A Study on the Copper Effect on gold leaching in copper-ethanediamine-thiosulphate solutions

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Abstract. A simple, fast and sensitive square-wave voltammetry (SWV), cyclic voltammetry (CV) and tafel method for the determination of various factors of gold in thiosulphate solution in this paper. We present our study on the effect of copper(II) on the leaching of gold in thiosulphate solutions. The current study aims to establish the interaction of copper in the leaching process by electrochemical method.

1. Introduction
Thiosulphate gold leaching has received considerable attention as an alternative technology to the cyanidation of gold ores due to environmental reasons [1-2]. But the high consumption is the major problems in thiosulphate leaching due to containing copper. Copper(II) ions and ammonia play a key role in leaching process [1,4]. The consumption of thiosulphate was largely reduced when ethylenediamine was used as an additive for the leaching of gold by Xia [3], however, the effects on gold leaching in thiosulphate solutions should be monitored and controlled which hasn’t been reported by electrochemical method such as square wave voltammetry(SWV) and Cyclic voltammetry(CV) in copper-ethane diamine-thiosulphate solutions, we present our study on the effect of ethylenediamine ammonia addition and copper(II) on the leaching of gold in thiosulphate solutions. The current study aims to establish the interaction of copper and thiosulphate in the leaching process by electrochemical method.

2. Experiments
2.1. Materials
The water used was deionized and distilled, all chemicals used were of analytical reagent grade. All experiments were performed at room temperature.

2.2. Analytical techniques
Electrochemical analysis was carried out using multifunctional microcomputer electrochemical analyser (mec-16, Jiangsu electro analysis instrument Co, Ltd), All potentials were measured relative to the saturated calomel electrode, a three-electrode system including Pt and Au working electrode, a Pt counter electrode and a saturated calomel electrode (SCE) as reference electrode was applied. The pH measurements were made using pH/Eh meter (PHS-25, Shanghai Precision & Scientific Instrument Co, Ltd).
2.3. Leaching
Leaching of pure gold was performed in a 250-ml reactor using a magnetic stirrer. The pure gold was suspended in the reactor with a nylon thread ensuring no contact with the reactor wall during leaching. The stirring speed was maintained at 250 min\(^{-1}\). All solutions were oxygenated to simulate the real situation.

3. Results and Discussion

3.1. Electrochemical behaviour of leaching solution

![Graph showing square wave voltammetry at two electrodes in the Cu\(^{2+}\)-ethane diamine-thiosulphate system](image)

**Fig. 1** Square wave voltammetry at two electrodes in the Cu\(^{2+}\)-ethane diamine-thiosulphate system \((C_{\text{en}}=0.05M, C_{\text{Cu}^{2+}}=0.004M, C_{\text{S}_2\text{O}_3^{2-}}=0.08M, \text{pH}=10)\)

As shown in Fig.1, it was seen that square wave voltammetry at two electrodes in solution of thiosulphate-copper(II)-ethylenediamine, curve 1 corresponds to a Pt electrode, curve 2 corresponds to a Au electrode, the difference behaviour between the two electrodes is that the peak at 0.2V only appears at a Au electrode which corresponds to the stripping peak of Au. The previous experiment has shown that the peak at -0.610V corresponds to the reduction peak of thiosulphate and the peak at -0.424V corresponds to the reduction peak of copper(II). It is found that the reduction peak potential shifts positive at a Au electrode compared to a Pt electrode indicating the reduction reactions more easily occur at a Au electrode, then the three peaks were used as characteristic peaks for analysing.
Fig. 2 Cyclic voltammogram at Au electrode in the \( \text{Cu}^{2+} \)-ethanediamine-thiosulphate system (\( C_{\text{en}} = 0.05 \text{M}, C_{\text{Cu}^{2+}} = 0.004 \text{M}, C_{\text{S}_2\text{O}_3^{2-}} = 0.08 \text{ M}, \text{pH} = 10 \))

Cyclic voltammetry (CV) in 0.1M thiosulphate+0.001 copper (II)+0.02M ethylenediamine solution at a Au working electrode was shown in Fig.2. The two nearly reversible redox peaks were shown in Fig.2, b peaks corresponds to the stripping peak of Au and c peaks corresponds the reduction peak of thiosulphate which is in concert with Fig.1, As can be seen in the Fig.1 there is a peak e which corresponds to the reduction peak of copper (II).

These signals help to analyze the corresponding ions for monitoring the leaching process.

3.2. Effect of copper(II) concentrations on the Au leaching

Fig. 3 The effect of the concentration of copper ion in the \( \text{Cu}^{2+} \)-ethane diamine-thiosulphate system (\( C_{\text{en}} = 0.05 \text{M}, C_{\text{Cu}^{2+}} = 0.004 \text{M}, C_{\text{S}_2\text{O}_3^{2-}} = 0.08 \text{ M}, \text{pH} = 10 \))

\( \text{Cu (NH}_3\text{)}_4^{2+} \) is easy to transfer into copper(II) hydroxide in the \( \text{Cu}^{2+} \)-ammonia-thiosulphate system, but \( \text{Cu (en)}_2^{2+} \) is more stable over a wide pH range in the \( \text{Cu}^{2+} \)-ethylenediamine-thiosulphate system. A broader pH range enables practical application in the \( \text{Cu}^{2+} \)-ethylenediamine-thiosulphate system.
Xia [3] reported Cu (en)$_3^{2+}$ and Eq. (1)-(6) was involved in the processing. It is found that Cu (S$_2$O$_3$)$_3^{5-}$ and Cu(en)$_2^{2+}$ is the primary species of copper in the leaching solution.

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\begin{align*}
2\text{en}^+ + \text{Cu}^{2+} &\rightarrow \text{Cu(en)}_2^{2+} \quad (1) \\
\text{Cu}^{2+} + 2\text{OH}^- &\rightarrow \text{Cu(OH)}_2 \quad (2) \\
\text{Cu}^{2+} + 4\text{OH}^- &\rightarrow \text{Cu(OH)}_4^{2-} \quad (3) \\
\text{Cu(en)}_2^{2+} + \text{OH}^- &\rightarrow \text{Cu(OH)}_2 + 2\text{en} \quad (4) \\
\text{en}^+ + \text{Cu}^+ &\rightarrow [\text{Cu(en)}]^+ \quad (5) \\
[\text{Cu(en)}]^+ + 3\text{S}_2\text{O}_3^{2-} &\rightarrow [\text{Cu(S}_2\text{O}_3)_3]^{5+} + \text{en} \quad (6)
\end{align*}
\]

The effect of varied copper(II) was studied by using square wave voltammetry under the condition of constant thiosulphate and ethylenediamine concentrations, the relationship between gold stripping peak current and the concentration of varied copper(II) is can be seen in the Fig.3. With increase of the concentration of copper(II), gold stripping peak current increases first and then decreases. It was found that gold stripping peak current reaches maximum when the the concentration of copper(II) is 0.0004mol/L. There is the best copper(II) concentration which contributed to maximum gold stripping peak current. As was known that the catalytic action of copper ions can speed up the dissolution of gold in thiosulphate solutions [4-5]. From the Fig.4, it appears opposite effects on gold stripping when the concentration of copper(II) is beyond 0.0004mol/L, the reason may be a reduced concentration of thiosulphate or passivation on gold surface.

**Fig. 4** The effect of the concentration of copper ion on copper ion current in the Cu$^{2+}$-ethane diamine-thiosulphate system (C$_{\text{en}}$ =0.05M, C$_{\text{S}_2\text{O}_3^{2-}}$=0.08 M, pH =10)

The relationship between reduction peak current of copper (II) and the concentration of copper(II) is can be seen in the Fig.4, the linear equation is y=0.6581x+0.00029 (R=0.9372) when copper(II) concentration is within the range of 0.002-0.01mol/L, in the optimal condition, the peak current of analytes had no a good linear relationship with the copper (II) concentration in a certain rang which shows that concentrations of reducible copper (II) ions reduced. The cause may be an insoluble substance informed. This indicates that the increase of copper ion concentration will have two effects:
on the one hand, it's good for gold leaching, on the other hand, it will consume too much reagent, therefore, it is necessary to control the concentration of copper ions.

4. Conclusion
The effects on gold leaching in thiosulphate solutions could be monitored and controlled by electrochemical method such as square wave voltammetry (SWV) and Cyclic voltammetry(CV) in copper-ethanediamine-thiosulphate solutions, the paper shows that with increase of the concentration of copper (II), gold stripping peak current increases first and then decreases; the increase of copper ion concentration will lead to an insoluble substance informed.

Acknowledgments
This work was financially supported by Yunnan Education Department(2016ZDX092).

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