

Study of gold leaching from refractory gold ore by new non-cyanide leaching agent

Wan-Fu Huang¹ and Hao Wu²

¹Professor, Jiangxi University of Science and Technology, Ganzhou, China

² PhD candidate, University of Science and Technology Beijing, Beijing, China

Corresponding author's E-mail: sim2008@sina.com

Abstract

Leaching of gold by cyanide has brought great harm to the environment and staff due to highly toxic. This research introduces a leaching approach to extract gold from gold ores with high sulfur and arsenic contents using a new non-cyanide leaching agent(HJ-1). The properties of ore, mechanism and process of leaching were studied. The results confirm that the gold was mainly oxidized into trivalent and complexed with SCN⁻ as Au(SCN)₄⁻ in HJ-1 leaching system. And it is shown through the research of process mineralogy that there were 2.7% of As and 9.206% of S closely associated with gold. Although the grade of gold was highly 98.34g/t, it also was deemed to refractory gold ore. By compared the leaching conditions and pretreatment methods, high temperature roasting-acid leaching has been adopted. After roasted at 750 °C for 2 hours and grinded for 6 min, the gold leaching rate can reach as high as 94.09% after 3h leaching under the optimized condition of initial pH 2.0, concentration of leaching agent 0.8mol/L, concentration of oxidant 0.05mol/L, and leaching temperature 298 K.

Keywords: High arsenic gold ore, non-cyanide leaching agent, Gold leaching, Leaching mechanism

1. INTRODUCTION

Because of the depletion of gold resources and the increasing demand for gold, refractory gold ore has attracted great attention and became important mineral to extract gold (Liu JZ et al., 2010). Leaching is the main means of gold extraction from refractory gold ore, and cyanide process is predominant means of gold leaching due to mature technology, wide adaptability, stable index, handy operation and high economy (Jeffrey MI et al., 2000). However, cyanidation is susceptible by impurities and time-consuming, especially leaching agent is highly toxic, which would cause harm to the environment and staff. Therefore, cyanide process has come to the edge of elimination (Ma CJ et al., 2015). It is urgent to develop a new, low toxic, efficient and economical non-cyanide leaching process (Huang WF et al., 1998). On this basis, gold leaching with thiocyanate have been proposed for the gold extraction due to strong binding-capacity of SCN⁻ with Au⁺, Au³⁺ (Pang XT et al., 1992). Thiocyanate leaching, on the one hand, has some attractive advantage such as high reaction selectivity, slight environmental risks and simple subsequent processing. On the other hand, thiocyanate leaching has stronger adaptive capacity to environment, higher leaching efficiency than other cyanide-free leaching (Wu H et al., 2016).

In this paper, the process mineralogy of flotation concentrate has been studied. On the basis of mineral character, the HJ-1 leaching of refractory gold ore by mixed leaching agent based on ammonium thiocyanate has been researched yet. The leaching process parameters were determined and the better leaching effect was obtained. Finally, a leaching process which is environmental protection and high efficiency was explored.

2. MATERIALS AND PROCEDURES

2.1. Ore sample and material composition

Table 1 shows the main chemical composition of refractory flotation gold concentrate. As shown in Table 1, the content of S was 9.206 % and the content of Fe was 12.694 % in flotation concentrate, and it was rich gold ore because the content of Au was 98.34 g/t. As is known to all, As-bearing gold ore is leached ineffectively. Thus, the ore was refractory gold ore because the content of As was 2.706% (Luo XH et al., 2016).

Table 1 Chemical composition of the sulfide gold concentrate

Element	O	Na	Mg	Al	Si	P	S	K	Ca	Ti
Content/%	37.780	1.356	1.224	7.945	19.710	0.043	9.206	1.599	1.073	0.542
Element	Cr	Fe	Co	Ni	Cu	Zn	As	Mo	Pb	Au ^a
Content/%	0.011	12.694	0.039	0.040	0.090	0.070	2.706	0.003	0.033	98.34

^a Unit g/t.

Analysis of the gold size by MLA (Mineral liberation analyzer) were shown in Table 2. The size of natural gold was between 2~20 μ m in ore, the gold size which is less than 20 μ m was close to 90%, also the size which is less than 10 μ m was more than half of total. It can be known that the gold in the ore was very fine. The disseminated grain size of gold was relatively fine and size of raw ore was coarse, thus gold liberation in the ore was unsatisfactory.

Table 2 Particle size of natural gold

Particle size/ μ m	Distribution rate/%	Cumulative rate/%
40	1.34	100
-40+20	10.09	98.66
-20+10	37.03	88.57
-10+5	32.47	51.54
-5+2	15.56	19.07
-2	3.51	3.51

Mineralogical analyses of the flotation gold concentrate using SEM (Scanning electron microscopy) indicate that the mineral composition was relatively simple. The metal minerals of ore sample were predominantly pyrite, arsenopyrite, and rutile. Moreover, the content of pyrite was 42.71%, the content of rutile was 1.26%, and the content of arsenopyrite was highly 5.62%. The nonmetallic minerals of ore sample were quartz and feldspar. Moreover, the content of quartz was 45.19% and the content of feldspar was 3.59%. Among these, pyrite was the mainly gold-carrying mineral. The result of mineralogical analyses is shown in Table 3.

Table 3 The result of mineralogical analyses

Mineral composition	Pyrite	Arsenopyrite	Rutile	Chalcopyrite	Sphalerite	Quartz	Feldspar	Sericite	Chlorite
Content /%	42.71	5.62	1.26	trace	trace	45.19	3.59	trace	trace

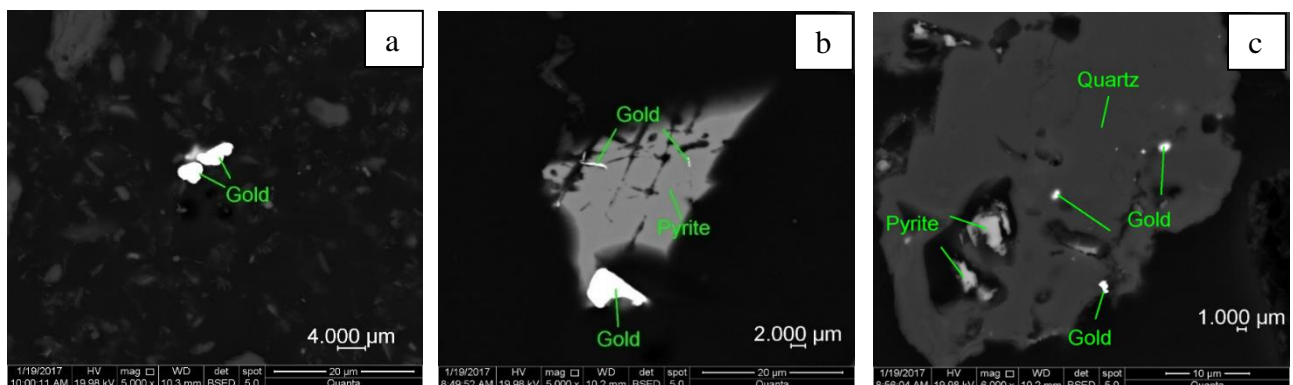


Figure 1 SEM image of ore

According to the analysis of SEM image, most of the natural gold in the ore is in the form of monomers (Figure a). Some of the natural gold is embedded in pyrite as irregular fine veins or flakes, and attached to the edge of pyrite (Figure b). A small part of natural gold is associated included by silicate minerals (Figure c).

The occurrence of gold is shown in table 4, it can be known from the picture that gold liberation in the ore was unsatisfactory because the exposure rate of natural gold is relatively few. Gold enwrapped by sulfides accounts for 30.89%, and a small amount is wrapped in silicate minerals and oxide. Based on the results of the MLA measurements, it can be known that the sulfide of inclusions is mainly pyrite and few arsenopyrite. The gold particles wrapped in sulfide are relatively fine, most of them is less than 20 μ m. oxide of inclusions is mainly pyrite secondary mineral such as oulopholite and jarosite which wrapped gold secondly.

Table 4 The occurrence of gold

The state of gold	Exposed gold	Wrapped gold by carbonate or oxide	Wrapped gold by sulfide	Wrapped gold by silicate	Total
Grade/(g/t)	53.12	3.51	30.38	11.33	98.34
Content/%	54.02	3.57	30.89	11.52	100.00

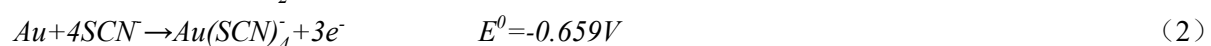
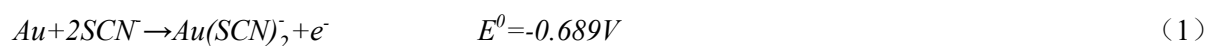
2.2. Experimental method

First of all, the influence of grinding time on grinding fineness was determined through grinding at the condition of ore quantity 1kg and grinding concentration 67% by XMQ-240 \times 90 Cone mill. Then the ore which have been grinded was roasted for 2h by QXR1400-40 muffle furnace. Roasted ore and leaching agent were took in beaker and the gold ore is agitation leached by JJ-4motor agitator. The pH of leaching liquor was measured by pH meter and leaching temperature was controlled by water bath. After leaching, leaching liquid and leaching slag were separated by filtration, the leaching rate of gold was calculated on the basis of the analysis of gold content in leaching liquid and leaching slag.

3. RESULTS AND DISCUSSION

3.1. Thermodynamic analysis

HJ-1 leaching solution is mainly composed of leaching agent and oxidant. Leaching agent is a mixture based on thiocyanate, and oxidants are usually one or several of Fe³⁺, MnO₂, O₂, and H₂O₂ based on the different nature of the ore (Broadhurst JL et al., 1993). The gold particles begin to dissolve electrochemically when ore is leached by HJ-1. This moment, the surface of gold particle is divided into anode region and cathode region (Liang CJ et al., 2015). In the anode region, the Au is oxidized to Au³⁺ and Au⁺ by oxidants, and then combine SCN⁻ as Au(SCN)₂⁻, Au(SCN)₄⁻ to enter solution. In the cathode region, the oxidant is deoxidized by getting electrons (Chen JX et al., 1997). HJ-1 leaching agent makes Au complexed under oxidizing conditions, and the process of leaching gold is completed accompany with transfer and diffusion of electron (Senanayake G, 2004). The reaction of anode region and cathode region is shown in Eq. (1), (2) and (3).



Take Fe³⁺ as example of reaction in the cathode region:



In order to solved the balance of chemical reaction in HJ-1 leaching solution, directly indicated the

relationship between potential, pH and ion concentration, thermodynamic formula and reactive balance in HJ-1 leaching solution were calculated based on the data of thermodynamics and acid-base dissociation (Wang ZK et al., 2006; Senanayake G, 2007), as shown in Table 5. And the Eh-pH diagram of Au-SCN-H₂O system was drew as shown in Figure 2.

Table 5 and Figure 2 indicated that Au was mainly oxidized to positive tervalence and combine into Au(SCN)₄⁻ in HJ-1 leaching solution. In the leaching process, Au (SCN)₂⁻ and Au⁺ cannot existed in the solution. This conclusion is consistent with previous research. Under standard conditions, Au(OH)₃ did not exist in thermodynamically stable water. Au(SCN)₄⁻ existed stably in leaching solution when the pH is less than 9.62, and the stable region in the graph increased gradually with the decreased of pH. Therefore, pH of leaching solution should be neutral or acidic when using HJ-1 leaching agent. In addition, the pH of leaching solution should be kept below 3 when Fe³⁺ is used as oxidant. Because Fe³⁺ begins to hydrolyze and precipitate when pH exceeds 3, Solution potential and oxidant concentration would be reduced.

The concentration of SCN⁻ increased with the increased of HJ-1 concentration in the leaching system. At the same time, the leaching reaction would be more rapid because the electrode potential of leaching reaction decreased gradually, and the Gibbs free energy of reaction gradually increased. After a period of time, the leaching reaction could not proceed because the concentration of Au(SCN)₄⁻ increased and SCN⁻ concentration dropped to a limit.

Table 5 Thermodynamic formula and reactive balance

Chemical reaction	Equilibrium condition
$Au+2SCN^- \rightarrow Au(SCN)_2^- + e^- \quad (4)$	$E=0.689-0.0592 \log \frac{[SCN^-]^2}{[Au(SCN)_2^-]}$
$Au+4SCN^- \rightarrow Au(SCN)_4^- + 3e^- \quad (5)$	$E=0.659-0.0197 \log \frac{[SCN^-]^4}{[Au(SCN)_4^-]}$
$Au(SCN)_4^- + 3OH^- \rightleftharpoons Au(OH)_3 + 4SCN^- \quad (6)$	$\log \frac{[SCN^-]^4}{[Au(SCN)_4^-]} = -13.46 + pH$
$Au(SCN)_4^- + 3H^+ + 3e^- \rightarrow Au + 3HSCN + SCN^- \quad (7)$	$E=0.609-0.0592pH-0.0197 \log \frac{[HSCN]^3 [SCN^-]}{[Au(SCN)_4^-]}$
$Au(SCN)_2^- + 2SCN^- \rightarrow Au(SCN)_4^- + 2e^- \quad (8)$	$E=0.644-0.0296 \log \frac{[Au(SCN)_2^-][SCN^-]^2}{[Au(SCN)_4^-]}$

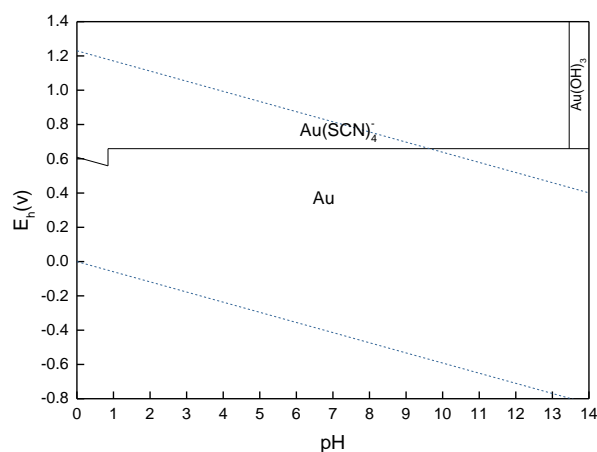


Figure 2 Eh-pH diagram of Au-SCN-H₂O

3.2. Roasting temperature

It can be known from phase composition that the metal minerals of ore sample were predominantly pyrite, arsenopyrite, and the nonmetallic minerals were quartz. In order to determine the optimum

temperature for roasting, DTA (Differential thermal analysis), TG (Thermogravimetric analysis) and DTG (Derivative thermogravimetry) were conducted in air atmosphere. The result is shown in Figure 3.

The DTA curve indicates minerals are endothermic from 25°C to 750°C because of a widely endothermic peak (Tang DW et al., 2013). It can be known that mineral weight gradually decreases with increasing temperature and the TG curve becomes steeper between 520°C and 600°C from Figure 2. And between 520°C and 600°C, the mineral weight decreased by 15%, indicating that the phase of the ore has changed. According to the DTG curve, there are two peaks of weight loss between 520°C and 600°C, which indicate that two transformation reactions occur during the process.

Comprehensive analysis shows that there are mainly pyrite (FeS_2) and arsenopyrite (FeAsS) in ore before 520°C (Liu HZ, 2013). After 520°C, FeS_2 and FeAsS are oxidized and decomposed gradually. FeS_2 and FeAsS convert to Fe_2O_3 at 550°C and 590°C respectively, and sulfur and arsenic are removed out ore as a result. when the temperature exceeds 750°C, the oxidation pretreatment is basically completed because minerals are no longer endothermic, and change of mineral weight is not obvious. Therefore, the final roasting temperature is determined to be 750°C.

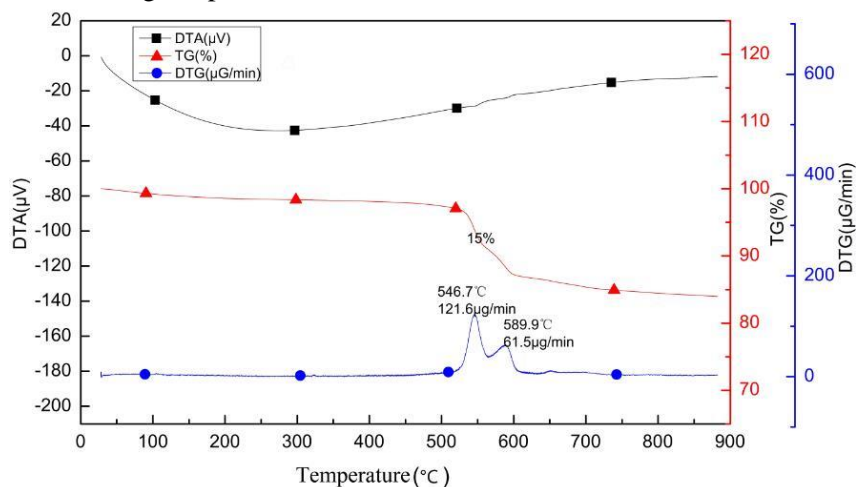


Figure 3 The result of DTA, TG and DTG

3.3. Effect of grinding fineness

The purpose of grinding is to maximize the dissociation or exposure of useful minerals, so that the useful minerals contact adequately with the leaching agent (Wu H et al., 2016). The grinding time is short, the degree of mineral dissociation or exposure is insufficient, thus the target mineral cannot fully contact with the leaching agent (Bai PC et al., 2012). However, excessive grinding will increase energy consumption, and lead to sliming ore pulp, increasing the difficult of filtration. Eventually, leaching effect becomes worse and cost becomes increasing. Therefore, the relationship between the grinding fineness and leaching efficiency was researched.

Table 6 shows the relation between grinding fineness and time under the condition that grinding concentration is 67% and grinding capacity is 100g.

Table 6 The relation between grinding fineness and time

Grade (mm)	Grinding time					
	2min	3min	4min	5min	6min	7min
+0.074	17.17%	11.55%	6.90%	5.66%	3.92%	1.44%
-0.074 +0.037	22.39%	23.24%	20.65%	15.72%	15.79%	11.34%
-0.037	60.44%	65.21%	72.45%	78.62%	80.29%	87.23%
Total	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%

The grinding products were leached for 3h respectively in a solution with a HJ-1 concentration of 0.8mol/L, a ferric sulfate concentration of 0.05mol/L, a pH of 2, a stirring speed of 600 rad/min, a liquid to solid ratio of 5 at 25 °C. The results are shown in figure 4.

Table 6 shows that the fineness of ore decreases with the increase of grinding time. In the ranges of grinding time (3–6min), Au extraction increased with the increases of grinding time and afterward kept roughly steady. The results presented in Figure 4 show that at 6min leaching rate was 92.59%, mineral fineness of -0.037mm accounted for 80.29%, mineral fineness of -0.074mm accounted for 96.08%.

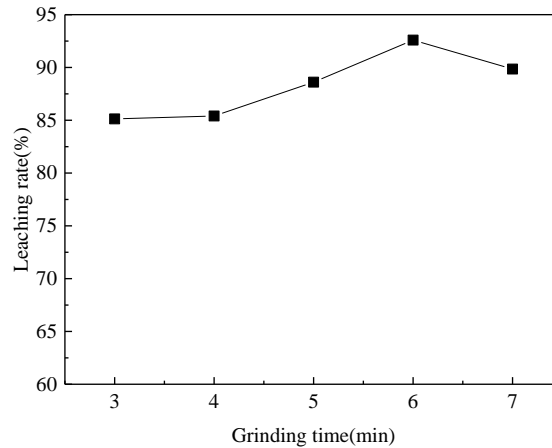


Figure 4 Relationship between grinding fineness and leaching effect

3.4. Effect of reagent system on leaching gold

The leaching reagent system mainly includes concentration of leaching agent, concentration of oxidant and pH value. In a certain range, the leaching speed and leaching rate increases with the increase of the concentration of leaching agent. When the oxidant concentration is relatively low, it is unfavorable for Au to be oxidized and dissolved. When the oxidant concentration is relatively high, it will oxidize leaching agent and increase the amount of leaching agent. And the thermodynamic analysis shows that pH of leaching solution should be neutral or acidic when using HJ-1 leaching agent. In addition, the pH of leaching solution should be kept below 3 when Fe^{3+} is used as oxidant.

Based on thermodynamic analysis, the concentration of the leaching agent, the concentration of oxidant and pH in leaching solution were studied. Ore after roasting and grinding were leached for 3h in a solution with a stirring speed of 600 rad/min, a liquid to solid ratio of 5 at 25 °C. Dosage range of reagent system and leaching results were shown in Figure 5.

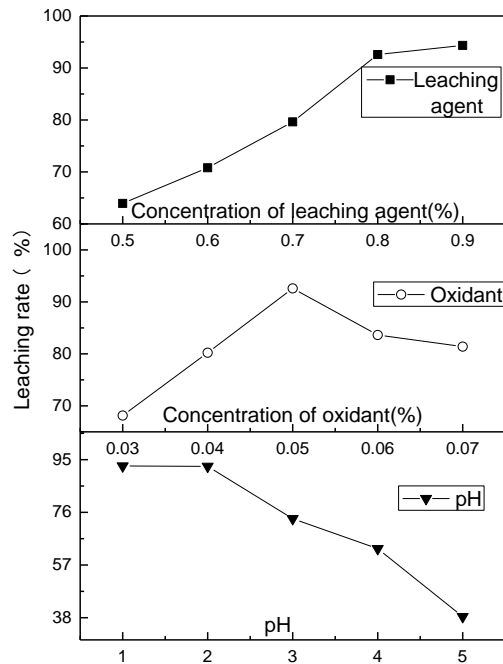


Figure 5 Effect of reagent system on leaching efficiency

Figure 5 shows gold extraction at different concentration of leaching agent, oxidant and pH. Figure 5 indicates that in the ranges of leaching agent (0.5–0.8mol/L), Au extraction increased with the increases of grinding time. And after 0.8mol/L, Au extraction kept roughly steady. In addition, gold extraction increased first and then decreased with the concentration of oxidant Fe^{3+} increased from 0.03mol/L to 0.07mol/L. The maximum rate of gold leaching was 92.59% when the concentration of oxidant was 0.05mol/L. When the oxidant concentration was relatively high, SCN^- would be oxidized and ullage of leaching agent HJ-1 would be increased. Consequently, the gold extraction would be reduced. Meanwhile, it is evident that gold extraction does not change significantly with increase of pH from 1 to 2. And then, from 2 to 5 of pH, gold extraction declined obviously due to precipitation and hydrolysis of Fe^{3+} when pH exceeded 3. Since the initial pH of leaching solution is about 2, excessive regulation of pH will increase the cost and not increase the leaching rate. From the above, appropriate reaction conditions were established as follows: leaching agent 0.8mol/L, oxidant 0.05mol/L and pH2.

3.5. Effect of operational factors on leaching gold

The operational factors mainly include liquor-to-solid ratio, leaching temperature and leaching time. In the reaction of gold leaching, the ratio of liquid to solid is directly related to the diffusion of HJ-1 and oxidant in solution (Alkan M et al., 2005). Low ratio of liquid-to-solid will lead to higher viscosity of ore pulp and more flowing difficultly between ore particles and leaching liquor. But, low ratio of liquid-to-solid also will increase the processing capacity of equipment, reduce the consumption of leaching agent (Yang DJ et al., 2002). In addition, shorter leaching time would make leaching reaction inadequately. But longer leaching time would increase time cost and increase the impurity ion in the ore pulp, which would impact the gold extract and increase the difficulty of subsequent processing (Mohammadi E et al., 2017).

Based on the optimum reagent system, the operation factors of gold leaching were investigated. Ore after roasting and grinding were leached in a solution with a stirring speed of 600 rad/min, a HJ-1 concentration of 0.8mol/L, an oxidant concentration of 0.05mol/L and pH of 2. The liquor-to-solid ratio, leaching temperature and leaching time were investigated and leaching results were shown in Figure 6.

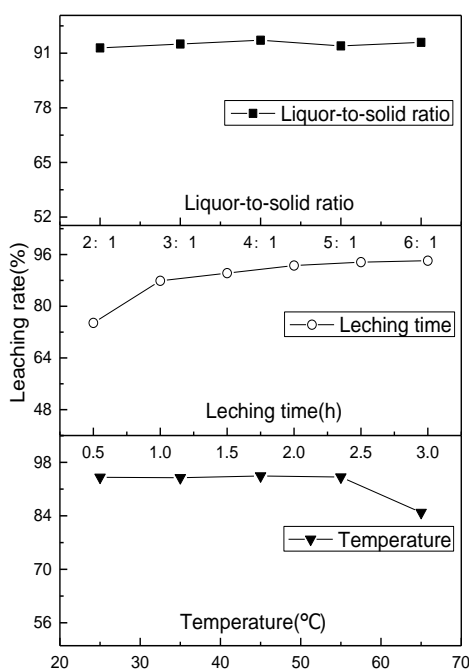


Figure 6 Effect of operational factor on leaching efficiency

It is evident that gold extraction changes inconspicuously with increase in liquor-to-solid ratio from 2 up to 6. Also, as it is seen, the gold extraction increases with increase in time and attains 90.24% after 1.5h leaching. And gold extraction increases slowly in the range of 1.5h to 3h. In addition, it is obvious to observe that gold extraction changes inconspicuously when the temperature is below 55°C. And the leaching rate decreases rapidly from 94% to 84.88% at 65°C, due to decomposition of leaching agent HJ-1 by excessive temperature. All things considered, appropriate operational factors were established as follows: liquor-to-solid ratio 4, leaching temperature 25°C and leaching time 3h.

4. CONCLUSIONS

Based on the research of process mineralogy on refractory gold ore, the experimental study of leaching process was carried out. In addition, the theoretical analysis of gold leaching by HJ-1 was researched from the viewpoint of thermodynamics.

1. The content of S was 9.206 % and the content of As was 2.706 % in flotation concentrate, and it was rich gold ore because the content of Au was 98.34 g/t. The metal minerals of ore sample were predominantly pyrite, arsenopyrite. gold liberation in the ore was unsatisfactory. Thus, the ore was refractory gold ore.
2. Au was mainly oxidized to positive tervalence and combine into $Au(SCN)_4^-$ in HJ-1 leaching solution. In the leaching process, $Au(SCN)_2^-$ and Au^+ cannot existed in the solution. And pH of leaching solution should be neutral or acidic when using HJ-1 leaching agent.
3. The optimum leaching process of HJ-1 was determined by experiment as follow: After roasted at 750°C for 2 hours and grinded for 6 min, the gold leaching rate of ore can reach as high as 94.09% after 3h leaching under the optimized condition of initial pH 2.0, concentration of leaching agent 0.8mol/L, concentration of oxidant 0.05mol/L, and leaching temperature 298 K.

5. ACKNOWLEDGMENTS

This study was financially supported by the Key Projects in the National Science & Technology Pillar Program during the Twelfth Five-year Plan Period of China (Fund No. 2012BAB10B03).

6. REFERENCES

- Liu JZ, Huang WF (2010). Progress of gold leaching process from the high arsenic gold ore, *Morden Mining*, 26, 26-29.
- Jeffrey MI, Breuer PL (2000). The cyanide leaching of gold in solutions containing sulphide, *Minerals Engineering*, 13, 1097-1106.
- Ma CJ, Li JY, Liu RJ (2015). A review of thiocyanate hydrometallurgy for the recovery of gold, *Applied Mechanics & Materials*, 768, 53-61.
- Huang WF, Wang DZ, Hu YP (1998). Theory and practice of leaching gold by thiosulfate, *Gold*, 19, 34-36
- Pang XT, Zhang SY (1992). Study of leaching gold and silver by thiocyanate process, *Gold*, 13, 33-37.
- Wu H, Huang WF, Qiu F, Hu XF (2016). Review of gold leaching by thiocyanate, *Precious Metals*, 37, 72-78.
- Luo XH, Huang WF (2004). Study and advances of associated gold and silver recovery, *Morden Mining*, 20, 5-7.
- Broadhurst JL, Perez JGHD (1993). A thermodynamic study of the dissolution of gold in an acidic aqueous thiocyanate medium using iron (III) sulphate as an oxidant, *Hydrometallurgy*, 32, 317-344.
- Liang CJ, Ma CJ (2015). Gold leaching from waste circuit boards with thiocyanate in neutral environment, *Precious Metals*, 36, 56-62.
- Chen JX, Pang XT (1997). Study on kinetics of leaching gold in Fe(III)-SCN system, *Hydrometallurgy of China*, 16, 16-21.
- Senanayake G (2004). Analysis of reaction kinetics, speciation and mechanism of gold leaching and thiosulfate oxidation by ammoniacal copper(II) solutions, *Hydrometallurgy*, 75, 55-75.
- Wang ZK, Chen DH, Chen L (2006). Thermodynamic criterion for oxidant selection in thiocyanate gold leaching, *Nonferrous metals*, 58, 26-28.
- Senanayake G (2007). Review of rate constants for thiosulphate leaching of gold from ores, concentrates and flat surfaces: Effect of host minerals and pH, *Minerals Engineering*, 20, 1-15.
- Tang DW, Yang C, Wang R, Huang BF (2013). The study of pyrolysis experiment about some refractory gold mine in guizhou province, *Precious Metals*, 34, 51-54.
- Liu HZ (2013). Present situation and Prospect of roasting oxidation of refractory gold ores at home and abroad, *Metallic Ore Dressing Abroad*, 42, 5-10.
- Wu H, Huang WF, Wen JL, Qiu F (2016). Experimental study of recovering sulfide ore from tungsten gravity tailings in Jiangxi, *Nonferrous Metals Science and Engineering*, 7, 100-104.
- Bai PC, He Y, Chen FF, Li KK (2012). Experimental Study on Cyanide Leaching Efficiency Influenced by Fineness of Grinding and Secondary Grinding and Leaching, *Gold Science and Technology*, 20, 71-73.

Alkan M, Çigdem H, Yilmaz Z (2005). The effect of alkali concentration and solid/liquid ratio on the hydrothermal synthesis of zeolite NaA from natural kaolinite, *Microporous & Mesoporous Materials*, 86, 176-184.

Yang DJ, Liao YS, Xu YF, Peng JR (2002). Experiment study of leaching gold in pyrite with thiourea, *Gold*, 23, 28-30.

Mohammadi E, Pourabdoli M, Ghobeiti-Hasab M, Heidarpour A (2017). Ammoniacal thiosulfate leaching of refractory oxide gold ore, *International Journal of Mineral Processing*, 164, 6-10.