

The Pretreatment of Refractory Gold Concentrate by using Mechanochemical Activation and Nitric Acid Oxidation Method

Hyok Sin, Chang-Sok Kim, Ryong-Ju Cho, Gang-Hyok Kim

Faculty of Chemical Engineering, Kim Chaek University of Technology, Yonggwang Street, Kyogu 60,
Pyongyang, Democratic People's Republic of Korea

Abstract- Hydrothermal oxidation pretreatment of refractory gold ores is an effective pretreatment of refractory gold ores, which has been widely used in recent years due to high rate of desulfurization, low environmental pollution and high reaction rate. In this paper, we describe the thermodynamic studies of nitric acid oxidation and the factors affecting gold extraction when pyrite and arsenopyrite-based gold concentrates are pretreated by mechanical activation and nitric acid oxidation. The factors affecting gold extraction are nitric acid concentration, mechanical activation time, and liquid-solid ratio. As a result, the decomposition of pyrite and arsenopyrite in nitric acid medium was proceeded from nitric acid concentration above 1mol/L at room temperature, and at the present of the mechanical activation, the decomposition was proceeded from nitric acid concentration above 0.5mol/L. After pretreatment using mechanical activation and nitric acid oxidation, the cyanidation leaching rate for gold concentrate was over 87%.

Keywords: Refractory; gold concentrate; mechanochemical activation; nitric acid oxidation; cyanide leaching.

I. INTRODUCTION

In recent years, the amount of gold production all over the world increase continuously, the manageable gold ore resources which adopt to cyanidation has been depleted, and then the refractory ore of low grade, thin size, or containing harmful impurities of sulfur, arsenic and copper become the main resources for the gold production. Generally, in the sulfide-rich arsenic-bearing refractory gold ore, the fine gold grains is been poikilitic in the pyrite and arsenopyrite, or is impregnated so, though the ore is ultrafinely grinded, gold particles is not exposed, therefore gold leaching rate is very low[1-3].

Also, during the leaching process, because arsenide is act with cyanide and consume the leaching agent and oxygen, so it prevents the gold leaching. To extract the gold from the refractory gold ore effectively, the oxidation pretreatment must be conducted prior to leaching to oxidize the sulfide bearing gold particles and convert their physical and chemical properties[4,5]. The pretreatment of refractory gold ore include the dry pretreatment such as roasting oxidation and the wet one such as

pressure oxidation, bio-oxidation and chemical oxidation [6,7,8].

Roasting is the traditional method commonly used in nonferrous metallurgy and is the most widely used method for treating refractory sulfide ores containing carbon, arsenic and copper. The aim of roasting is to dissolve the sulfide and expose the gold particles to cyanidation, and also to remove the sulfide containing arsenic, antimony, into the volatile oxide and to recover the dust. Materials such as coal are burned out and disappear. After roasting, the gold that existed in the microscopic granules is relatively concentrated and a good kinetic condition of the next step, the cyanidation process, is provided.

The advantages of roasting are the maturity of the process, the reliability of the technology and the good overall recovery. The disadvantage is that even with the recovery of the operating SO₂, As₂O₃, and other crude gases, the remaining minor gas components pollute the environment, the production cost increases due to the complexity of the dedusting devices and the long dedusting process[9, 10]. The pressurized oxidation method has the advantage of having a higher gold leaching rate than the roasting method, being able to treat

concentrates with higher sulfur content, and directly treating the ore. However, it is a highly corrosive medium and has the disadvantage of high equipment investment and complex operation.

The oxidation of sulfide minerals by microorganisms is the sulfide of the donor of electrons, the final acceptor of electrons is oxygen, and the former of electrons from donor to acceptor is considered to be a kind of electrochemical reaction that the microorganism is responsible for. In this case, the main role of microorganisms is to directly oxidize the mineral matrix. In the first phase of the interaction between the sulfide substrate and the bacteria, the microorganisms attach to the substrate and then the chemical change of the substrate itself begins to occur. The microbial oxidation method has the disadvantage of having a long oxidation pretreatment time and a complex process condition, while it has the advantages of having a high degradability, high recovery of gold and silver, high recovery of gold and silver, low capital investment and production cost for sulfides such as pyrite and arsenopyrite.

The chemical oxidation method includes chlorination process and nitric acid oxidation method, and the nitric acid oxidation method has recently studied due to high effectiveness and short processing time[11,12,13]. The representative nitric acid oxidation method were ARSENO method, NITROX method and CAOL method[9,14,15].

ARSENO method can oxidize the pyrite and arsenopyrite completely at 85°C under oxygen atmosphere in 15 minutes. This method is used in industry, but it is difficult to supply oxygen. NITROX method use air instead of oxygen, but produced elemental sulfur cover the surface of gold particle, so leaching rate is low. COAL method was developed recently, and processing temperature is 100°C and processing pressure is 1 atm and dispersion agent is used for moving the produced elemental sulfur from the surface of gold particle to the solution. But it is difficult to find the reasonable dispersion agent and to increase the dispersion efficiency.

Recently, the experience that the mechanochemical activation was applied in the cyanide leaching to increase leaching rate was reported[16,17]. However, due to the various impure substance, cyanide consumption is high. Also, the experience that the ultrasonic wave was applied in the nitric acid oxidation to promote the pretreatment efficiency was reported[19]. The ultrasonic wave can make the high temperature and high pressure instantaneously on the surface of mineral particle, so the reaction rate is accelerate and it is easy to convert the elemental sulfur to sulfate. However, the ultrasonic equipment is very expensive and power consumption is also high.

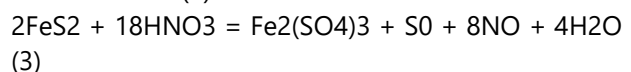
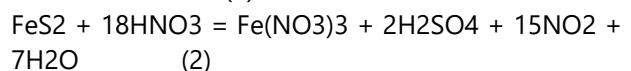
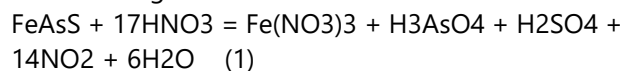
The role of mechanochemical activation is similar to ultrasonic treatment. So we applied the mechanochemical activation in the nitric acid oxidation pretreatment to promote the pretreatment efficiency, to decrease the nitric acid consumption and to reach the gold leaching rate as above 87%.

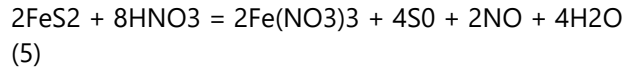
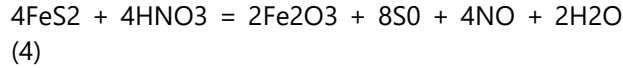
II. THE THERMODYNAMICS OF PYRITE AND ARSENOPYRITE IN THE NITRIC ACID

According to the literature data, ore gold associations with sulphides is considered to be able to approach 90% [20]. To render gold from the crystalline structure of the sulfide and to make it accessible for cyanidation a pretreated operation is necessary.

The thermodynamic evaluation of the pyrite and arsenopyrite behavior under the conditions studied was carried out with the help of "HSC Chemistry 6" software; the chart of the Pourbaix E- pH diagram(Fig. 1, 2), calculations of values of the standard Gibbs energy for the temperature range 25-85°C were shown in Table 1.

Pyrite and arsenopyrite can react with nitric acid in the following reactions:





When oxygen is supplied, forming nitrogen monoxide NO in aqueous solutions is converted into nitric acid according to the overall reaction:

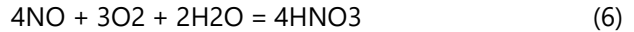


Table 1. Calculations of values of the changed Gibbs energy, kJ.mol for the temperature range 25~85° C for Eq. (1)~(6)

Temperature, °C Equation, ΔG, kJ/mol

Temperature, °C	Equation, ΔG, kJ/mol					
	1	2	3	4	5	6
25	-327.6	-547.7	-1,317.2	-646.8	-274.5	-195.1
35	-317.8	-543.3	-1,328.1	-652.6	-238.6	-185.4
45	-308.4	-538.1	-1,338.9	-658.3	-142.7	-175.7
55	-296.2	-535.6	-1,349.6	-664.1	-103.3	-166.0
65	-287.2	-531.8	-1,360.3	-669.9	-97.0	-156.3
75	-278.6	-526.4	-1,371.0	-675.7	-58.1	-146.7
85	-266.3	-520.4	-1,381.6	-681.4	-17.2	-137.1

On the basis of the results of the thermodynamic calculations of Table 1, it has been established that the process of leaching of sulfide minerals in nitric acid is thermodynamically probable in a wide temperature range from 25 to 85° C.

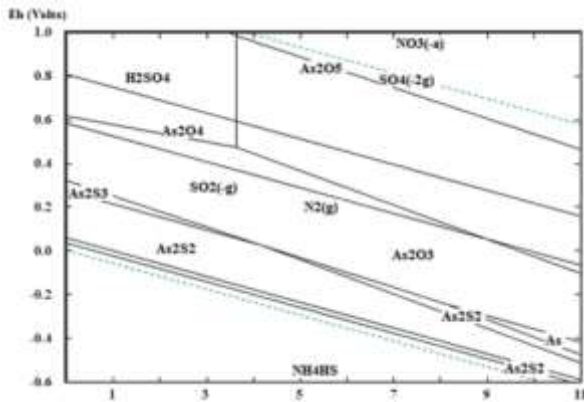


Fig. 1. Equilibrium E-pH diagram for system As-S-N-H₂O

It can be noticed from the analysis of the Pourbaix diagram(Fig. 1), that at an elevated pH and a negative redox potential of the system, arsenic can be in the form of sulphide crystals, as well as in metallic form. With growth of redox potential and acidity of the medium, however, arsenic might be oxidized to higher oxides.

The oxidation of iron(Fig. 2) at low values of the redox potential(up to 0.45 V), formation of S₀ and Fe₂O₃ throughout the considered range is observed. To transfer iron to the trivalent form, a high potential of the system E > 1.1 V is required.

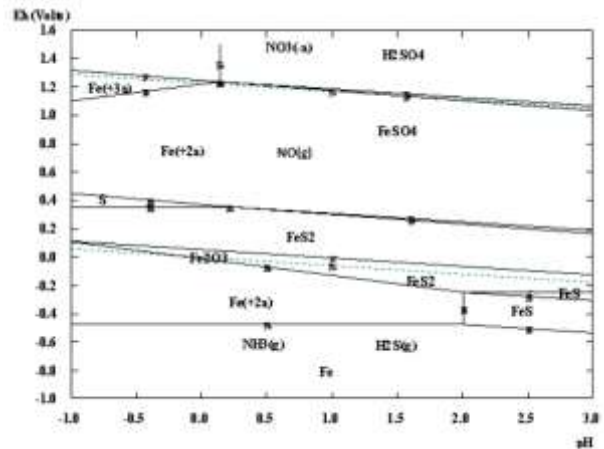


Fig. 2. Equilibrium E-pH diagram for system Fe-S-N-H₂O.

III. EXPERIMENTAL

The chemical composition of sample was shown in Table 2. The XRD pattern and SEM image was shown in Fig. 3 and Fig. 4 respectively.

Table 2. The chemical composition of gold concentrate

Element	Au, g/t	Cu	Fe	Pb	Zn	S	SiO ₂
Content, %	15.5	2.32	28.99	0.77	0.05	33.29	29.89

To research the mineralogical composition, XRD analysis was proceeded.

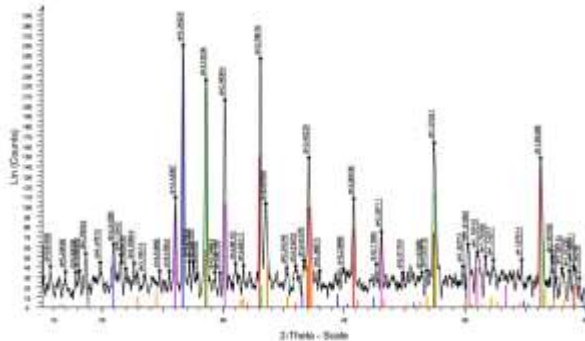


Fig. 3. XRD pattern of gold concentrate.

In the XD-3 type XRD analyzer, the source was CuK α , movement rate was 2°/min, voltages was 30kV and current was 20mA. The result was shown in the Fig 3. As shown in the Fig 3, the main metal minerals in the concentrate are pyrite and arsenopyrite. The gangue mainly contains SiO₂.

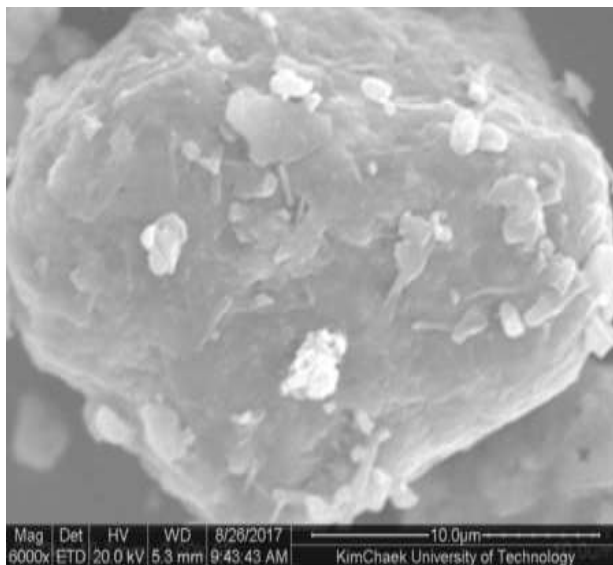


Fig. 4. SEM image of gold concentrate.

From the chemical composition and XRD analysis, the calculated mineralogical composition of gold concentrate was shown in the Table 3.

Table 3 The main mineralogical composition of sample

Minerlogical composition	FeS ₂	CuFeS ₂	ZnS	PbS	SiO ₂
Content, %	57.78	6.67	0.08	0.89	29.98

The gold particles in the concentrate is mainly dispersed in sulfide mineral such as pyrite and chalcopyrite in the fine or ultrafine-sized natural gold phase. The traditional cyanide leaching rate of gold concentrarate was about 30~35%.

To grind the concentrate, we used a continuous ball mill. The inside volumn is 3L and it is rotated by reduction electromotor. The rate of revolution is 150rpm and the grinding media is ceramics ball. The cyanidation of pretreated gold concentrate is proceeded at cyanide concentration 0.2%, pH 10.5 and the leaching time 24h. The gold concentration of leaching solution is measured by using the atomic absorption analyser.

IV. RESULTS AND DISCUSSION

The gold leaching rate at various nitric acid concentration without mechanochemical activation.

- The effect of nitric acid concentration. To confirm the efficiency of mechanochemical activation pretreatment, we pretreated the concentrate at various nitric acid without mechanochemical activation. The decomposition was acutely begun when the nitric acid concentration was more than 1mol/L. At this time, the liquid-solid ratio was 6, sufficient value.

After pretreatment, pulp was filtered and the residue was washed, and then it was leached by cyanide. The gold leaching rate at various nitric acid concentration was shown in Fig. 5.

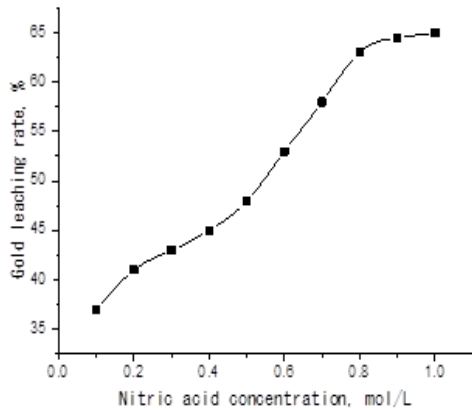


Fig 5. The gold leaching rate at various nitric acid concentration.

(Liquid-solid ratio 6)

As shown in Fig. 5, the gold leaching rate at 1 mol/L of nitric acid concentration is not very high as about 65%, because the produced elemental sulfur during the oxidation process covered the surface of gold particles, so it hindered the diffusion of cyanide and oxygen to the surface of gold particles.

The mechanochemical activation can dissociate the generated elemental sulfur from the gold particle surface and facilitate the diffusion of leaching agent to the surface of gold particle, so it can increase the gold leaching rate.

- The effect of liquid-solid ratio.

To determine the suitable liquid-solid ratio, after the pretreatment at various liquid-solid ratio with 1mol/L of nitric acid concentration, the cyanidation was proceeded.

The liquid-solid ratio was changed from 2 to 7.

At low liquid-solid ratio, we can distinguish the many sulfur clot in the ore pulp, with the growth of liquid-solid ratio, the amount of sulfur clot was decreased. The reason is that the whole amount of nitric acid with the growth liquid-solid ratio was increased so that the sulfur was oxidized to sulfate.

The gold leaching rate at various liquid-solid ratio was shown in Fig 6.

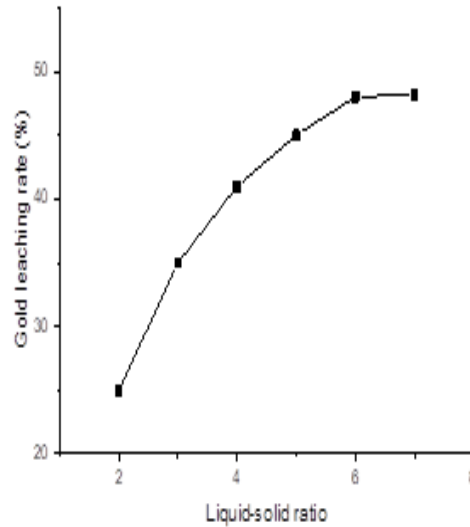


Fig 6. The gold leaching rate at various liquid-solid ratios at pretreatment.

The gold leaching rate was increased with the growth of liquid-solid ratio at pretreatment, however, at the more than liquid-solid ratio 6, the change of the gold leaching rate was not significant. From this experimental result, we can find that the enough liquid-solid ratio can facilitate the diffusion of oxidation agent and the separation of the generated elemental sulfur.

Determination of mechanochemical activation time.

We made 33% of pulp from the concentrate which - 200mesh particle content was 20%, and then put it to be 1L of ball mill and ground it, and measured the particle size at various grinding time. The results were shown Fig. 7.

As shown in the Fig. 7, in 1h of grinding time, - 200mesh particle content was more than 95%, and in the more grinding time, particle size did not big change. Therefore, we found that the reasonable mechanochemical activation time was about 1h.

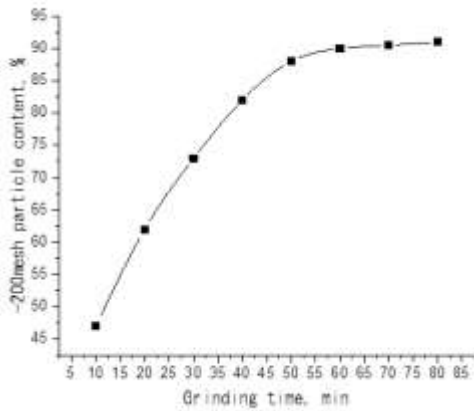


Fig. 7. The particle size change of concentrate at various grinding time.

The gold leaching rate at various nitric acid concentration with mechanochemical activation.

We measured the gold leaching rate at various nitric acid concentration (0.1mol/L~1mol/L) with mechanochemical activation. At this time, from the 0.5mol/L of nitric acid concentration, decomposition reaction was proceeded acutely.

The results of gold leaching rate were shown in Fig. 8.

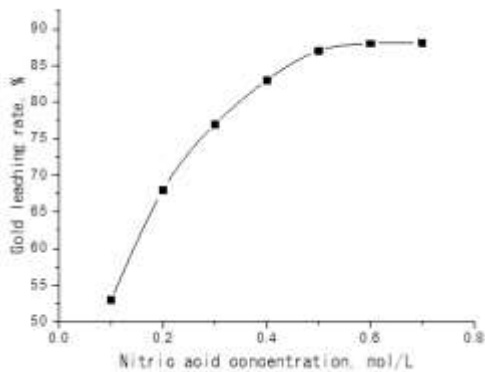


Fig. 8. The gold leaching rate at various nitric acid concentration with mechanochemical activation

As shown in the Fig. 8, the mechanochemical activation increased the efficiency of nitric acid oxidation pretreatment remarkably. Also, the consumption of nitric acid for the pretreatment was decreased significantly.

During the mechanochemical activation, when the grinding ball and mineral grains were crashed each other, the temperature of surface was instantaneously increased to 1000K [16], so that pretreatment oxidation reaction was rapidly facilitated. Due to the friction between the mineral and grinding ball, the generated elemental sulfur can easily separate and gold particles can easily contact leaching agent and oxygen.

V. CONCLUSION

Mechanical activation can significantly enhance the nitric acid oxidation pretreatment effect of refractory gold concentrate and reduce nitric acid consumption. During mechanical activation, the dissolution reaction was intense from 0.5 mol/L nitric acid concentration, which was fully exposed to gold particles by separating elemental sulfur formed on the surface of gold particles by tribological action. At this time, gold leaching rate was more than 87%.

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