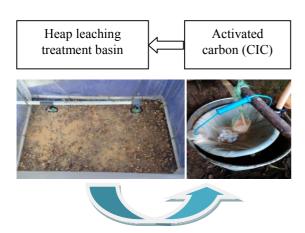


Figure 1. Concentrate Circulation

Atomic absorption spectroscopy analysis. From the AAS, the ppm feed (feed) and concentrate for each test was obtained. The AAS test is conducted at LIPI Geotek laboratory, Bandung.

Activated carbon burning. The activated carbon containing gold metal is burned to obtain the bullion, which is a mixture of gold, silver, and other metals.

Recovery. In cyanidation, the law of conservation of the weight of the metal is applied. The weight of the input metal must be equal to the weight of the output metal plus the weight of the accumulated metal. Au recovery is obtained from equation (7).

$$Au \ Recovery = \frac{Au \ weight \ in \ concentrate}{Au \ weight \ in \ feed} \ x \ 100\% \tag{7}$$

Results and Discussion

Au in Feed and Concentrate. The Au concentrations in the feed and concentrate are obtained from a calibration curve. The curve was made in the 0.2000-2.0000 ppm and the 0.0034-0.0522 absorbance response with equations Abs = 0.026984Conc -0.0020197 and $R^2 = 0.9995$. The result of AAS analysis of rock samples and concentrate per test with the weight of processed gold ore of 150 kg each is presented in Table 1.

To calculate the weight of Au contained in the concentrate, the concentrate density must be calculated first as presented in Table 2. The concentrate density was measured using pycnometer.

Based on Table 1 and Table 2, for feeds weighing 150 kg and concentrate of 70 liters per test, Au weight contained in the feed and concentrate were obtained as presented in Table 3.

Table 1. Au Content in Feed and Concentrates

Test -	Au Content (ppm)	
	Feed	Concentrate
1	3.3259	0.9055
2	5.5460	2.5703
3	4.1504	2.7699
4	5.5135	4,1691
5	4.5980	3.6693

Table 2. The Concentrate Density

Test	Concentrate Density (g/mL)
1	0.9894
2	0.9887
3	0.9857
4	0.9738
5	0.9705

Au Recovery. Based on equation (7), Table 1, and Table 3, the Au recovery obtained is presented in Table 4.

AgNO₃ Effect on Au Recovery. The effect of AgNO₃ concentration on Au recovery is presented in Figure 2.

Figure 2 shows how addition of AgNO₃ to 150 kg of feed affects Au recovery. Recovery increased with addition of AgNO₃, and was highest at the addition of 4 g of AgNO₃. Besides Au, Ag is very present in gold ore; therefore, adding AgNO₃ during leaching would increase the amount of Au⁺ ions in the concentrate. Furthermore, Ag⁺ (from ore pretreatment and AgNO₃) would react with S²⁻ ion (from impurities mineral) to form Ag₂S precipitate [20], thereby minimizing the possibility of equations (5) and (6). This would increase the amount of Au⁺ ion which binds to CN⁻ ion, especially since S²⁻ ion would react with oxygen and CN⁻ ion to form [S₂O₃]²⁻ and CNS⁻ ion as in (5) and (6), respectively. If the reactions depicted by (5) and (6) occur, the oxygen supply in equation (1) would reduce. In cleaning and leaching processes, liquid oxygen,

Table 3. Au Weight in the Feed and Concentrate

Test	Au Weight in	Au Weight in
rest	Feed (g)	Concentrate (g)
1	0.4989	0.0627
2	0.8319	0.1779
3	0.6226	0.1911
4	0.8270	0.2842
5	0.6897	0.2493

Table 4. Au Recovery

T	AgNO ₃ Addi-	Au Recovery
est	tion(g)	(%)
1	0	12.57
2	1	21.38
3	2	30.70
4	3	34.37
5	4	36.15

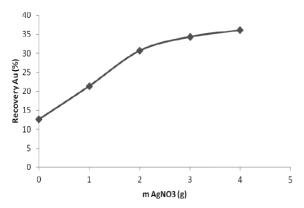


Figure 2. Effect of AgNO₃ Concentration on Au Recovery

cyanide, and water are needed. Oxygen was mainly introduced through a sprinkler. It was also obtained from the air above the leaching basin and the air contained in concentrate, which was continuously circulated for 24 hours. Cyanide ion bonded with Au to form a complex ion Au (CN)²⁻. The reaction that occurs during leaching is shown in equation (8) [17, 18].

$$4 \text{ Au}_{(s)} + 8 \text{ CN}^{-}_{(aq)} + O_{2(g)} + 2 \text{ H}_{2}O_{(l)}$$
 → $4 \text{ Au}(\text{CN})_{2(aq)}^{-} + 4 \text{ OH}^{-}_{(aq)}$ (8)

Although the Au recovery obtained in this study is still below 50%, there is a 23.57% increase in recovery due to pretreatment. Pretreatment was done by adding AgNO₃ to the concentrate so that Au recovery increased from 12.57% to 36.14%. The improvement in Au recovery in this study is higher than those of Qiu and Wei Li, where pretreatment improved recovery by 8.34% for Qiu and 3.45% for Wei [6, 16]. Qiu et al were able to increase the leaching of Au from 85% (without pretreatment) to 93.34% (with pretreatment) [6], while Wei et al increased Au recovery from 85.44% (without pretreatment) to 88.89% (with pretreatment) [19].

In this research, the Au recovery is still below 50% because the grain size of ore (ca. 0.5 cm) is too fine for heap leaching. Grain size that is too fine can disrupt percolation of concentrate in piercing the collision of ore granules during circulation. A good grain size for heap leaching is about 1–2.5 cm, while for sizes below 1 cm, vat leaching processing method is best employed [1].

In this study, Au recovery can be increased by roasting pretreatment to reduce sulfide minerals in order to achieve an Au recovery of 60–80% [15]. This study shows that there is a good potential for AgNO₃ to improve Au recovery. A better recovery of above 50% can also be obtained by changing the size of the ore to about 1-2.5 cm to improve percolation of concentrate.

Conclusion

For five tests, Au concentrations contained in the feed (ore) were 3.3259 ppm, 5.5460 ppm, 4.1504 ppm, 5.5135 ppm, and 4.5980 ppm. Similarly, those in the concentrate were 0.9055 ppm, 2.5703 ppm, 2.7699 ppm, 4.1691 ppm, and 3.6693 ppm. It was found that AgNO₃ can increase Au recovery from 12.57% to 36.15%, and the optimal concentration of AgNO₃ to increase Au recovery was 4 g per 150 kg ore (feed).

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