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## Gold recovery from refractory gold concentrates by pressure oxidation pre-treatment and thiosulfate leaching

Li Yu <sup>1</sup>, Shimei Li <sup>1</sup>, Quanjun Liu <sup>1\*</sup>, Jiushuai Deng <sup>2,1\*</sup>, Bin Luo <sup>1</sup>, Yuanqin Liang <sup>1</sup>, Liuchuang Zhao <sup>1</sup>, Hao Lai <sup>1</sup>

<sup>1</sup> State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, PR China

<sup>2</sup> School of Chemical Engineering and Technology, China University of Mining & Technology (Beijing), Beijing 100083, China

Corresponding author: [kmliujq@163.com](mailto:kmliujq@163.com) (Quanjun Liu)

**Abstract:** Naturally, refractory gold is enclosed by sulfide minerals such as pyrite and arsenopyrite and a higher content of organic carbon, which results in difficulty in the recovery of gold. In this study, the flotation gold concentrate before and after pressure oxidation (POX) was analyzed. The analysis of the Eh-pH diagram revealed that pyrite/arsenopyrite would be dissolved in higher oxidation potential. Results of SEM-EDS showed that the surface of minerals became very rough and structure of some particles was destroyed after POX. The XRD measurement showed that pyrite was oxidized to jarosite, and gangue minerals such as quartz and organic carbon were hardly changed. The process of thiosulfate leaching of gold was designed and optimized according to Miscellaneous implemented by Response Surface Methodology (RSM). Based on the results of ANOVA, leaching model was significant. In leaching,  $[S_2O_3^{2-}]$  played an important role and the interactions between  $[S_2O_3^{2-}]$  and  $[Cu^{2+}]$  were significant. The effect of [HA] was relatively weak. Optimum process parameters of the initial reagent concentration were 505.00 mM for  $[S_2O_3^{2-}]$ , 34.77 mM for  $[Cu^{2+}]$ , and 0.50 mM for [HA]. Under these conditions, the Au extraction value was about 86.21%, which was significantly higher than that obtained with leaching directly.

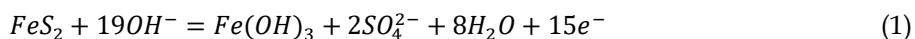
**Keywords:** gold, pressure oxidation, thiosulfate, leaching, RSM

### 1. Introduction

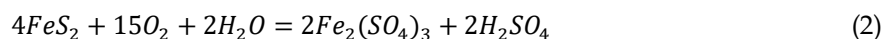
Gold was an important rare and precious metal, always coexists with sulphide minerals such as pyrite and arsenopyrite (Azizi et al., 2010; Nunan et al., 2017). Due to the depletion of high-grade gold ores with large-scale gold ore mining, the attention of gold production enterprises is switching towards refractory gold ores gradually (Karamanev et al., 2001; Zhu et al., 2012).

There are two reasons for refractory of gold: (a) The content of organic carbon in the ores is higher and carbon could be enriched in the flotation process. The higher content of carbon in the flotation concentrate would cause "pre-robbing" in the cyanidation stage, and the recovery amount of gold would decrease. (b) The gold in Carlin-type deposits is encapsulated as fine particles (sometimes at a molecular level) in the crystal structure of sulphides, typically pyrite with or without arsenopyrite matrix (Li et al., 2006). Even though the particle size can be reduced by fine grinding, the gold could not be exposed. Mohammadi et al. investigated ammoniacal thiosulfate leaching of refractory oxide gold ore, and they obtained maximum gold extraction of 55% (Mohammadi et al., 2017). Shen et al. had researched the direct thiosulfate leaching of gold from refractory ore, and they achieved gold recovery of only 70% (Shen et al., 2013). Li et al. studied the best conditions of roasting and oxidizing refractory gold-bearing sulfur concentrates in the muffle furnace, and the optimized technological parameters for thiosulfate leaching were ascertained through optimal experiments. The results show

that gold recovery is difficult by thiosulfate leaching without any pre-treatment, and the recovery of gold only is 10.1%. After roasting and oxidizing, the gold leaching rate increases substantially. The leaching rate of gold reaches 71.2% with the optimal leaching technological parameters (Li et al., 2013). Leaching of the gold was difficult and the 5~70% recoveries of gold were lower than that obtained for other gold ores (excess of 95%). Compared with carbonaceous matter, the gold encapsulated in sulfide minerals has a more significant effect on the leaching value of gold. Previous studies had provided a number of methods to distribute the "protective containment" of gold, for example, bio-oxidation (Lindstrom et al., 2003), ozone-oxidation (Elorza-Rodriguez et al., 2006; Li et al., 2009; Li et al., 2015), roasting (Lehmann et al., 2000), electro-chlorination (Zhu et al., 2012), and pressure-oxidation (Lampinen et al., 2015). Bio-oxidation obtains required oxidation ratio requires a long time. The roasting process of gold bearing sulfur concentrate consumes a lot of energy and releases pollutants such as SO<sub>2</sub> into the air. Couldn't achieve a satisfactory recovery by electro-chlorination, Zhu et al. had researched leaching of refractory gold ores by ultrasonic-assisted electro-chlorination, the application of ultrasound could reduce the reaction time greatly. However, ultrasound would damage the electrode surface, which makes this method unstable for industrial applications. Pressure oxidation (POX) was known as an effective oxidizing pre-treatment to decompose sulfide minerals such as pyrite. The POX currently includes two major classes: acid or alkaline environment (Lampinen et al., 2015; Li et al., 2006). Generally, it is accepted that the oxidation of pyrite in an alkaline environment is expressed by equation (1), in which the ferric ion precipitates on the pyrite surface or existing in form of ferric hydroxide in suspension liquid (Li et al., 2006).



Li et al. researched pyrite pre-oxidation in alkaline environment, they observed that that an iron-, silicon-, and calcium-bearing compound, with variable amounts of sulfur, commonly surrounded pyrite grains, which caused low sulfide oxidation and low gold extraction (Li et al., 2006). Further, POX in an alkaline environment is expensive owing to the requirement of heavy consumption of NaOH or Na<sub>2</sub>CO<sub>3</sub>, so it is not suitable for practical applications. Compared with that is an alkaline environment, the economy of pressure oxidation in acid is event since a low pH value could be maintained by sulfuric acid generation from the oxidation reaction of the sulfide mineral. The chemical reaction is shown in equation (2) (Chan et al., 2015).



Some researchs found that the cyanide leaching value of gold increased sharply when the flotation concentrate was treated by pressure oxidation in acid (Dong et al., 2015; Luo et al., 2015). Now, the flotation-pressure oxidation-cyaniding technology was taken to deal with the refractory gold ore in shuiyindong despite, the recovery of gold was obtained about 82~85%. Furthermore, increasing restrictions on cyanidation techniques used in gold production have been imposed, so the company is searching for a new alternative technology. The thiosulfate was regard as an appropriate alternative for cyanide. The use of thiosulfate in the presence of ammonia and Cu<sup>2+</sup> has been regarded as an appropriate choice, and extensive research work has been carried out in this area with comprehensive published reviews. Lampinen et al. found that the pressure oxidized (in an acid environment) gold concentrate was effectively leached in an ammoniacal thiosulfate leaching solution (Lampinen et al., 2015). Furthermore, Xu et al. suggested that HA (sodium humic acid) was used to improve the leaching, and could improve gold extraction of flotation concentrate treated by oxidative roasting (Xu et al., 2015).

Pressure oxidation technology for the treatment of refractory gold concentrates has been deployed in some countries. Shuiyindong gold deposit is one of the Carlin-type deposits which is a typical difficult-to-treat gold deposit, located in Guizhou province in western China. It was the first application of acid pressure oxidation in China. The composition of the flotation concentrate is very complex, there is some gangue mineral would exert an effect on pressure oxidation and leaching process. Therefore, condition experiments were used to design the technological process is necessary to obtain a higher gold recovery. In this study, the differences in the flotation concentrate of gold before and after pressure oxidation were analysed. The process of thiosulfate leaching of gold were researched by employing the response surface methodology (RSM). The block flow diagram process steps of this study is shown in



when no bubbles are generated. The experiments were conducted in a 1 L autoclave (GSHA-2, Weihai Xintai Chemical Machinery Co., Ltd., China). The pulp was placed in the autoclave and deionized water up to 1 L was added. The pulp was heated to 200°C for about 7 min, at a heating power of 1.5 kW and the stirring speed of pre-oxidation was fixed at 500 rpm. The temperature of react was steady at 200±10°C which was controlled by adjusting the quantity of cooling water, and a PID automatic temperature control instrument was used in the heating control system. Oxygen was fed during the entire reaction process, and the reaction pressure was maintained at 2.5 MPa. The reaction was stopped when the reaction temperature was decrease without cooling water. The oxygen feed was stopped and stirring was initiated when the pulp temperature decreased to 80°C. Then, the lid of the autoclave was removed, and the pulp was taken out when the pulp temperature reached 40°C. After pre-oxidation tests, the pulp was filtered and dried for the analysis and leaching tests.

### 2.3. Leaching

Leaching tests were carried out in 1000 mL glass beakers and using a mechanical agitator (RW20, IKA, Germany). The stirring speed was fixed at 600 rpm, the room temperature was controlled to 25±3°C, and 100g pressure oxidized sample powder was added into a beaker with 200 mL pure deionized water for each leaching. After agitation for 5 min, the pH of the pulp was firstly adjusted to 10.5±0.5 by using a sodium hydroxide-ammonium sulfate mixed solution. Then copper sulfate (CuSO<sub>4</sub>), sodium humate (HA), and sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) were added to the glass reactor. Then, the pH value of the solution was kept steady by readjustment every 20 min with the addition of sodium hydroxide-ammonium sulfate mixed solution. After leaching, the residues were immediately vacuum filtered, dried, and weighed. The gold leaching value was calculated by the following equation:

$$\varepsilon = \frac{m_1\alpha - m_2\theta}{m_1\alpha} \times 100\% \quad (3)$$

where  $m_1$  is 100 g,  $m_2$  is the mass of residues,  $\alpha$  is grade of gold in pressure oxidized sample,  $\theta$  is grade of gold in residues.

### 2.4. Characterization

All samples were adequately rinsed with pure deionized water and then dried under vacuum 24 h before X-ray diffraction and Scanning electron microscope and Energy Dispersive Spectrometer analyses. Element content and chemical phase analysis of samples were analysed by Kunming Metallurgical Research Institute. Scanning electron microscope and Energy Dispersive Spectrometer (SEM-EDS, VEGA3, TESCAN, Czech Republic) was employed to provide morphological analysis and the composition of the concentrates and product of pre-oxidation. The magnification time was fixed at 2000 or 5000. Prior to the measurement, the samples were ground, and then gold coated using an ion coater under vacuum environment. The qualitative analysis of main mineral phases of were detected by X-ray diffraction (XRD, D/Max 2200X, Rigaku, Japan) at 40kV×30mA, Cu K $\alpha$  radiation ( $\lambda=1,54056$  Å) and  $2\theta$  from 10 to 90°, and the results analysed by MDI Jade 6.5 software.

### 2.5. Experimental design

Response surface methodology (RSM) is an effective statistical technique for modelling and analysing problems where the response is influenced by several factors and the aim is to get an optimum response. In order to conduct the leaching experiments, the exploratory plan was developed to optimize and investigate the influence of the important factors toward Au extraction utilizing Miscellaneous module of Design-Expert 8.0.6 Trial version (Stat-Ease, Inc., Minneapolis, MN, USA). The procedure of experimental design and optimization has been represented in the form of a flowchart as shown in Fig. 2.

The value of Au extraction (Y, %) was taken as the response variable, where the concentrations of thiosulfate (A, mM), Cu (B, mM) and HA (C, mM) were considered as the independent variables (factors). Their data range were determined by previous experience and listed in Table 3. As shown in Table 3 the total number of required experimental runs was 27 (3k), where k is the number of factors (k=3). Conducting tests on the basis of testing program designed by Design-expert 8.0.6.1 software.

Testing program and results were fitted to a quadratic model. The generalized second-order polynomial model used in the response surface analysis can be described in the form given in Eq. (4) (Chen et al., 2015).

$$R = a_0 + \sum_{i=1}^k \alpha_i x_i + \sum_{i=1}^k \alpha_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \alpha_{ij} x_i x_j + \varepsilon \quad (4)$$

where R is the dependent response, k represents the number of variables,  $a_0$  is the constant term,  $a_i$  is the linear and interaction coefficient, respectively;  $x_i, x_j$  are the variables,  $a_{ii}$  is the coefficients of the quadratic parameter, the terms  $x_i x_j$  are the interaction,  $a_{ij}$  is the coefficients of the interaction parameters and  $\varepsilon$  represent the residual associated with the interaction (Khosravi et al., 2017).

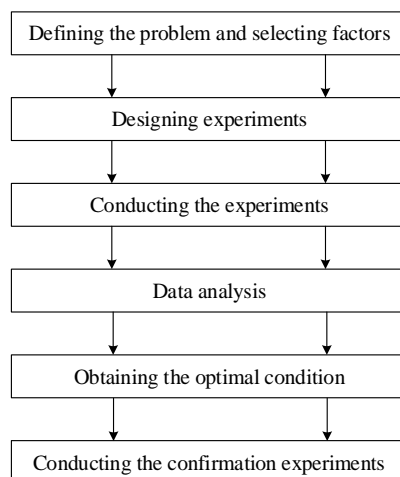


Fig. 2. Procedure of leaching experimental design

Table 3. The affecting the extraction process of gold and their levels

Factor	Symbol	Factorial levels		Target
		Low(-1)	High(+1)	
[S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ], mM	A	100	600	Maximum
[Cu <sup>2+</sup> ], mM	B	0	50	
[HA], mM	C	0	50	

### 3. Result and discussion

#### 3.1. Pre-oxidation

##### 3.1.1. Eh-pH diagram of the FeS<sub>2</sub>-FeAsS-H<sub>2</sub>O system

The thermodynamic data used in Eh-pH diagrams of the FeS<sub>2</sub>-FeAsS-H<sub>2</sub>O system at 25 °C and 200 °C were taken from the HSC Chemistry Software Version 6.0 (Outokumpu Research Oy, Finland). S, Fe and As were chosen as the main elements, the ion concentration of the system was set as at 0.1 mol/L. According to the computed results of HSC, the Eh-pH diagrams were drawn by origin 2017.

The Eh-pH diagrams of the FeS<sub>2</sub>-FeAsS-H<sub>2</sub>O system at 25°C and 200°C are presented in Fig. 3. As shown in the Fig. 3, the area surrounded by the green dashed lines is the stability region of FeAsS, while the area surrounded by the red dashed lines is the region with a high prevalence of FeS<sub>2</sub>. Pyrite and arsenopyrite were stable in the low oxidation-reduction potential range and the stability region of pyrite (red dashed lines) was encompassed by arsenopyrite (green dashed lines) (Ke et al., 2017). Based on thermodynamics principle, the stability of pyrite was better than that of arsenopyrite. Thus, the oxidation and decomposed of pyrite needs more attention in the pre-oxidation of the flotation concentrate of gold. With the increase in the potential, the arsenopyrite phase was transformed to arsenic sulfide (As<sub>4</sub>S<sub>4</sub>, As<sub>2</sub>S<sub>3</sub>), arsenite (HAsO<sub>3</sub><sup>-</sup>), and arsenate (H<sub>3</sub>AsO<sub>4</sub>, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup> and AsO<sub>4</sub><sup>3-</sup>). In the high oxidation-reduction potential range, arsenate reacted with Fe<sup>3+</sup> to form (FeAsO<sub>4</sub>) when 0.81 < pH < 3.41, and reducing the quantity enter in the solution. Compared with the Eh-pH diagrams of the

$\text{FeS}_2$ - $\text{FeAsS}$ - $\text{H}_2\text{O}$  system at 25°C, the stability region of the pyrite and arsenopyrite become obviously smaller and the thermodynamic property of arsenopyrite was more stable than that of pyrite. In the high pH range, the crystal structure of pyrite and arsenopyrite were broken, however, the process required the addition of a large amount of alkali to raise the pH value of the pulp. Thus, it is less cost-effective than mineral dissolution. The oxidation process of pyrite and arsenopyrite is an exothermic reaction and produces large quantity of protonic acid; the characteristic can keep the reaction on appropriate temperature and pH value. Compared with an alkaline environment, POX in the acid environment is more economically advantageous. In the high potential range, sulphur exists in the form of sulfite ( $\text{HSO}_4^-$ ) or sulfate ( $\text{SO}_4^{2-}$ ). Elemental sulfur could not be formed in the oxidation process, avoiding gold secondary included by it. The iron exists in the form of  $\text{FeAsO}_4$  when  $\text{pH} < 5.75$ , and  $\text{Fe}(\text{OH})_3$  when  $\text{pH} > 5.75$ . The arsenic in the solution is the form of arsenic acid ( $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ ), so it is necessary to consider arsenic pollutant in the waste water treatment. The results of Eh-pH diagram are for reference only it lacks the thermodynamic data of some materials.

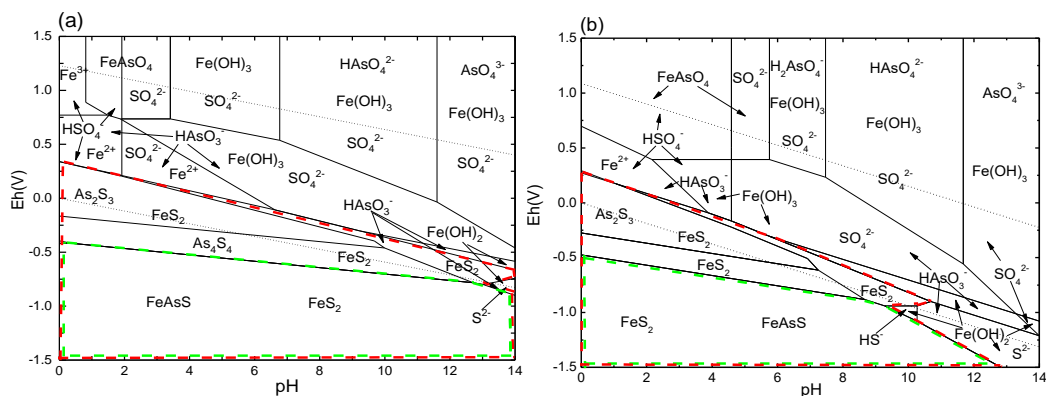


Fig. 3. Eh-pH diagrams of the Fe-As-S- $\text{H}_2\text{O}$  system at (a) 25 °C, (b) 200 °C

### 3.1.2. Mineral composition

The XRD results for the flotation concentrate and product of POX are shown in Fig. 4. As shown in Fig. 4(a), pyrite ( $\text{FeS}_2$ ) is the main mineral in the flotation concentrate of gold, and the others are arsenopyrite and quartz; these results agree with chemical analysis as shown in the Table 2. After pre-oxidation, pyrite and arsenopyrite could not be found in the sample. As indicated in Fig. 4(b), pyrite was oxidized, generating jarosite. Quartz was barely changed in the process of pre-oxidation. Fractional gangue mineral was dissolved in the acid solution, and  $\text{Ca}^{2+}$  react with sulfate radical to generate the precipitate ( $\text{CaSO}_4$ ) were found by XRD analysis. Minerals were dissolved and reconstruction in POX, gold which has been exposed maybe secondary locked by new crystals such as Jarosite. It has been reported in previous literature that jarosite was also generated in other pre-treatments. However, jarosite would

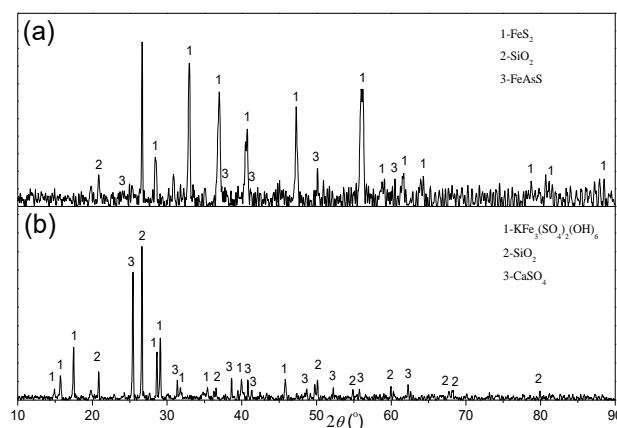
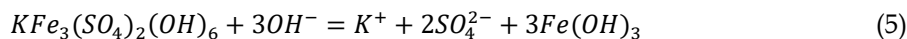


Fig. 4. XRD analysis of the ore sample. (a) The flotation concentrate of gold, (b) The product of the pressure oxidation

be resolve in the alkaline leaching process, the chemical reaction is shown in Eq. (5) (Chan et al., 2015)



Combining with the results of chemical analysis shown in Table 4, the content of total carbon decreased but that of organic carbon increased after POX. This indicates that carbonated minerals could dissolve but organic carbon hardly reacted in POX. For the analysis mentioned above, the negative impact of organic carbon would still exist in the case of cyanide leaching. However, the crystal structure of pyrite was broken down and gold would be exposed in POX; furthermore, the impact of organic carbon on the system of thiosulfate leaching. The results are same as those for the analysis of Eh-pH diagrams of the Fe-As-S-H<sub>2</sub>O system.

Table 4. The results of chemical analysis of the flotation concentrate after POX

Component	Au	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>	Fe	As
Content / %	2.72×10 <sup>-3</sup>	5.89	8.64	14.45	30.24	6.94	0.34
Component	S	TC	TOC	Cu	Pb	Zn	Sb
Content / %	10.45	6.74	6.38	<0.05	<0.05	<0.05	<0.05

### 3.1.3. Analysis of surface

The samples before and after POX were subjected to SEM/EDS study in order to analysis their surface morphology and chemical composition; the results are show in Fig. 5 and Fig. 6. As shown in Fig. 5, the surface area of samples is changed. Compared with the without prepared sample (Fig. 5), the surface of sample after POX becomes very rough and the structures of some particles are destroyed. In addition, the EDS analysis results, show that the main component of the flotation concentrate of gold (Fig.6) was carbon organic matter (1#), pyrite/arsenopyrite (2#, 3#, 4#), and quartz (5#), and the result agrees was in accord with chemical analysis results. After pre-oxidation, the weight proportion of Fe is decreased and O is increased; further, the contents of Al, Mg, and Ca increased distinctly. The results indicate that the sulfide ores (pyrite and arsenopyrite) were oxidized and dissolved in the process of POX. The elements Fe and S existed in the form of ferric salts and sulfate, and as indicated by XRD analysis, the main component of the material (8#, 10#) was jarosite. Carbon organic matter (6#) and quartz (7#) barely changed but some sulfate adhered on them. The elements Al, Mg, and Ca come from basic gangue mineral were react with sulfate and generate precipitation (9#) in the product of POX. According to above analysis, a conclusion is drawn that the oxidation, dissolution and recrystallization of the sulfide ore results in the exposure of the encapsulated gold. A part of the gold could react with the leaching agent, and thus, gold extraction will increase significantly.

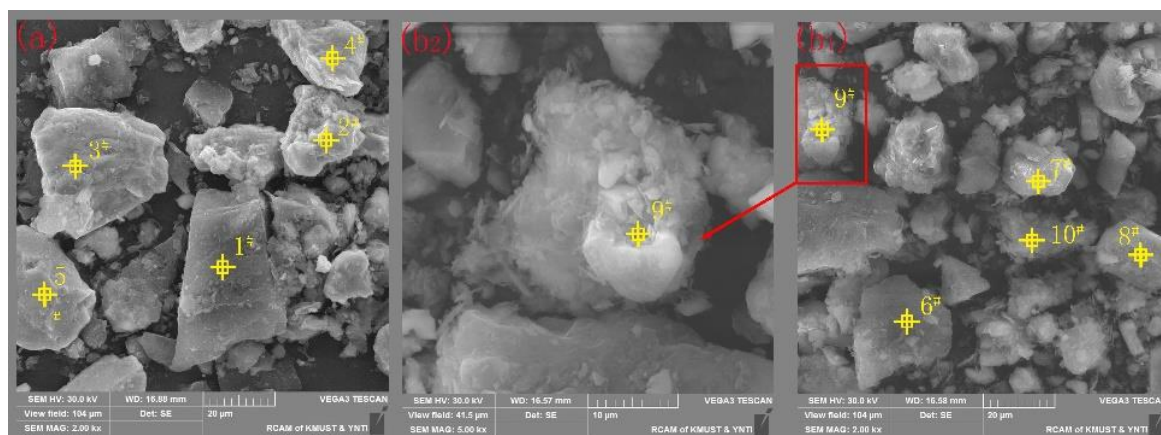


Fig. 5. Scanning electron micrographs of flotation concentrate (a) before POX; (b) after POX

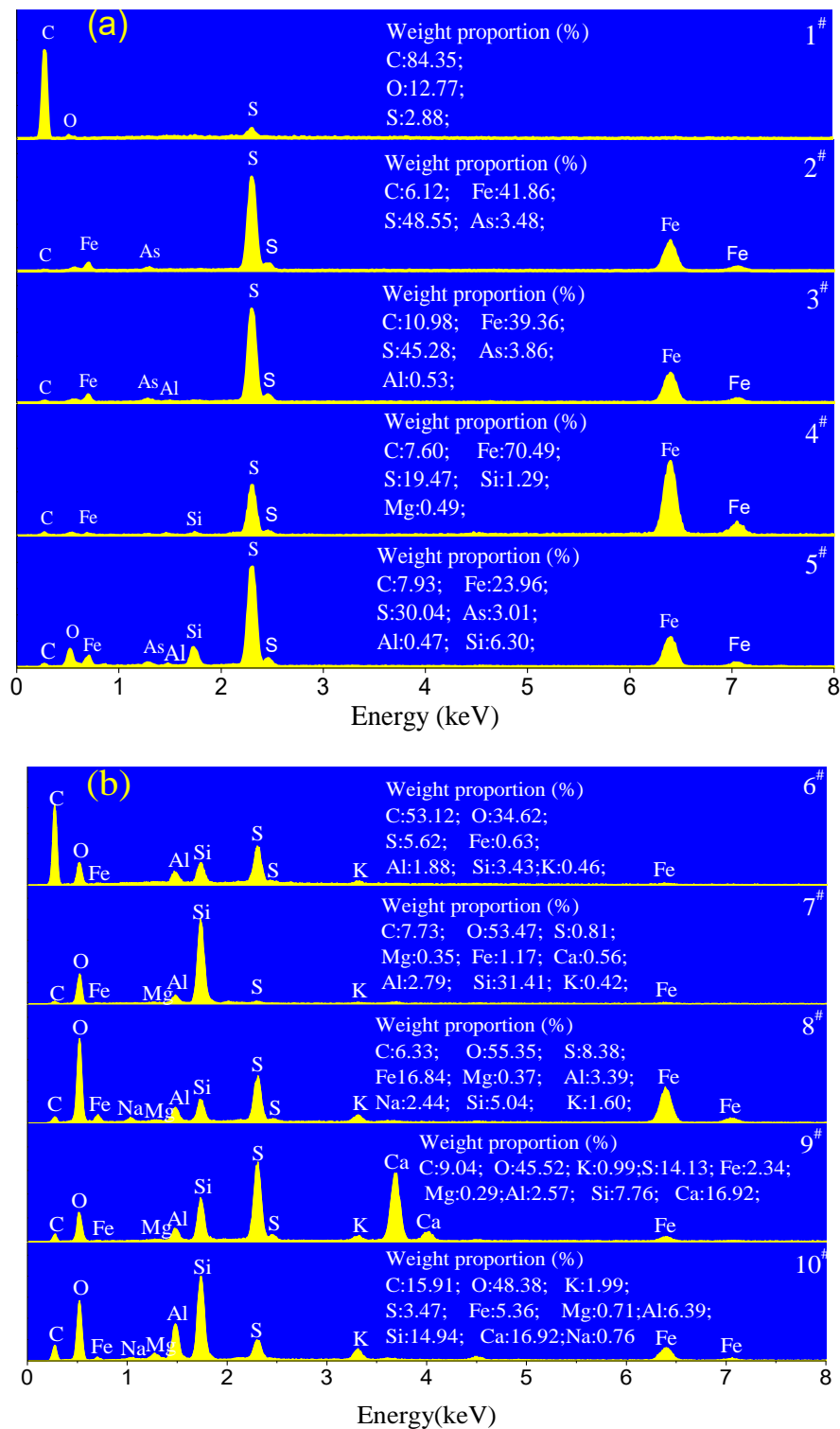


Fig. 6. Energy dispersive spectrum of flotation concentrate (a) before POX; (b) after POX

### 3.2. Leaching

#### 3.2.1. Empirical model and statistical analysis

The experimental design is shown along with the actual and predicted value in Table 5. The analyses of variance (ANOVA) and response surfaces were performed using the Design Expert software. The optimum preparation conditions were estimated through regression analysis and three-dimensional (3D) response surface plots of the independent variables and each dependent variable.



Table 5. Experimental design and results of actual and predicted value

Run no.	A:[S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ], mM	B:[Cu <sup>2+</sup> ], mM	C:[HA], mM	Au extraction, %	
				Actual value	Predicted value
1	100	0	0	13.31	8.37
2	100	0	0.25	17.47	14.44
3	100	0	0.5	23.71	19.05
4	350	0	0	42.22	47.57
5	350	0	0.25	46.43	52.57
6	350	0	0.5	50.21	56.10
7	600	0	0	44.41	42.90
8	600	0	0.25	48.02	46.82
9	600	0	0.5	51.31	49.27
10	100	25	0	22.24	25.38
11	100	25	0.25	27.72	30.61
12	100	25	0.5	31.95	34.37
13	350	25	0	73.26	73.27
14	350	25	0.25	78.06	77.41
15	350	25	0.5	80.61	80.09
16	600	25	0	79.24	77.28
17	600	25	0.25	84.42	80.35
18	600	25	0.5	83.21	81.95
19	100	50	0	7.75	9.40
20	100	50	0.25	12.59	13.77
21	100	50	0.5	15.34	16.69
22	350	50	0	72.13	65.97
23	350	50	0.25	74.63	69.26
24	350	50	0.5	75.79	71.10
25	600	50	0	74.24	78.66
26	600	50	0.25	76.78	80.88
27	600	50	0.5	78.11	81.63

Table 6. ANOVA results of quadratic model to predict the extraction of gold

Source	Squares	df	Mean Square	F-Value	P-Value	Significant
Model	18048.64	9	2005.405	96.19723	< 0.0001	*
A-	11133.3	1	11133.3	534.0533	< 0.0001	*
B-	1254.504	1	1254.504	60.17729	< 0.0001	*
C-	209.7152	1	209.7152	10.05983	0.0056	
AB	904.8033	1	904.8033	43.4025	< 0.0001	*
AC	13.9968	1	13.9968	0.671412	0.4239	
BC	8.619075	1	8.619075	0.413448	0.5288	
A <sup>2</sup>	2887.304	1	2887.304	138.501	< 0.0001	*
B <sup>2</sup>	1633.17	1	1633.17	78.34151	< 0.0001	*
C <sup>2</sup>	3.226667	1	3.226667	0.15478	0.6989	
Residual	354.3957	17	20.8468			
Cor Total	18403.04	26				
Adj R-Squared	0.97997					
Pred R-Squared	0.94900					
Adeq Precision	26.4793					

The tests results were fitted by Design-expert 8.0.6.1. The final equation representing the gold extraction rate (R) in terms of coded factors was obtained as functions of [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] concentration (A), [Cu<sup>2+</sup>] concentration (B) and [HA] concentration (C):

$$R = 77.41 + 24.87 \times A + 8.35 \times B + 3.41 \times C + 8.68 \times AB - 1.08 \times AC - 0.85 \times BC - 21.94 \times A^2 - 16.50 \times B^2 - 0.73 \times C^2 \quad (6)$$

The ANOVA was used to determine the significance of the leaching tests model and its adequacy and also to determine the effects of the factors (Table 6). The ANOVA demonstrated that the equation adequately represented the real relationship between the significant variables and the value of gold extraction. The Model F-value of 96.20 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. P-values were used for the significance test of parameters. Simply, the null hypothesis is rejected when the P-value is smaller than the selected confidence level (e.g. 95%,  $\alpha = 0.05$ ) (Yazici and Deveci, 2014). P-value less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, A<sup>2</sup>, B<sup>2</sup> are significant model terms.

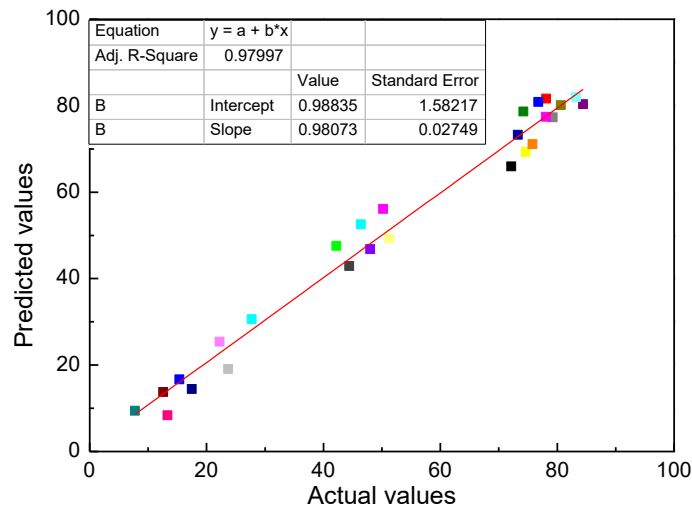


Fig. 7. Plot of the experimental and predicted responses

As shown in Fig. 7, the intercept and slope of fitting straight is 0.98835 and 0.98073 respectively (the value is very close to 1) indicated that good correlation between the test and the standard estimations, R<sup>2</sup> value indicates 97.997% of the experimental data can be explained by the model thereby supporting the anticipated model (Ha et al., 2014). In addition, in the present work, the distinction amongst R<sup>2</sup> and R<sup>2</sup>-Adjust values was under 0.03097 (Table 6) which proves that the model did not contain irrelevant terms.

### 3.2.2. Effects of factors and 3D response surface plot

Fig. 8 shows the perturbation plot of the effects of the main factors on the leaching value of gold. The effect of all the factors were compared at a particular point in the design space. The steep slope or high curvature in a factor indicates that the gold extraction is sensitive relatively to that factor. It can be seen from Fig. 8 that the ranking of the significant factors is as follows: A > B > C.

As shown in Fig. 10, the influence of factors on the gold extraction could be better understood by using 3D response surface plots and contours. The plots could give some information about the primary impact of three factors. The 3D response surface graphs for the relationship between two factors when the other factors were held at optimal levels for the gold leaching value are indicated in Fig. 10(a-c).

Compared with Cu<sup>2+</sup> and HA, thiosulfate has a significant effect on the gold leaching value. As indicated in Fig. 10(a), gold extraction has a quicker growth rate with the increase in the thiosulfate concentration in the initial range of 0 to 0.4 M. This is because excess thiosulfate amount increases the rate at which cupric tetramine is reduced to cuprous thiosulfate. When the concentration was beyond the range, gold extraction began to increase slowly. On the one hand, the concentration of thiosulfate was adequate relatively. Similar phenomena have been found in the gold-cyanide system, the reaction not being controlled cyanide diffusion oxygen diffusion and other test parameter at high cyanide concentrations. On the other hand, secondary reaction could be produced, such as some degradation of

thiosulfate ions to tetrathionate at high thiosulfate concentrations, as shown in Eq. (7) (Camelino et al., 2015).

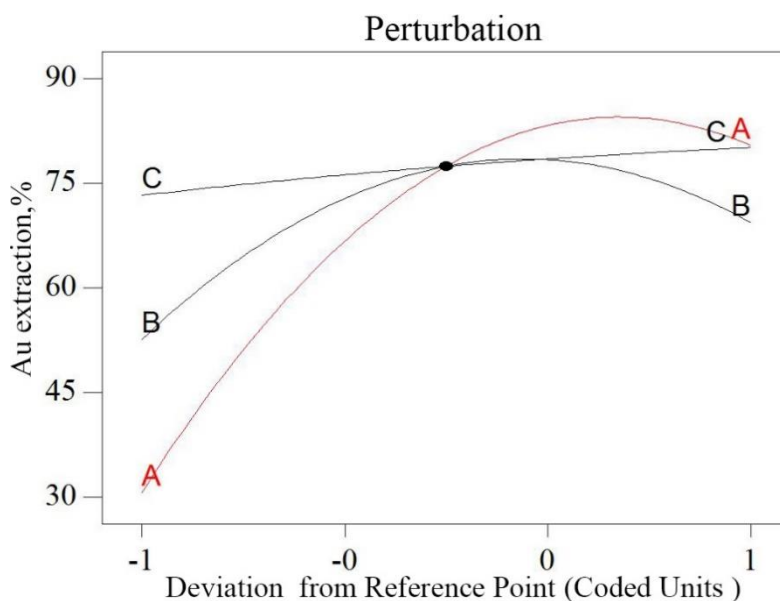


Fig. 8. Perturbation plot showing the relative significance of factors on Au extraction

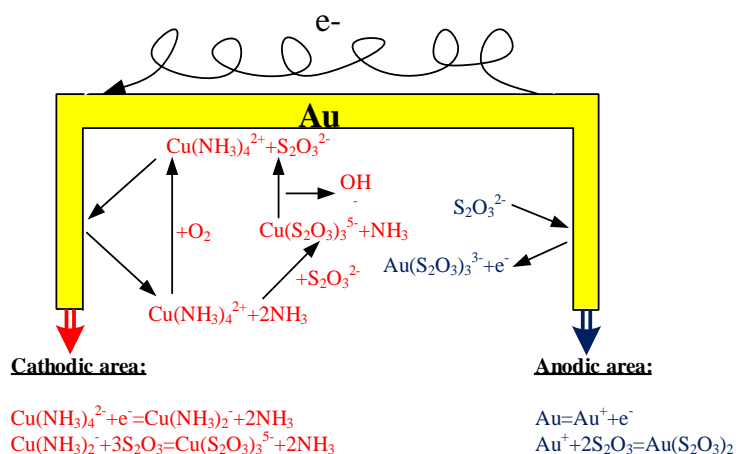
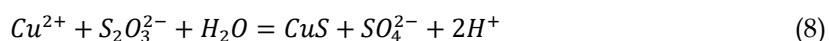
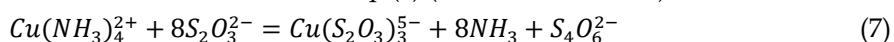


Fig. 9. Behaviour of gold in an ammoniacal-thiosulfate system

The leaching behavior of gold in an ammoniacal-thiosulfate system is shown in Fig. 9. It indicates that gold reacts with the thiosulfate and produces  $\text{Au}(\text{S}_2\text{O}_3)_3^{2-}$ , and thiosulfate plays the role of a leaching agent.  $\text{Cu}^{2+}$  as the oxidizing agent and catalyst facilitates the leaching process. The interactions between thiosulfate and  $\text{Cu}^{2+}$  has been determined in previous research. Thus, it is necessary to consider the influence of thiosulfate and  $\text{Cu}^{2+}$  on the process of gold leaching. RSM plays an important role in selection of the most appropriate initial concentration of thiosulfate and  $\text{Cu}^{2+}$ . As shown in the Fig. 10(b),  $\text{Cu}^{2+}$  could not induce the gold to dissolve, but the process of gold leaching by thiosulfate could be strengthened by  $\text{Cu}^{2+}$ . The process of chemical reaction is shown in Fig. 9. The gold extraction decreases in a high concentration of  $\text{Cu}^{2+}$ . It is widely considered that thiosulfate was oxidized by  $\text{Cu}^{2+}$ , since excessive  $\text{Cu}^{2+}$  elevated the pulp potential and accelerated the thiosulfate oxidation subsequently. The processes may take place via the reaction as shown in Eq. (8) (Aazami et al., 2014).



As shown in Table 6 and Fig. 8(c), the linear and quadratic effect of the concentration of HA was statistically not significant, and the interaction effect between HA and thiosulfate or  $\text{Cu}^{2+}$  was not

significant too. Combined with the results shown in Fig. 10(c), HA has a positive effect to increase the gold extraction; however, the effect was weak. HA could weaken the interaction between thiosulfate and  $\text{Cu}^{2+}$ , and decrease the decomposition of thiosulfate. Furthermore, HA avoided passivation species from coating the surfaces of gold and gold-bearing minerals, and increased the extraction of gold (Lampinen et al., 2015).

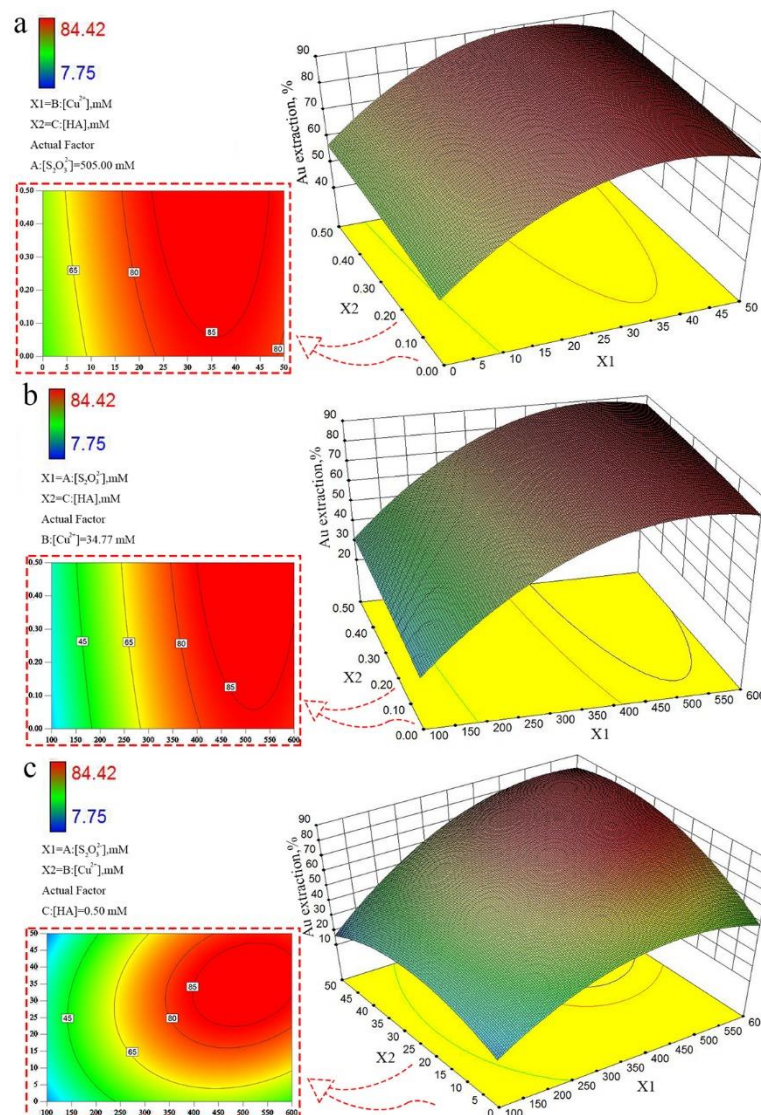


Fig. 10. 3D response surface plots and contours showing the effect of two factors on the extraction value of gold; (a)  $[\text{Cu}^{2+}]$  and  $[\text{HA}]$ ; (b)  $[\text{S}_2\text{O}_3^{2-}]$  and  $[\text{HA}]$ ; (c)  $[\text{S}_2\text{O}_3^{2-}]$  and  $[\text{Cu}^{2+}]$

### 3.2.3. Optimization

The Au extraction was optimized to obtain the maximum extraction rate using the Design Expert software. Fig. 10 demonstrates the trend of factors for movement towards the optimal point. Optimum initial reagent concentrations were 505.00 mM for  $[\text{S}_2\text{O}_3^{2-}]$ , 34.77 mM for  $[\text{Cu}^{2+}]$ , and 0.50 mM for  $[\text{HA}]$ . The predictive Au extraction value in these conditions was about 88.93%. To confirm the validity of the model, two confirmation experiments were carried out at the predicted optimum conditions. The results of the flotation concentrate of gold (using POX and without POX) leaching tests are shown in Fig. 11. After pre-oxidation, the leaching effect increased significantly, and the gold leaching rate was only 21.22% by direct leaching. The results indicate that the mineral crystals were destructive and the gold encapsulated in the sulfide was exposed. The part of gold could react with thiosulfate and dissolved into the solution; thus, the recovery of gold was increased. Further, the confirmatory experiments indicated the optimized values of the parameters were successfully established by the software. Under

optimal conditions, the value of Au extraction achieved was about 86.21% and exceeded the results in other process parameters.

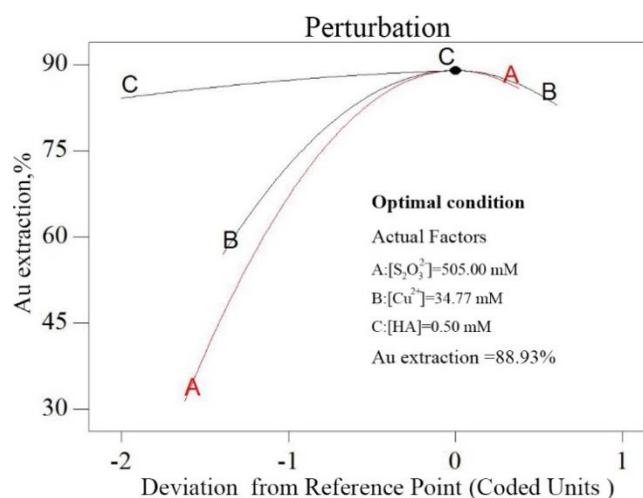


Fig. 11. Perturbation plot showing the optimal conditions of factors to obtain the maximum extraction of gold

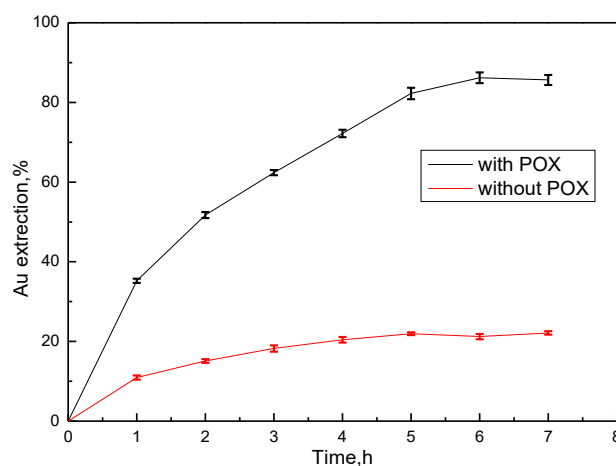


Fig. 12. The results of leaching tests (with or without POX) in the optimal conditions

#### 4. Conclusions

In this study, the process of pressure oxidation-thiosulfate leaching of flotation concentrate of gold was investigated. After POX, pyrite/arsenopyrite dissolved at a high oxidation potential, and the surface of minerals became very rough while the structure of some particles was destroyed. The content of element O increased, but that of S and Fe decreased distinctly. Pyrite was oxidized to jarosite and gangue mineral such as quartz and organic carbon were hardly changed.

For leaching tests, RSM was used to optimize and investigate the influence of the important factors. The result of ANOVA indicated that the leaching tests model is significant, and a good correlation between the test results and the standard estimations is obtained. The ranking of the significant factors is  $[S_2O_3^{2-}] > [Cu^{2+}] > [HA]$ . The interactions are significant between  $[S_2O_3^{2-}]$  and  $[Cu^{2+}]$ . HA as an assist, which can positive effect to increase the gold extraction. Based on the results of RSM, the optimum process parameters were 505.00 mM for  $[S_2O_3^{2-}]$ , 34.77 mM for  $[Cu^{2+}]$ , and 0.50 mM for  $[HA]$ . With these conditions, the Au extraction value achieved was about 86.21%, which proved that the model was useful in the leaching tests.

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## References

- AAZAMI, M.; LAPIDUS, G.T.; AZADEH, A. 2014. *The effect of solution parameters on the thiosulfate leaching of Zarshouran refractory gold ore*. International Journal of Mineral Processing, 131: 43-50.
- AZIZI, A.; PETRE, C.F.; OLSEN, C.; LARACHI, F. 2010. *Electrochemical behavior of gold cyanidation in the presence of a sulfide-rich industrial ore versus its major constitutive sulfide minerals*. Hydrometallurgy, 1013-4: 108-119.
- CAMELINO, S.; RAO, J.; PADILLA, R.L.; LUCCHI, R. 2015. *Initial studies about gold leaching from printed circuit boards PCB's, of waste cell phones*. Proc Mat Sci, 9: 105-112.
- CHAN, T., M. COLLINS, J. DENNETT, J. STIKSMA, J. JI, R. KALANCHEY, AND R. BEREZOWSKY. 2015. *Pilot plant pressure oxidation of refractory gold-silver concentrate from Eldorado Gold Corporation's Certej Project in Romania*. Can Metall Quart, 54: 252-260.
- CHEN, A.R.; WANG, S.X.; ZHANG, L.B.; PENG, J.H. 2015. *Optimization of the microwave roasting extraction of palladium and rhodium from spent automobile catalysts using response surface analysis*. International Journal of Mineral Processing, 143: 18-24.
- DONG, Z.; HAN, Y.; GAO, P. 2015, *Research Status on Chemical Pre-oxidation for Carlin- type Gold Ore*. METAL MINE, 12.: 92-97.
- ELORZA-RODRIGUEZ, E.; NAVA-ALONSO, F.; JARA, J.; LARA-VALENZUELA, C. 2006. *Treatment of pyritic matrix gold-silver refractory ores by ozonization-cyanidation*. Minerals Engineering, 191: 56-61.
- HA, V.H.; LEE, J.C.; HUYNH, T.H.; JEONG, J.; PANDEY, B.D. 2014. *Optimizing the thiosulfate leaching of gold from printed circuit boards of discarded mobile phone*. Hydrometallurgy, 149: 118-126.
- KARAMANEV, D.; MARGARITIS, A.; CHONG, N. 2001. *The application of ore immobilization to the bioleaching of refractory gold concentrate*. International Journal of Mineral Processing, 621-4: 231-241.
- KE, Y.; SHEN, C.; MIN, X.B.; SHI, M.Q.; CHAI, L.Y. 2017. *Separation of Cu and As in Cu-As-containing filter cakes by Cu<sup>2+</sup>-assisted acid leaching*. Hydrometallurgy, 172: 45-50.
- KHOSRAVI, R.; AZIZI, A.; GHAEDRAHMATI, R.; GUPTA, V.K.; AGARWAL, S. 2017. *Adsorption of gold from cyanide leaching solution onto activated carbon originating from coconut shell-Optimization, kinetics and equilibrium studies*. J Ind Eng Chem, 54: 464-471.
- LAMPINEN, M.; LAARI, A.; TURUNEN, I. 2015. *Ammoniacal thiosulfate leaching of pressure oxidized sulfide gold concentrate with low reagent consumption*. Hydrometallurgy, 151: 1-9.
- LEHMANN, M.N.; O'LEARY, S.; DUNN, J.G. 2000. *An evaluation of pretreatments to increase gold recovery from a refractory ore containing arsenopyrite and pyrrhotite*. Minerals Engineering, 131: 1-18.
- LINDSTROM, E.B.; SANDSTROM, A.; SUNDKVIST, J.E. 2003. *A sequential two-step process using moderately and extremely thermophilic cultures for biooxidation of refractory gold concentrates*. Hydrometallurgy, 711-2: 21-30.
- LUO, X.; LI, J.; ZHOU, W.; FENG, J.; MA, R. 2015. *Research on the Dosage of Sodium Cyanide Used for Leaching Refractory Gold Ore after Pressure Oxidation Procedur*. Precious Metals, 04: 51-55+62.
- LI, F.; DING, D.X.; HU, N.; PENG, Z.C.; CHEN, W. 2014. *Roasting oxidation-thiosulfate leaching of gold from refractory gold-bearing sulfur concentrates*. The Chinese Journal of Nonferrous Metals, 24.: 831-837.
- LI, J.; DABROWSKI, B.; MILLER, J.D.; ACAR, S.; DIETRICH, M.; LEVIER, K.M.; WAN, R.Y. 2006. *The influence of pyrite pre-oxidation on gold recovery by cyanidation*. Minerals Engineering, 199: 883-895.
- LI, Q.C.; LI, D.X.; QIAN, F.J. 2009. *Pre-oxidation of high-sulfur and high-arsenic refractory gold concentrate by ozone and ferric ions in acidic media*. Hydrometallurgy, 971-2: 61-66.
- LI, Y.L.; LI, D.X.; LI, J.B.; WANG, J.; HUSSAIN, A.; JI, H.; ZHAI, Y.J. 2015. *Pretreatment of cyanided tailings by catalytic zonation with Mn<sup>2+</sup>/O<sup>3-</sup>*. J Environ Sci-China, 28: 14-21.
- MOHAMMADI, E., POURABDOLI, M., GHOBEITI-HASAB, M., AND HEIDARPOUR, A. 2017. *Ammoniacal thiosulfate leaching of refractory oxide gold ore*. International Journal of Mineral Processing 164, 6-10.
- NUNAN, T.O.; VIANA, I.L.; PERXOTO, G.C.; ERNESTO, H.; VERSTER, D.M.; PEREIRA, J.H.; BONFATTI, J.M.; TEIXEIRA, L.A.C. 2017. *Improvements in gold ore cyanidation by pre-oxidation with hydrogen peroxide*. Minerals Engineering, 108: 67-70.
- SHEN, Z.H.; ZHANG, Q.; MAO, S.; YE J.J. 2013. *Leaching of micro-disseminated gold ore deposit in guizhou by thiosulfate*. Mining And Metallurgical Engineering, 33-5.: 85-90.

- XU, B.; YANG, Y.B.; JIANG, T.; LI, Q.; ZHANG, X.; WANG, D. 2015. *Improved thiosulfate leaching of a refractory gold concentrate calcine with additives*. *Hydrometallurgy*, 152: 214-222.
- YAZICI, E.Y.; DEVECI, H. 2014. *Ferric sulphate leaching of metals from waste printed circuit boards*. *International Journal of Mineral Processing*, 133: 39-45.
- ZHU, P.; ZHANG, X.J.; LI, K.F.; QIAN, G.R.; ZHOU, M. 2012. *Kinetics of leaching refractory gold ores by ultrasonic-assisted electro-chlorination*. *Int J Min Met Mater*, 196: 473-477.