

Cyanidation of Oxidized Gold Ore by Nitrite

Revi Timora Salajar¹, Maryono²

¹(Widyaiswara of Center for The Development of Human Resources for Geology, Minerals and Coal - Ministry of Energy and Mineral Resources – Republic of Indonesia)

²(Researcher of Research and Development Center of Mineral and Coal Technology - Ministry of Energy and Mineral Resources – Republic of Indonesia)

ABSTRACT: The low yield of gold in the direct cyanidation process of sulfide refractory gold ore has led to various attempts to modify the cyanidation process directly to increase its gold yield. One of them is by conducting a pre-processed of sulfide refractory gold ore with the use of oxidative materials before the cyanidation process. The effect of natrium nitrite as an oxidative material on pre-processed sulfide refractory gold ore has been investigated. The important variables in the test are the concentration of natrium nitrite, percentage of solid, and duration of pre-cyanidation process. The concentration of natrium nitrite has a significant effect on the level of gold gain. Optimum gold yield was achieved at 1.40 M natrium nitrite concentration and percentage of solid is 20%. This gold recovery is 99.47% with duration time of pre-cyanidation process is 6 hours. Meanwhile, the optimum silver recovery was achieved at 1.40 M natrium nitrite concentration and percentage of solid is 20% with duration time of pre-cyanidation process is 12 hours. This silver recovery is 18.40%.

The results of this study provide the possibility that direct cyanidation of sulfide refractory gold ores with the use of pre-treated oxidative materials allows it to remain competitive in commercial applications.

KEYWORDS: refractory gold ore, leaching, cyanide, natrium nitrite.

Date of Submission: 20-09-2021

Date of acceptance: 05-10-2021

I. INTRODUCTION

The process of extracting gold from ores by cyanidation process was first applied by MacArthur and Forrest in 1887 [1]. Until now, the cyanidation process is still used to extract gold from its ore due to the solubility level of cyanide compounds in dissolving gold and silver is the highest among other gold compounds (Table 1)[2].

Table 1. Stability constant of gold compound

Complex	Gold(I)		Gold(III)	
	β_2		Complex	β_4
$\text{Au}(\text{CN})_2^-$	$2 \times 10^{38}\ddagger$		$\text{Au}(\text{CN})_4^-$	$\sim 10^{26}$
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	5×10^{28}		AuI_4^-	5×10^{47}
$\text{Au}(\text{CS}(\text{NH}_2)_2)_2^-$	$2 \times 10^{23}\ddagger$		$\text{Au}(\text{SCN})_4^-$	10^{42}
AuI_2	4×10^{19}		AuBr_4^-	10^{32}
$\text{Au}(\text{SCN})_2^-$	$1,3 \times 10^{17}$		AuCl_4^-	10^{25}
AuBr_2^-	10^{12}			
AuCl_2^-	10^9			

*Values of stability constants used in this chapter are taken from the tabulations of Sillen (Sillen and Martell, 1964) unless otherwise indicated.

‡Hancock and Finkelstein (1970).

†Calculated from standard reduction-potential data reported by Groenewald (1975).

The more complex gold carrier mineral, the higher consumption of cyanide reagent. Therefore, we should propose a cyanidation process modification of various types of gold ore to remain competitiveness. Various studies have been carried out in the reaction of formation of complex compounds of gold cyanide (AuCN^{2-}) and inhibitors of the carrier mineral.

In the direct cyanidation process of refractory gold ores, the dissolution reaction of gold by cyanide compounds (CN^-), is inhibited by the presence of sulfide minerals. The most commonly associated sulfide

minerals in sulfide refractory gold ores are the mineral Pyrite (FeS_2), Chalcopyrite (CuFeS_2), Sphalerite (ZnS), and Galena (PbS)[3].

The sulfide minerals of refractory gold ores, act as a protective layer against gold particles. This makes the gold recovery in direct cyanidation process to be low. In addition, the reaction occurs for the formation of base metal cyanide complexes as shown for the mineral pyrite by forming Ferrocyanide compounds ($\text{Fe}(\text{CN})_6^{4-}$) Fig. 1 [2].

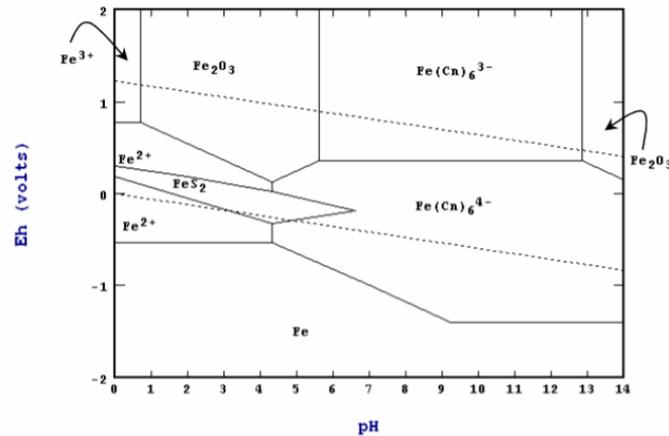


Fig.1. Eh-pH Diagram of Fe-S-CN-H₂O[2]

The formation of base metal cyanide complex compounds will cause a decrease in the effectiveness of the cyanide-gold reaction. Therefore, to increase gold recovery in the cyanidation process of sulfide refractory gold ores, it is necessary to pre-treat the sulfide mineral oxidation process, so that the sulfide mineral protective layer can be removed. Various methods of sulfide mineral oxidation processes have been widely applied, such as through the pyrometallurgical pathway by roasting process, chemical oxidation under pressure, or biological oxidation (bacterial leaching). Furthermore, the development of pre-processing of sulfide refractory gold ores through hydrometallurgical pathways with oxidative materials under atmospheric conditions, such as using peroxides as oxidative materials. Sodium nitrite is used to oxidize the sulfur component in sulfide minerals to sulfate ions which are dissolved in the leach solution.

II. RESEARCH METODOLOGY

The refractory gold ore, originating from Mandailing Natal District, North Sumatera, Republic of Indonesia. This ore has been processed through a grinding and sifting process until it reaches a size of 50% - 200#. Grinding is done by dry method, while sampling is done by Cone and Quartering Method.

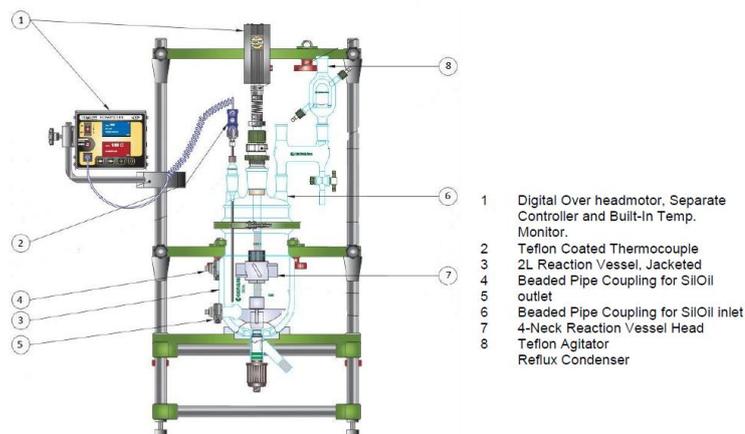


Fig. 2. Cyanidation glass reactor

The experiment was carried out using a cyanidation glass reactor as shown in Fig. 2[4], with as much as 2 liters of distilled water as solvent at a rotation speed 90 rpm, room temperature, for 20 hours. The purpose of this experiment was to observe the effect of increasing the concentration of sodium nitrite (NaNO_2) on the recovery of gold in refractory ore. In the pre-cyanidation process, the variables used were the percentage of solid, the concentration of NaNO_2 , and the pre-processing time. Meanwhile, the cyanidation process, variables used

were the percentage of solid and the concentration of NaNO_2 as shown in Table 2. Particles size analysis of the ore ground sample showed that the particle size distribution of smaller than -200# was more than 50%.

Table 2. Experimental variables

Parameter	Quantity
Sample size	50%-200#
Process Temperature	Room temperature
Cyanide strength	1,20%
NaNO_2 concentration	1,40 – 1,80 M
Agitation rate	90 rpm
Percentage of solid	20 – 40%
Pre-cyanidation time	6 - 12 hours
Cyanidation time	20 hours
pH	12 – 13

III. RESULTS AND DISCUSSION

Characterization of the ore sample was performed by the analytical method of X-ray diffraction (XRD) to determine its mineral composition, as shown in Table 3 and Fig. 3.

Table 3. Mineral Composition of the leaching test sample (by XRD Method)

Mineral	%
Quartz (SiO_2)	66,6
Pyrite (FeS_2)	11,8
Arsenopyrite (FeAsS)	1,9
Sphalerite (Fe,ZnS)	4,4
Chalcopyrite (CuFeS_2)	1,8
Mooihoekite ($\text{Cu}_9\text{Fe}_9\text{S}_{16}$)	3,1
Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)	10,3

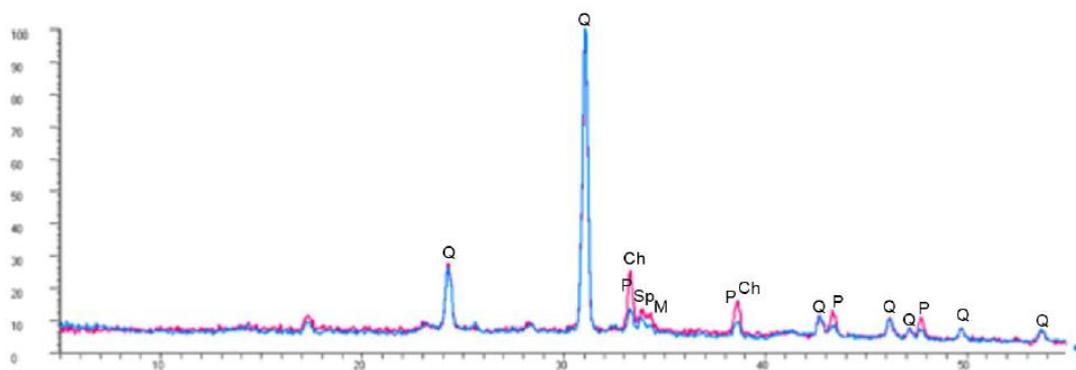


Fig. 3. X-ray Diffractogram, with the mineralogical species found in the leaching test samples

X-ray Fluorescence (XRF) was used to analyze the concentration of the major element. Meanwhile, gold and silver were analyzed by fire assay and atomic absorption spectroscopy (AAS). The result of element analysis is presented in Table 4.

Table 4. Major element composition of the leaching test sample (by XRF Method)

Element	Concentration (ppm)
<i>Au</i>	9,35
<i>Ag</i>	148
<i>Cu</i>	1,53
<i>Pb</i>	1,79
<i>Fe</i>	12,57

Zn	6,60
As	0,83
S	12,70
Si	12,68

The ore used in this experiment is ore with a particle size fraction of 50%-200#. Pre-cyanidation is done by adding sodium nitrite at two concentration variables, 1.4 M and 1.8 M. The use of NaNO_2 is to dissolve sulfide so that it does not inhibit the cyanidation process because Sulphur in the ore, will bind CN^- to form SCN^- .

Effect of NaNO_2 addition and solid percentage in six hours pre-cyanidation of gold

The experimental conditions were 20-40% solids, NaNO_2 concentration 1.4 – 1.8 M, NaCN strength 1.20%, pre cyanidation operating time was 6 hours, while the cyanidation process lasted for 20 hours. The following is the result of the gold-silver recovery, Figure 4.



Fig. 4. Gold and Silver recovery at 1,20% - CN constant (six hours pre-cyanidation)

Effect of NaNO_2 addition and solid percentage in twelve hours pre-cyanidation of gold

The experimental conditions were 20-40% solids, NaNO_2 concentration 1.4 – 1.8 M, NaCN strength 1.20%, pre cyanidation operating time was 12 hours, while the cyanidation process lasted for 20 hours. The following is the result of the gold-silver recovery, Figure 5.

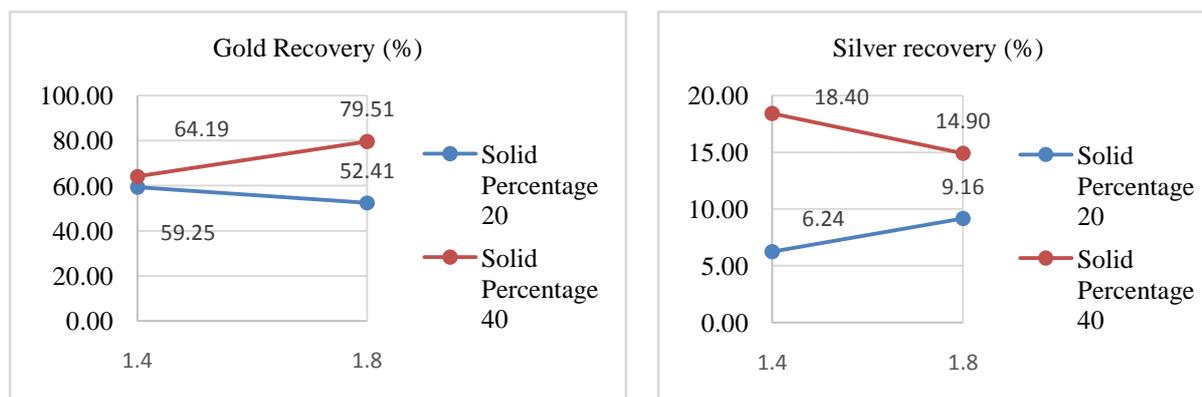


Fig. 5. Gold and Silver recovery at 1,20% - CN constant (twelve hours pre-cyanidation)

NaNO_2 in the cyanidation process of sulfide refractory gold ore is used to increase dissolved gold. It will dissolve into aurocyanide anion, Figure 6.

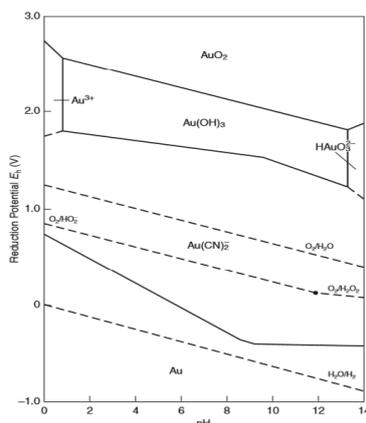
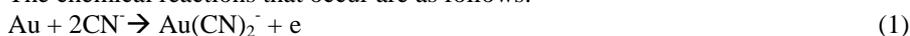
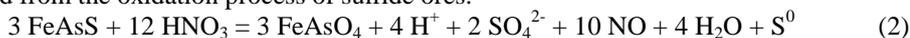


Fig. 6. Potential-pH Diagram of Au-H₂O-CN⁻ at 25⁰ C

The chemical reactions that occur are as follows:

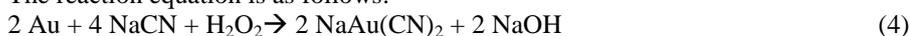


Gold can be dissolved into aurocyanide anions from refractory sulfide gold ores. Sulphur must be decomposed first. In reactions (2) and (3), NO₃ reacts to produce sulfuric acid and sulfur. Furthermore NO_(g) is produced from the oxidation process of sulfide ores.



In the cyanidation process, gold ore requires dissolved oxygen to achieve the effectiveness of the reaction to form gold cyanide compounds, Au(CN)₂⁻ and Au(CN)₄⁻. Therefore, oxygen aeration during the cyanidation process of gold ore is necessary. It suggested that the dissolution of gold-silver in cyanide and H₂O₂ media without oxygen is slow and only plays small role[5].

The reaction equation is as follows:



The oxidation reaction of sulfide minerals by NaNO₂ makes gold particles free from the protective layer of sulfide minerals. Thus, it is expected that the dissolution reaction of gold particles by cyanide ions to form Au(CN)₂⁻ compounds can take place effectively. Excess NaNO₂ results in an oxidation reaction of cyanide ion (CN⁻) to cyanate (CNO⁻) as shown by the reaction equation (5):



Based on the aspect of thermodynamics (Eh-pH diagram) as can be seen in Figure 7[6], the cyanate compound (CNO⁻) is very stable. The formation of cyanate compounds causes a decrease in the concentration of cyanide ions, resulting in a decrease in the effectiveness of the cyanidation process.

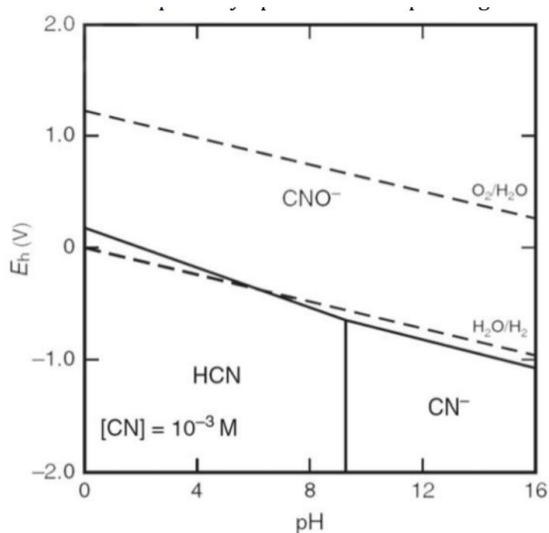


Fig. 7. Eh-pH diagram of cyanate ion

The following is the relationship between pH and the stability of CN⁻ ionic compounds. If the pH is close to 9, HCN gas will be formed. When pH more than 9.5, HCN gas will not be formed (Figure 8.)[6].

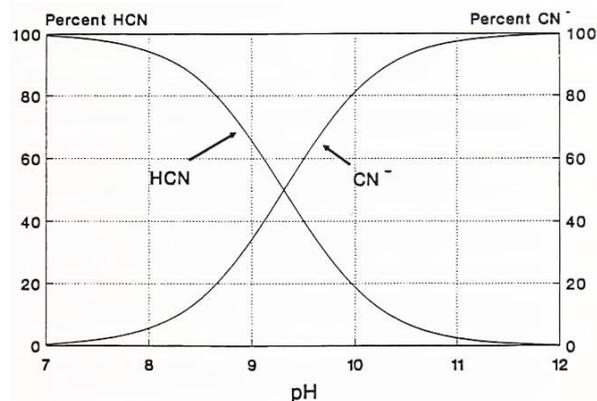


Fig. 8. HCN and CN⁻ – pH diagram

IV. CONCLUSION

The experimental result show that natrium nitrite influences the extraction yield, both for gold and silver. The percentage of solid affects the extraction yield for both gold and silver significantly. Likewise, the duration of the pre-cyanidation time affects the recovery of gold and silver. Therefore, further research is needed to enable optimal extraction of gold and silver to be achieved which is higher than what has been obtained from this study. The research results that have been obtained can be another alternative to be applied in the pre-cyanidation process to increase the recovery of gold and silver from the ore. This has the potential to play a role in the future as an option in the refractory gold ore processing

REFERENCES

- [1] F. Habashi, "Extractive metallurgy of activated minerals," *Miner. Eng.*, vol. 13, no. 10–11, p. 1191, 2000.
- [2] J. O. Mardsen and C. I. House, *The Chemistry of Gold Extraction*, Second Edi. Society for Mining, Metallurgy, and Exploration, Inc., 2009.
- [3] T. T. Chen, L. J. Cabri, and J. E. Dutrizac, "Charactrsizing Gold in Refractory Sulfide Gold Ores and Residues," *JOM*, pp. 20–22, 2002.
- [4] S. Suratman, "Gold recovery of refractory sulfide concentrates using direct cyanide leaching with nitrite as an oxidant," *Indones. Min. J.*, vol. 19, no. 3, pp. 153–165, 2017.
- [5] F. Habbashi and R. Emas, *Handbook of Extractive Metallurgy Edited by Fatbi Habashi Volume III : Precious metals, refractory metals, scattered metals, radioactive metals, rare earth metals*, vol. III. 1997.
- [6] E. Y. Yazıcı, H. Deveci, E. Yılmaz, F. Ahlatcı, and O. Celep, "Recovery of Cyanide From Effluents Using Carbon Dioxide," *Mugla J. Sci. Technol.*, vol. 3, no. 2, pp. 171–177, 2017.