DISSOLUTION KINETICS OF GOLD AND SILVER IN CYANIDATION①

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ABSTRACT

The dissolution kinetics of gold and silver cyanidation of Cu–Au sulfide concentrate has been investigated at ambient temperature in consideration of effects of various parameters, such as particle size of ores, hydrodynamics of the process and initial cyanide concentration as well as oxygen partial pressure. The experimental data are mathematically treated with an approach based on the shrinking core model. A phenomenological expression describing the rate and rate constants for cyanidation of the concentrate is developed from the treatment. The dissolution of gold and silver is explained by an electrochemical mechanism in which the rate determining step is the diffusion of cyanide and dissolved molecular oxygen through a porous layer formed during the minerals dissolutions.

Key words: dissolution kinetics Cu–Au sulfide concentrate cyanidation electrochemical mechanism

1 INTRODUCTION

Since it was found one hundred years ago, the conventional cyanidation technology for gold and silver recovery has been used efficiently in industries due to its economy and process simplicity. The cyanidation process of gold extraction has been dramatically improved in terms of increased efficiency, shorted operating duration, reduced costs and cyanide consumption in the results of considerable efforts and great progress in fundamental researches and its interaction with industrial activities.

The overall reaction of gold cyanidation is given by

$$\mathrm{Au+2CN^-+O_2/22+H_2O=} \\ \mathrm{Au(CN)_2^-+OH^-+H_2O_2/2} \qquad (1)$$

and a microscopic expression for the rate of gold cyanidation has been derived as

$$Rate=\frac{2AD_{\mathrm{CN}}D_{\mathrm{O}}[\mathrm{CN}^-][\mathrm{O}_2]}{\delta(D_{\mathrm{CN}^-}[\mathrm{CN}^-]+4D_{\mathrm{O}}[\mathrm{O}_2])} \qquad (2)$$

where D_{CN^-}, D_{O} are the diffusion coefficients of CN^- and O_2 respectively, δ is the thickness of the diffusion film, and A the surface area of reacting gold[1,2].

For an ore leaching process, however, the kinetics of gold cyanidation depends on more experimental parameters. This paper is one of

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the basic studies on leaching of gold and silver from a Cu–Au sulfide concentrate, and reports the results of systematic investigation on the kinetics of direct cyanidation.

2 METHOD

Table 1 shows the elemental analysis and mineral compositions of the Cu–Au concentrate used in the study.

Table 1 Elemental analysis and mineral compositions of the concentrate

Element	Cu	Fe	Pb	Zn	S
wt–%	9.3	36.4	1.84	0.77	30.7
Element	As	Ni	Hg	Au / mg	Ag / mg
wt–%	0.024	0.004	0.0018	55.0~56.3	150
Mineral	$CuFeS_2$	ZnS	PbS	FeAsS	FeS_2
wt–%	20.7	1.15	2.12	0.0033	11.9
Mineral	$FeS_{1.1}$	Silicate			
wt–%	37.0	20.9			

where all chemicals used were reagent grade and deionized water was used for the preparation of all solutions.

The experiments were performed at ambient temperature in a stirred baffled glass reactor with a capacity of about 0.5 L. pH of the leaching solutions was measured and recorded with a combined glass electrode on- line during the experiments. Determination of the metal concentration in leaching solutions were carried out using a Perkin–Elmer Model 603 atomic absorption spectrophotometer. The concentration of oxygen and free CN in liquors was determined as described in ref. [3].

3 RESULTS

Preliminary experiments showed that the solid / liquid ratio seems not to play a significant role in the leaching of Au and Ag from the concentrate. A ratio of 10 g concentrate / 100 mL leaching solution was used throughout the study. The effect of the hydrodynamics in the leaching process is shown in Fig. 1.

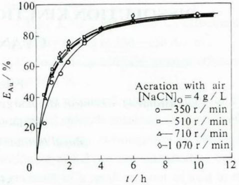

Fig.1 Effect of stirrer rotation speed and leaching time (t)on gold dissolution(E_{Au})

It is seen that the stirring speed has very little influence on the leaching and is fixed at 700 rpm during the kinetic study. The effect of the particle size on the dissolution of gold is also insignificant, as shown in Fig. 2. Grinding the concentrate to particles through 120 mesh is used in all experiments.

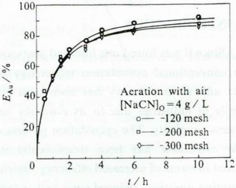

Fig.2 Effect of particle size and leaching time (t) on gold dissolution(E_{Au})

The influence of the initial concentration of cyanide on the dissolution of gold and silver has been studied in detail. The experiments were performed with aeration, i.e. bubbling air during leaching. The results are plotted in

Fig.3.

The effect of the aeration of the solution is investigated by bubbling with pure oxygen, mixture of oxygen and compressed air, as well as without any aeration. The quantification of the oxygen relative concentration is respectively given as 1.0, 0.50, 0.21 and 0.01. The experimental results are given in Fig. 4.

The concentration of free cyanide in solution is measured and plotted in Fig.5 as a function of leaching time for experiments at different initial cyanide concentrations.

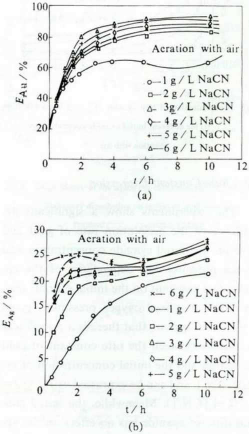

Fig.3 The dissolution of gold (E_{Au}) and silver (E_{Ag}) at different initial concentration of cyanide

(a)—gold; (b)—silver

(Aeration with air)

4 DISCUSSION

4.1 *The Kinetic Model of Leaching*

In order to determine the appropriate rate control model, the experimental data are mathematically treated using the regression method in the basic considerations of a shrinking core model, non-porous solid particle and kinetic equations derived for three different rate controlling steps. The rate equations are described as follows.

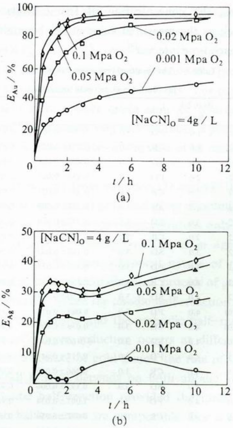

Fig.4 Effect of oxygen partial pressure on gold and silver dissolution(E_{Au}, E_{Ag})

(a)—gold; (b)—silver

(Aeration with O_2, air and without aeration)

General rate equation $y = R_o t$
Rate control step according as $y = R_o t$
Film diffusion $\alpha / C_{free\,\mathrm{CN}}$;
Chemical reaction $[1-(1-\alpha^{1/3})] / C_{free\,\mathrm{CN}}$;
Diffusion through a porous layer
$[1-3(1-\alpha)^{2/3}+2(1-\alpha)] / C_{free\,\mathrm{CN}}$.

Here t–leach time, h; $C_{free\mathrm{CN}}$– the concentration of free CN, $\mathrm{kg/m^3}$; α–dissolved fraction of gold; R_0–apparent rate constant, $\mathrm{L \cdot g^{-1} \cdot h^{-1}}$.

The slopes and correlation coefficients estimated with different equations are listed in Table 2 for gold dissolution. In these calculations, the concentration of free cyanide is taken as the measured value at the beginning of each time interval[4]

Table 2 The results of regression calculation for control model of gold dissolution

$[O_2]$	$[\mathrm{NaCN}]_o$ / $\mathrm{Kgm^{-3}}$	RCM	LT / h	R_o	R^2
0.2	1.0	FD	3.0	1.09 ± 0.10	0.9765
0.2	1.0	CR	3.0	0.633 ± 0.043	0.9534
0.2	1.0	SD	3.0	0.407 ± 0.009	0.9985
0.2	2.0	FD	3.0	0.635 ± 0.045	0.9854
0.2	2.0	CR	3.0	0.307 ± 0.021	0.9908
0.2	2.0	SD	3.0	0.274 ± 0.009	0.9965
0.2	3.0	FD	3.0	0.372 ± 0.019	0.9848
0.2	3.0	CR	3.0	0.189 ± 0.008	0.9936
0.2	3.0	SD	3.0	0.189 ± 0.005	0.9986
0.2	4.0	FD	3.0	0.307 ± 0.012	0.9898
0.2	4.0	CR	3.0	0.159 ± 0.011	0.9905
0.2	4.0	SD	3.0	0.159 ± 0.008	0.9932
0.01	4.0	FD	3.0	0.089 ± 0.010	0.9648
0.01	4.0	CR	3.0	0.036 ± 0.009	0.9898
0.01	4.0	SD	3.0	0.0160 ± 0.0001	0.9998
0.5	4.0	FD	3.0	0.717 ± 0.041	0.9903
0.5	4.0	CR	3.0	0.466 ± 0.037	0.9815
0.5	4.0	SD	3.0	0.193 ± 0.006	0.9983
1.0	4.0	FD	3.0	1.047 ± 0.074	0.9854
1.0	4.0	CR	3.0	0.682 ± 0.050	0.9841
1.0	4.0	SD	3.0	0.214 ± 0.015	0.9907

Where RCM–rate control model; LT–limit of leach time used in estimation of kinetic model; FD–liquid film diffusion control; CR–chemical reaction control; SD–diffusion control through a porous layer; R^2—correlation coefficient.

The maximum value of correlation coefficients listed in Table 2 indicates that the mechanism given by the equation of diffusion control through a porous product layer is valid for gold dissolution during the initial period of cyanidation. This rate process model is used throughout the subsequent data processing.

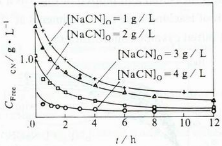

Fig. 5 **Concentration of free cyanide ($C_{free\mathrm{CN}}$) Vs. leach time (t) for different initial cyanide concentrations, aeration with air**

4.2 *Rate Constant Expression*

The experiments show a significant dependence of the dissolution rate of gold and silver on the initial cyanide concentration and oxygen pressure. The dependence of the apparent rate constant on the initial cyanide concentration at a fixed oxygen pressure is given in Fig. 6. It appears that there is a non–linear correlation between the rate constant of gold dissolution and the initial concentration of cyanide $[\mathrm{CN}^-]$, and can be expressed as $R_0(\mathrm{Au}) = k_1 / (1+k_2[\mathrm{CN}^-])$. Meanwhile, the initial concentration of cyanide has no effect on the apparent rate constants of silver dissolutions. Fig.7 shows the dependence of the initial rate constants of silver dissolution on the relative concentration of dissolved oxygen concentration by an equation as $R_0 = k_3[O_2] / (1+k_4[O_2])$.

The overall expression for initial apparent rate constant R_0 can be derived by combining the relative equations as

$$R_0(\mathrm{Au}) = \frac{p_1[\mathrm{O}_2]}{p_2[\mathrm{CN}^-] + [\mathrm{O}_2] + p_3} \quad (4)$$

$$R_0(\mathrm{Ag}) = \frac{p_1[\mathrm{O}_2]}{p_2 + [\mathrm{O}_2]} \quad (5)$$

4. 3 *Dissolution Mechanism*

The analysis of the kinetic data for gold dissolution indicates that the rate limiting step is diffusion through a porous (product) layer. On the other hand, the cyanidation reaction does not point out the formation of any solid product. In fact, there is a significant difference between dissolution of gold disk and concentrate cyanidation. The gold in the concentrate is partly closed by matrix minerals, e.g. sulfides, and indirectly contacted with solutions. During the cyanidation of the concentrate, moreover, there are several reactions that may cause the formation of a solid product layer. Some electrochemical measurements supported the assumption on the formation of basic and intermediate complexes, such as $\mathrm{AuOH}_{abs}^{[7]}$, $\mathrm{AuCN}_{abs}^{[8]}$, absorbed on the gold surface. The layer may also be a result of a precipitation of iron oxide, e.g. FeOOH[9], or passivation from copper oxide and / or hydroxyl film[10]. These may very well establish a porous layer on gold surfaces in the view of its real action.

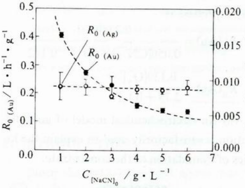

Fig.6 Dependence of the apparent rate constant (R_o) of gold and silver dissolution on initial cyanide concentration($C_{[\mathrm{NaCN}]}$ aeration with air

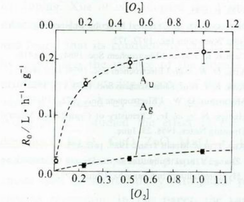

Fig.7 Dependence of the apparent rate constant (R_o) of gold and silver dissolution on oxygen partial pressure $[\mathrm{O}_2]|[\mathrm{NaCN}]_0 = 4$ kg / m^3

It is clear from equation (3) and (4) that the reaction rate of gold and silver dissolution depends on the oxygen concentration only at low oxygen concentration. This is in agreement with the electrochemical nature of the process. In the electrochemical process of gold dissolution, where the anodic half–reaction of gold cyanidation and the cathodic half–reaction of oxygen reduction occurs at different sites on surface of gold grains, the rate of the overall process depends on both anodic and cathodic half–reaction provided the rates of both half-reaction are comparable. For a fixed high cyanide concentration, the dissolution reaction is determined by the cathodic half reaction at low oxygen partial pressure. In this case, the rate is controlled by diffusion of oxygen molecules and increases with increasing oxygen partial pressure. It finally approaches a nearly constant value for which the rate becomes proportional to the free CN concentration, indicating a shift from predominantly cathodic to predominantly anodic half reaction.

The plots of the leached fraction of silver vs. time (Fig. 3b) show a maximum and a minimum. It was reported that the dissolved silver takes part in precipitations, and that Ag may form solid AgCN at the low pH, low concentration of CN^- and high concentration of oxygen[10]. Equilibrium calculations[11] shows that Ag_2O or AgO may be formed while free CN is decreased during leaching, as given by the following reaction equations.

$$Ag(CN)_2^- + OH^- = \frac{1}{2}Ag_2O(s) + 2CN^- + \frac{1}{2}H_2O \quad (5)$$

$$Ag(CN)_2^- + \frac{1}{4}O_2 + OH^- = AgO(s) + 2CN^- + \frac{1}{2}H_2O \quad (6)$$

The phenomenon of decline of silver content in leach liquors may result from absorption or precipitation with sulfides in the concentrate as

$$2Ag(CN)_2^- + S^{2-} = Ag_2S(s) + 4CN^- \quad (7)$$

The reaction may progress towards the left as if the concentrations of sulfide in liquors is as high as 10^{-8} mol / L, and the cyanide is as low as 0.01 mol / L.

5 CONCLUSIONS

The following conclusions may be obtained from this study:

(1) A rate controlling model where the diffusion of cyanide ion and oxygen molecules through a porous layer on the surface of reacting grains appears to be suitable for describing the cyanidation of gold and silver in the Cu–Au concentrate. The phenomenological equations of rate process can be expressed as

$$y = \frac{1 - 3(1-\alpha)^{2/3} + 2(1-\alpha)}{C_{freeCN}} = R_0 t$$

(2) The effect of the initial concentration of cyanide and oxygen concentration on the dissolution rate of gold and silver is pronounced. The apparent rate constant can be respectively expressed as

$$R_0(Au) = \frac{0.231[O_2]}{0.056[CN^-] + [O_2] - 0.142}$$

$$R_0(Ag) = \frac{0.139[O_2]}{2.78 + [O_2]}$$

(3) An electrochemical model of gold dissolution is satisfactorily used to explain the kinetics of cyanidation of the concentrate.

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