A Kinetic Study Of Gold Leaching In CuBr₂-NaBr System

Encinas-Romero Martín A.*, Tiburcio-Munive Guillermo and Yánez-Montaño Mireya

Department of Chemical Engineering and Metallurgy, University of Sonora, Hermosillo, Sonora 83000, México *maencinas@ig.uson.mx

maencinas@iq.uson.mx

Abstract— The CuBr₂-NaBr system was applied as an alternative for the leaching of gold. The variables analyzed were agitation, temperature, cupric bromide concentration and ion bromide concentration. Two mechanisms of dissolution were apparent depending on temperature. The results show that the CuBr₂-NaBr system is suitable to dissolve gold by a complex dissolution Kinetic.

Keywords— Gold; Cupric Bromide; Sodium Bromide; Rotating Disc Study

I. INTRODUCTION

The mining of gold ores has led to intense researching in recent years, the reason for this is obvious, this material continues to be in high demand, and as a result its price is maintained at a reasonably high level and relative stability. This circumstance makes interesting the treatment of gold deposits that were once considered uneconomic, also there are continuing concerns regarding traditional processes.

For about 120 years, cyanidation has been the standard method for gold recovery. The cyanide process advantages lie in its low cost and technological simplicity; however, cyanidation has certain disadvantages, which are its high toxicity and its slow kinetics. Furthermore, cyanide solutions are not efficient for the leaching of certain classes of gold ores, which are considered to be refractory. Moreover, inhibition of the dissolution of gold, caused by certain metal ions and other species, which form ionic complexes with cyanide, reduces the availability of this ion for gold dissolution and increases its consumption [1].

There is therefore a need to develop safer technology for gold extraction. One of the most obvious trends is the use of halide chemistry; it was considered the most promising method for recovering gold, until the discovery of the cyanidation. Among the halogens, bromine has received increased attention in a number of investigations [2-7].

Using systems halide/Halogen gold mining has been documented in several studies. The use of bromine in the leaching of gold ores was first patented by Sheaffer. This process was modified by Himman, who discovered the need to use an excess of bromine and feedback during the dissolution of gold. The bromination process was analyzed by Cassel, who used an alkaline medium to recover bromine as bromate salts and produce bromine in situ by acidification. Subsequently Putman and Fink picked up the theme and patented the application of chlorine to the in-situ production of bromine. They also described the benefit of excess bromide and chloride in the process. Dadgar showed gold extraction with bromine provides a significant increase in the rate of extraction, particularly for gold concentrates. The same study demonstrated that conventional techniques can be used for solvent extraction, ion exchange, activated carbon and carburizing for gold recovery of the solution [1-3].

There is very little information on the use of cupric bromide as a leaching agent. Among the most important works lies the Hoepfner-Chambers process for extracting copper from copper sulfide concentrates, where a mixture of cupric bromide (CuBr₂) and sodium bromide (NaBr) proved to be an effective leaching agent. This reactive mixture has also been used for the extraction of silver, which showed that it requires high concentrations of bromide ions to maintain the silver in solution. Furthermore, this mixture was used for the leaching of lead from galena, showing a much faster kinetic of reaction system as compared with ferric chloride to the same conditions [4-8].

Therefore, this research proposes the use of cupric bromide as an alternative lixiviant for gold extraction in the presence of sodium bromide, evaluating the most suitable conditions for the process such as temperature, concentration of cupric bromide, concentration of bromide ions and stirring speed, thereby demonstrating the technical feasibility of the use of these agents in the dissolution of precious metals.

II. EXPERIMENTAL

Leaching was carried out in a 500 mL glass separable flask with a fitted lid having four necks. The center hole of the lid was used for accommodation of a stirring rod holding a gold disc (0.195 cm² in area and 0.5 cm thick, reagent grade 99.99%). Previously casted into 2.5 cm diameter araldite cylinders. Before every run the disc was grounded and polished to insure exposure of a new clean surface. The other three necks were used for the introduction of nitrogen gas into the leaching solution, thermometer and condenser, respectively.

Temperature was closely controlled by a heating jacket and a solid state controller. High purity nitrogen gas was passed through the solution for 30 minutes prior to each experiment to purge dissolved oxygen. A 10 mL sample of solution was withdrawn at predetermined intervals and the lead concentration was established by the atomic absorption spectrophotometry. For every sample withdrawn, an equal volume of barren solution was returned to the reaction flask.

III. RESULTS AND DISCUSSION

Figure 1 shows the effect of stirring speed on the dissolution rate of gold in CuBr₂-NaBr leaching system. In this figure, a linear variation of the amount of gold dissolved vs. time is seen, which is typical in rotating disk experiments. It can also be seen that with increasing agitation speed, the dissolution rate of gold increases as well, due to the decrease in the boundary layer effects. This behavior is accentuated in the range between 500 and 1000 rpm, after which this increase is stabilized.

Figure 2 shows the Levich graph which indicates a linear increase of the rate constant of gold dissolution vs. the square root of disc angular velocity, indicating under such conditions that gold dissolution is apparently controlled by diffusion.



Fig. 1. The Effect of stirring speed on the dissolution rate of gold in CuBr₂-NaBr leaching system. [CuBr₂] = 0.5 M, [NaBr] = 0.5 M, $T = 80^{\circ}$ C. (a) 100 rpm, (b) 500 rpm, (c) 700 rpm, (d) 1000 rpm, (e) 1500 rpm, (f) 1800 rpm.

Figure 3 shows the effect of cupric bromide concentration on the dissolution rate of gold in CuBr₂-NaBr leaching system. It can be observed that when the concentration of cupric bromide was increased, the dissolution rate of gold increased too. At concentrations lower than 0.05 M, the dissolution rate of gold is very slow. At concentrations between 0.5 and 0.75 M, the dissolution rate of gold increases and it reaches its greatest effect.

To determine the order of reaction with respect to the cupric bromide, the natural logarithm of the rate constant of gold dissolution vs. the natural logarithm of the corresponding cupric bromide concentration was plotted. The resulting graph is shown in Figure 4. The value of the slope indicates a reaction order of 1.5 with respect to cupric bromide. This reaction order is indicative of a complex reaction mechanism. This result may be explained due to the combined effects between bromide and cupric ions, which cannot be separated experimentally since the concentration of this leaching agent must vary.



Fig. 2. Graph of Levich equation. $[CuBr_2] = 0.5 M$, [NaBr] = 0.5 M, $T = 80^{\circ}C$.



Fig. 3. The effect of cupric bromide concentration on the dissolution rate of gold in $CuBr_2$ -NaBr leaching system. [NaBr] = 0.5 M, $T = 80^{\circ}$ C, rpm = 500. (a) 0.05 M, (b) 0.25 M, (c) 0.5 M, (d) 0.75 M.

To evaluate the exclusive effect of bromide ion concentration on the dissolution rate of gold in CuBr₂-NaBr leaching system, the total concentration of the bromide ion in solution was taken into account, which was varied from 0.005 to 0.75 M, maintaining constant the concentration of cupric ion in 0.5 M. The experimental results in Figure 5, show an increase in the dissolution rate of gold with the increase to bromide ion concentration, being more significant for 1.75 M. Also the graph in Figure 6 shows a reaction order of 1.0 with respect to the bromide ions.



Fig. 4. Graph to obtain the order of reaction with respect to the cupric bromide, for the dissolution of gold in $CuBr_2$ -NaBr leaching system. [NaBr] = 0.5 M, $T = 80^{\circ}C$, rpm = 500.



Fig. 5. The effect of bromide ion concentration on the dissolution rate of gold in $CuBr_2$ -NaBr leaching system. $T = 80^{\circ}C$, rpm = 500. (a) 1.005 M, (b) 1.05, (c) 1.25 M, (d) 1.5 M, (e) 1.75 M.

The effect of temperature on the dissolution rate of gold in CuBr₂-NaBr leaching system is shown in Figure 7. The greatest dissolution of gold is achieved at a temperature of 90°C at a dissolution rate of 0.144 mg Au/min.cm². Comparing this result with the gold cyanide system, this is about eight times higher. However, an operating temperature of 80°C is proposed because the temperatures above this value appear to be not practical.

Figure 8 shows the Arrhenius plot which indicates that the dissolution of gold in $CuBr_2$ -NaBr leaching system has two different control mechanisms, according to the operating temperature. In the range of high temperature (70-90°C), the activation energy resulted in a value of 5.23 kcal/mol, which indicates a control mechanism in the diffusion and mixed limit. For the low temperature range (40-60°C), the activation energy resulted in a value of 18.3 kcal/mol, which indicates a chemical reaction control. The

transition temperature between both mechanisms is about 62°C.



Fig. 6. Graph to obtain the order of reaction with respect to the bromide ion, for the dissolution of gold in CuBr₂-NaBr leaching system. $T = 80^{\circ}$ C, rpm = 500.



Fig. 7. Temperature effect on the dissolution rate of gold in $CuBr_2$ -NaBr leaching system. [$CuBr_2$] = 0.5 M, [NaBr] = 0.5 M, rpm =500. (a) 40°C, (b) 50°C, (c) 60°C, (d) 70°C, (e) 80°C, (f) 90°C.

The Eh-pH diagram for the Au-Br-H₂O system shown in Figure 9, indicates that in the region of pH 2 to 4, which comprises the pH range evaluated during this experimentation, the thermodynamically stable species are $AuBr^{2-}$ and $AuBr^{4-}$. The potential range for $AuBr^{2-}$, turns out to be smaller (0.68-0.81V) compared to that presented for the species $AuBr^{4-}$, (0.81-1.34 V).

The dissolution of gold in CuBr₂-NaBr leaching system can be associated with an electrochemical process where the anodic process indicated in the following reactions may occur:

$$Au^+ + 2Br^-$$
 → $AuBr_2^- + e$ $E^\circ = 0.96 V$
 $Au^{+3} + 4Br^-$ → $AuBr_4^- + 3e$ $E^\circ = 0.85 V$



Fig. 8. Arrhenius plot to obtain the activation energy for the dissolution of gold in CuBr₂-NaBr leaching system. [CuBr₂] = 0.5 M, [NaBr] = 0.5 M, rpm = 500.



Fig. 9. Eh-pH diagram for Au-Br system in aqueous solution. [species] = 10^{-5} M, T = 25° C

In both reactions the standard electrode potential is very high, which leads to the need for a strong oxidizing agent, in the process of dissolution of gold in CuBr₂-NaBr leaching system, cupric ions act as an oxidizing agent, while the bromide ions act as a complexing agent. Also, bromide ions exist in excess in this solution, which gives stability to the dissolved gold in the system. Sodium ions apparently are not involved in the reaction.

IV. CONCLUSIONS

The results of this research indicate that solutions of $CuBr_2$ -NaBr are suitable to dissolve gold. The dissolution rate of gold is strongly influenced by the stirring speed, temperature, and concentration of

bromide and cupric ions, resulting in a complex kinetic process, which involves a change of control mechanism with a transition temperature of about 62°C.

REFERENCES

[1] J.B. Hiskey, and P.H. Qi. "Leaching and Electrochemical Behavior of Gold Iodide Solutions, Part I. Dissolution Kinetics," [SME/AIME, Littleton, Colorado, pp. 1-8, 1990].

[2] T. Trand, and A. Davis. "Fundamental Aspects on the Leaching of Gold in Halide Media," [EPD Congress TMS/AIME, Warrendale, Pennsylvania, pp. 99-113, 1992].

[3] R.H. Sergent, B. Pesic, J.A. Quijano, and F.X. Salazar. "Recovery of Gold Using Bromine. Recuperación de Oro usando Bromo," [Memorias de la XX Convención Internacional de Minería AIMMGM. AC. Acapulco, Gro., México, pp. 726-730, 1993]

[4] A. Dadgar, and J. Howarth. "Advances in Bromine Gold Leaching Technology," [EPD Congress, TMS/AIME, Warrendale, Pennsylvania, pp. 126-136, 1992]

[5] A. Dadgar. "Extraction and Recovery of Gold from Concentrates by Bromine Process," Precious Metals, pp. 227-240, 1989.

[6] B. Pesic, and R.H Sergent. "Reaction Mechanism of Gold Dissolution with Bromine," Metallurgical Transaction B. Volume 24B, pp.419-431, 1993.

[7] G.W McDonald, H. Darus, and S.H. Larger. "A Copper Bromide Process for Hydrometallurgical Recovery of Copper," Hydrometallurgy, 24, pp. 291-316, 1990.

[8] M.A. Encinas-Romero, and S. Aguayo-Salinas. "Cupric Bromide Process for the Leaching of Galena," [Second Conference in Hydrometallurgy, Republic of China, pp. 227-230, 1993].