

# KINETICS OF GOLD LEACHING FROM SULFIDE GOLD CONCENTRATES WITH THIOSULFATE SOLUTION<sup>①</sup>

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## ABSTRACT

The reaction process for leaching gold from sulfide gold concentrates containing copper with ammonia-ammonium thiosulfate solution containing copper(II) can be divided into initial stage and later stage of reaction. Initial stage of reaction is controlled by interface reaction. Later stage of reaction is controlled by diffusion process of reaction through solid products layer. Whole leaching process is under the control of corrosion reaction of pyrite bearing gold. Action of ammonium sulfate in the system is probably as follows: (1)  $\text{NH}_4^+$  and  $\text{NH}_3$  forms a buffer solution; (2)  $\text{SO}_4^{2-}$  ion inhibits the oxidation and decomposition of  $\text{S}_2\text{O}_3^{2-}$  ion.  $\text{Cu}^{2+}$  ion in the system acts as an oxidant and oxygen makes the  $\text{Cu}^{2+}$  regenerate.

**Key word:** thiosulfate gold leaching kinetics sulfide ore

## 1 INTRODUCTION

Kinetics of leaching gold with an ammonia-ammonium thiosulfate containing copper have been researched early<sup>[1-6]</sup>. Someone thought that the process is controlled by diffusion process; another one thought that it is controlled by chemical reaction. But the following points are consistent.

(1) Copper ion catalyze this reaction of dissolution gold.

(2) Precipitation of element sulfur and sulfide of copper occur during the process of leaching gold.

(3) Adding sulfite to the thiosulfate solution can inhibit the precipitation of  $\text{S}^0$  and  $\text{CuS}$  or  $\text{Cu}_2\text{S}$ . Gong Qian *et al* have proposed leaching gold by thiosulfate-sulfate solutions instead of the thiosulfate-sulfite solution<sup>[7]</sup>. This text just researched the kinetic charac-

teristic of leaching gold from sulfide ores with thiosulfate solution containing sulfate ion to understand the effects of sulfate ion on the kinetics of leaching gold. The minerals bearing gold in the sulfide ores are mainly pyrite and chalcopyrite. Dissolution of pyrite is the most difficult. So that, basic characteristics of gold dissolution process should be with relation to basic characteristic of dissolution process of pyrite. The article tries to illustrate the kinetics data of leaching gold from sulfide ores by oxidation law of pyrite.

## 2 EXPERIMENTAL

### 2.1 Samples

Samples used were sulfide gold concentrate containing copper from float workshop and 80% of the ore, containing  $57.1 \text{ g} \cdot \text{t}^{-1}$

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Au, 50.2 g · t<sup>-1</sup> Ag. passed through 200 mesh.

By microscopic examination, the gold concentrate used in experiments contained; pyrite, chalcopyrite, bornite, malachite and limonite.

Gangue minerals are mainly quartz and calcite. The minerals bearing-gold are mainly pyrite, chalcopyrite and bornite.

## 2.2 Experimental Instruments and Methods

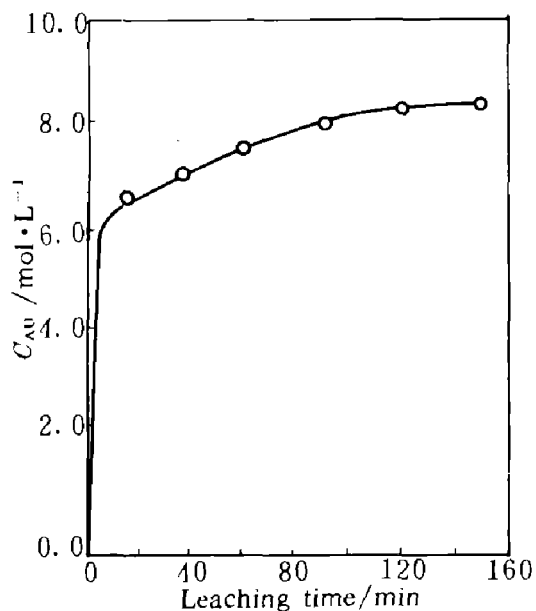
The tests were conducted in a four-necked, 500 mL round bottom flask. The stirring was accomplished using a direct drive over-head motor. Definite amount air was introduced for all the tests. The flask with four-necked was immersed in a thermostat with a variety of temperature within  $\pm 1$  °C. The air was first pre-saturated by passing through a solution with the same NH<sub>4</sub>OH concentration as experimental solution.

At the start of an experiments, after putting leaching solution into a four-necked flask which fixed up the thermostat and the solution was stirred and heated for 10 min, reaching the required temperature of solution, air was introduced, then ore was added. After 5 min, first solution sample was taken out to analyse gold concentration in solution, subsequently took one sample every 15 min and took out 2 mL each time. The analysis results of solution was compared with one of the residue leached, the relative error was about  $\pm 10\%$ , sometimes could reached about  $\pm 15\%$ . The leaching rate mentioned later were calculated using the results in leached solution and extraction percent were calculated using analysis results in residue leached after experiment. All reagents used in experiments were reagent grade. As there is element sulfur in the ammonium thiosulfate in solid state, the

(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution was filtered after preparation for use in experiments. Besides gold, silver and copper were also analyzed in the same sample solution during the experiments. Silver was analyzed with AAS. Experimental results about gold are only described in this paper, about silver and copper will be described in other article.

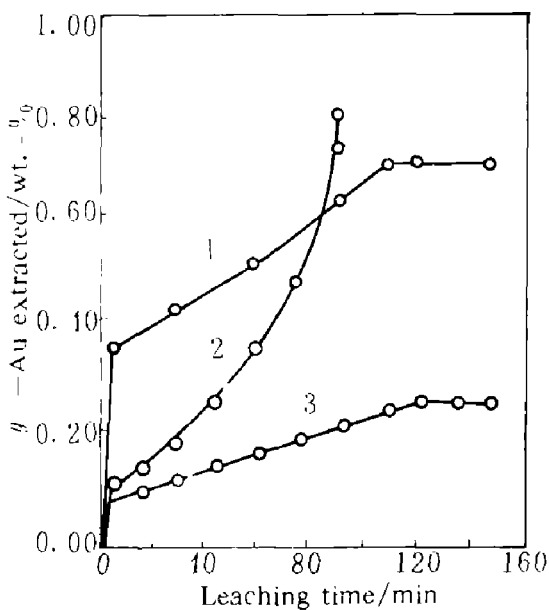
## 3 EXPERIMENTAL RESULTS

General outline of dissolving gold from sulfide gold concentrates with an ammonia- ammonium thiosulfate- ammonium sulfate solution are shown in Fig 1. It can be seen clearly from Fig. 1 that the processes of dissolution gold can be divided into two stages. Dissolution of gold is quite fast at the initial five minutes. Then the dissolution rate of gold remarkably decreases. Gold extraction reached maximum within 1.5 ~ 2 h. The results calculated are shown in Fig. 2. It can be seen from the leach model in accordance with various leaching model and the data in Fig. 1 that the process of leaching Au can also be divided into two stages. Dissolution process of gold from sixth minute to the end of gold dissolution can be described by diffusion process of reactants through solid reaction products layer, i. e. the model 3 in the Fig. 2. Although model 1 looks like to be suitable; after observing carefully, it was found that model 1 is unsuitable, because after 60 minutes, model 1 deviated from straight line. If the ore grain used in experiments is more fine, model 1 more remarkably deviated from straight line, as shown Fig 3. so that, model 3 was adopted. According to Fig. 2, all the experimental data were expressed by  $K_5$  and  $K_3$ .  $K_5$  is average dissolution rate (mol · s<sup>-1</sup>) of gold in initial 5 min.  $K_3$  is a constant (min<sup>-1</sup>) evaluated according to the model



**Fig. 1 Gold concentration  $C_{Au}$  in solution varies with time**

0.7 mol·L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; 1.0 mol·L<sup>-1</sup> NH<sub>4</sub>OH;  
L:S=6:1; 0.5 mol·L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; 50 °C;  
850 min<sup>-1</sup>; 1g·L<sup>-1</sup> Cu<sup>2+</sup>; 0.7L·min<sup>-1</sup> air



**Fig. 2 Leaching model**

1— $y = 1 - (1 - a)^{1/3} \times 10^2$ ; 2— $y = \frac{1}{3} \ln(1 - a) - [1 - (1 - a)^{1/3}] \times 10^2$ ; 3— $y = 1 - \frac{2}{3a} - (1 - a)^{2/3} \times 10^2 = K_3 t \times 10^2$   
 $a$ —extraction/wt.-%;  $t$ —time/min

3. It includes molar volume of reactants, diffusion coefficient of the reactants in solid

products layer, concentration of reactant, grain radius of ore and reaction time was usually 1.5 h.

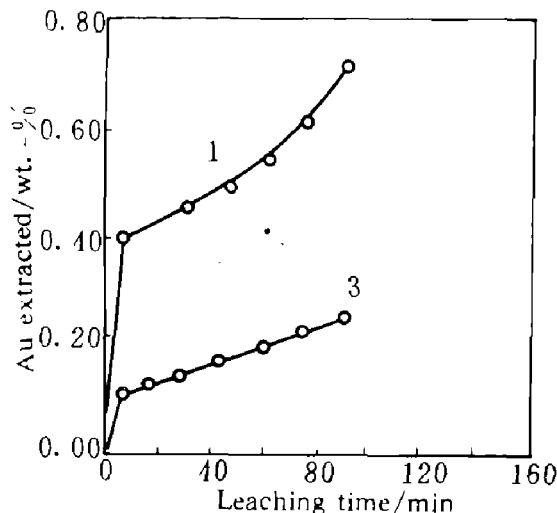
**3.1 Effect of Ammonium Sulfate Concentration**

The results were shown in Table 2. Leaching rate of gold and extraction of gold increased by adding ammonium sulfate to leaching solution. The results were shown as:

**Table 1 Effects of ammonium sulfate concentration**

(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> /mol·L <sup>-1</sup>	$K_3 \times 10^2$ /mol·s <sup>-1</sup>	$K_3 \times 10^4$ /min <sup>-1</sup>	Au extraction /wt.-%
0.6	1.0	1.37	89.0
0.2	1.2	1.53	91.0
0.5	1.3	1.63	91.0
0.8	1.5	1.71	96.3
1.0	1.4	1.73	95.8

\* 0.7 mol·L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; L:S=6:1; 850 min<sup>-1</sup>; 1.0 mol·L<sup>-1</sup> NH<sub>4</sub>OH; 50 °C; 90 min.; 1.0 g·L<sup>-1</sup> Cu<sup>2+</sup>; 0.7L·min<sup>-1</sup> air, particle size < 300 mesh



**Fig. 3 Leaching model**

The meaning of curves 1, 3 and other conditions are the same as those in Fig. 2.

$K_3 \propto [(NH_4)_2SO_4]^{0.12}$ . After adding ammonium sulfate, basic characteristic of leaching gold process do not vary, i. e.

whole leaching process can be all divided into two stages whether adding ammonium sulfate or not. Over high concentration of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in solution is disadvantageous to leaching gold.

### 3.2 Effects of Stirring Velocity

The relation of stirring velocity and leaching rate can be shown as  $K_5 \propto 9.3 \times 10^{-9} \times \omega^{1/2}$ ,  $K_s \propto 1.1 \times 10^{-1} \times \omega^{1/2}$ , where  $\omega$  is stirring velocity ( $\text{min}^{-1}$ ) which has a little effect on dissolution of gold indicates that effect of liquid phase diffusion process was in existence.

### 3.3 Effects of Temperature

Changing temperature from 20 C to 60 C, leaching rate and gold extraction increased as the temperature increased. But the increment value was not large. Active energy for  $K_5$  is 3.1  $\text{kJ} \cdot \text{mol}^{-1}$  and active energy for  $K_s$  is 10  $\text{kJ} \cdot \text{mol}^{-1}$ . The effect of temperature on  $K_s$  is more remarkable than for  $K_5$ .

### 3.4 Effects of Ammonium Thiosulfate Concentrations

Experimental results can be shown as  $K_5 \propto [(\text{NH}_4)_2\text{S}_2\text{O}_3]^{0.05}$ ,  $K_s \propto [(\text{NH}_4)_2\text{S}_2\text{O}_3]^{0.21}$ . The effects of thiosulfate concentration on  $K_5$  was very small. This showed that the  $\text{S}_2\text{O}_3^{2-}$  acts only as complex agent of gold and did not join the controlled-step reaction, because the complex action of thiosulfate ion with gold was faster.

### 3.5 Effects of Ammonia Concentration

Preliminary experiments showed that gold extraction obtained from leaching sulfide gold concentrate using ammonium thiosulfate solution containing  $\text{Cu}^{2+}$  without free

ammonia was very poor. After adding 0.5 mol.  $\text{L}^{-1}$  of ammonia to the leaching solution, gold extraction increased remarkably, but if continuing to add ammonia, increasing extraction was not very remarkable,  $K_5 \propto [\text{NH}_4\text{OH}]^{0.2}$ ;  $K_s \propto [\text{NH}_4\text{OH}]^{1.53}$ .

### 3.6 Effects of Cupric Ion Concentration

Experimental results conforms the following relation:  $K_5 \propto [\text{Cu}^{2+}]^{0.69}$ ,  $K_s \propto [\text{Cu}^{2+}]^{0.76}$ .

The effect of air amount on  $K_5$  is less and the effect on  $K_s$  is remarkable.  $K_s \propto Q_{\text{O}_2}^n$ , where  $Q_{\text{O}_2}$  is air amount entered.  $n$  is a constant about 0.5.

### 3.7 Effects of Ore Particles Size

The ore particle size is the average value of the diameter of upper-level screen mesh and next level screen mesh. The effects of ore size can be sum up as  $K_5 = 4 \times 10^{-9} \times 1/a$ ,  $K_s = 3.11 \times 10^{-6} \times 1/a \times 1/H$ , where  $\bar{a}$  is average diameter,  $H$  is thickness of solid products layer.  $K_5$  was reduced with ore size increase. The effect of reduced ore size on  $K_s$  have two aspects: (1) increasing diffusion interface, which is favourable to reaction; (2) increasing initial reaction rate and solid reaction products which is unfavourable for later reaction. If the effect of any factor in those two factors is larger, the experimental results reflects just the effect of that factor.

## 4 DISCUSSION

### 4.1 Main Reactions Series

In the leaching system, besides a series of decomposition and oxidation reactions of  $\text{S}_2\text{O}_3^{2-}$ , it also included mainly oxidation, dissolution and complex reactions of gold

and oxidation reactions of gold-bearing minerals etc. gold-bearing minerals are mainly chalcopyrite and pyrite. Decomposition of pyrite is the most difficult one. If leaching out gold contained in pyrite is required, first of all, pyrite should be decomposed. By analysis using scanning electron microscope, besides a part of gold exists in free state, most of the gold in ore is inlaid in pyrite. So that, kinetics process of leaching gold with thiosulfate solution should be controlled by corrosion reaction of pyrite. Results detected by X-ray diffraction indicate that the peak values of chalcopyrite in leached-residue were lower than in raw ore<sup>11</sup>, suggesting that chalcopyrite underwent destroy during leaching. Though the change of the peak values of pyrite was not markable, it can be seen from photographs, taken by scanning electron microscope. There are clear scar on leached-pyrite granula. The granula of pyrite has changed into loose and porous one. Sulfide gold concentrates containing iron first were leached using ammonia-ammonium thiosulfate solution containing copper and then leached residues were detected by X-ray diffraction. The results showed the peak value of pyrite in leached-residue is lower than raw ore, which indicates corrosion process of pyrite exist surely in leaching. Though oxidation of pyrite is as difficult as oxygen acting as oxidant, in local region with high copper concentration can be corroded as cupric ion acting as oxidant.

4.2 Initial Reaction and Later Reaction

The initial leaching reaction in the first 5 min should be the dissolving reaction of gold which included a part of free gold and gold exposed on surface of granulas of chalcopyrite, bornite and pyrite due to be oxidized. Then the granulas surface were cov-

ered by solid reaction products. The reaction enters into reaction stage of diffusion control of reaction reagents going through solid reaction products. Solid products probably includes ferric oxide and element sulfur yielded due to oxidation of chalcopyrite and pyrite and cupric sulfide precipitated from copper in solution. Reaction reagent diffusing inwards through products layer reacts with chalcopyrite and pyrite not be oxidized, gold is exposed out and then is dissolved. It also included that reaction reagent through microporous diffused to interior of ore particles reacts with free gold inside of ore granules. Stirring velocity has effects on both of  $K_3$  and  $K_4$ . But it was not so remarkable as the reaction is completely controlled by diffusion. This indicated that both of  $K_3$  and  $K_4$  included minor effect to liquid diffusion process.

1.3 Relationship Between Reaction Rate and Various Variables

The relationship between reaction rate and various variable can be summarized as following:

$$\begin{aligned}
 k_3 &= k_1 \times [Cu^{2+}]^{0.69} \times [NH_4OH]^{0.2} \\
 &\quad \times [(NH_4)_2SO_4]^{0.14} \\
 &\quad \times [(NH_4)_2S_2O_8]^{0.05} \\
 &\quad \times w^{1.2} \times 1/a \times e^{-31/RT} \\
 K_4 &= k_2 \times [NH_4OH]^{1.53} \\
 &\quad \times [Cu^{2+}]^{0.76} \\
 &\quad \times [(NH_4)_2S_2O_8]^{0.21} \\
 &\quad \times [(NH_4)_2SO_4]^{0.19} \\
 &\quad \times Q_{O_2} \times 1/a^2 \times 1/H \\
 &\quad \times w^{1.2} \times e^{-10/RT}
 \end{aligned}$$

$K_3$  with air amount entered is independent. So the oxidant in system can only be cupric ion. Action of oxygen only make cupric ion regeneration. So the effect of oxygen is not remarkable within short time. But when the leaching lasted for longer time,

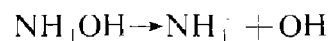
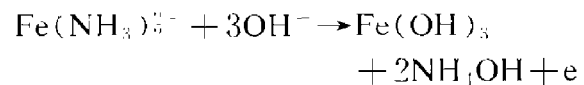
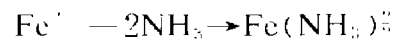
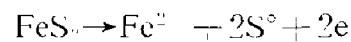
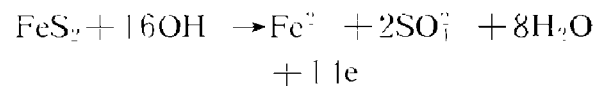
the effect of oxygen got more remarkable. Therefore, air amount entered remarkably influenced on  $K_5$ . Diffusion species of initial stage of reaction is cupric ion and diffusion of later stage of reaction include probably cupric ion and oxygen molecule. According to  $K_5 \propto [\text{NH}_4\text{OH}]^{1.5} \times [\text{NH}_3]^{0.76}$ , it can be explicitly indicated that the oxidant is  $\text{Cu}(\text{NH}_3)_2^{2+}$ . The proportion of cupric ion with  $\text{NH}_3$  is 1 : 2 in  $\text{Cu}^{2+} + 2\text{NH}_3 = \text{Cu}(\text{NH}_3)_2^{2+}$ . But it should be  $\text{Cu}(\text{NH}_3)_4^{2+}$  on the basis of the result obtained from thermodynamic analysis. Effect of  $\text{S}_2\text{O}_3^{2-}$  concentration on  $K_5$  was less. It showed that rate-controlling reaction does not involve  $\text{S}_2\text{O}_3^{2-}$ . Effects of both  $\text{NH}_4\text{OH}$  and  $\text{NH}_4^+$  probably were the result of the effect of pH. Leaching gold only using ammonium thiosulfate solution containing copper without  $\text{NH}_3$ , gold extraction was very low. If adding 0.5 mol  $\cdot \text{L}^{-1}$  ammonia into the leaching solution, gold extraction rises greatly. But if continuing to add ammonia to the leaching solution, increase of gold extraction was not remarkable. Change of pH in leaching solution is just as this trend. The pH of ammonium thiosulfate solution free from ammonia is lower but as adding a small amount of ammonia into the solution, pH of the solution remarkably increases. Because  $\text{NH}_4^+$  and  $\text{NH}_3$  composes a buffer solution  $\text{NH}_4\text{OH} = \text{OH}^- + \text{NH}_4^+$ , if adding ammonia into the solution continuously, change of pH of the solution is very small. The effects of pH on gold extraction is probably resulted from the effect of pH on the corrosion of pyrite. The reference [8] indicated at fixed potential the anodic current ( $i$ ) of pyrite in ammonia-ammonium sulfate solutions can be related with  $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{SO}_4$  and temperature using the following equation:

$$i = k \times [\text{NH}_4\text{OH}]^{0.18} \times [(\text{NH}_4)_2\text{SO}_4]^{0.11}$$

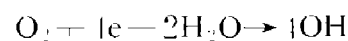
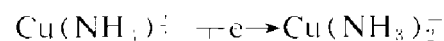
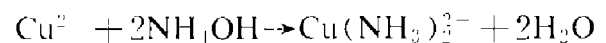
$$\propto \exp(-12.1/RT)$$

This is similar to the relation of  $K_5$  with these variables in the present paper, indicating the close relationship of gold dissolution with the corrosion of pyrite. The reaction order of  $(\text{NH}_4)_2\text{SO}_4 > 0$ , indicates another effect of  $\text{NH}_4^+$ . That is increasing ammonia concentration with an increase of  $\text{NH}_4^+$  concentration. The increase of  $\text{NH}_3$  is advantageous to the stabilization of  $\text{Fe}(\text{NH}_3)_4^+$ ,  $\text{Cu}(\text{NH}_3)_2^+$ ,  $\text{Au}(\text{NH}_3)_2^+$ , facilitating the corrosion of pyrite and the dissolution of gold. It was also indicated in reference [10] and [11] that  $\text{SO}_4^{2-}$  in ammonium sulfate can inhibit the oxidation decomposition of  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$ .

The relationship of the anodic current of pyrite with various variables were explained in reference [8] by means of the following reaction equations:



$\text{Cu}(\text{NH}_3)_2^+$  in ammonia-ammonium thiosulfate solution acts as an oxidant and oxygen makes the  $\text{Cu}(\text{NH}_3)_2^+$  regenerate. Therefore the following equations should exist in solution:



The relation of the dissolution rate of gold can be qualitatively explained using these reaction equations. The effect of ammonium sulfate on  $K_5$  is smaller than thiosulfate, indicating the complex reaction of  $\text{S}_2\text{O}_3^{2-}$  with Au influences the late dissolution of gold.

## 5 CONCLUSIONS

(1) Reaction process of leaching sulfide gold concentrates with ammonia-ammonium thiosulfate-ammonium sulfate solution containing copper can be divided into an initial stage and a later stage of reaction. The initial stage of reaction is under the control of interface reaction; the later stage of reaction is under the control of diffusion process of reactents through solid reaction products layer. All of two reactions stage included minor effect of liquid phase diffusion process. Diffusion component in initial stage of reaction is  $\text{Cu}^{2+}$  ion; in the later stage of reaction also contained oxygen besides  $\text{Cu}^{2+}$  ion.

(2) Cupric ion acts as oxidant, oxygen makes  $\text{Cu}^{2+}$  ion regeneration. Action of  $\text{S}_2\text{O}_3^{2-}$  is only to be a complex agent of gold and does not join in reaction of control step.

(3) Action of ammonium sulfate;

(a)  $\text{NH}_4^+$  and  $\text{NH}_4\text{OH}$  composes a buffer solution;

(b)  $\text{SO}_4^{2-}$  ion inhibites oxidation and decomposition of  $\text{S}_2\text{O}_3^{2-}$  ion.

(4) Leaching gold processes from sulfide gold concentrates with ammonia-ammonium thiosulfate-ammonium sulfate containing copper controlled by corrosion reaction

of pyrite.

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