

Degradation of Thiosulfate in the Process of Gold Leaching

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Thiosulfate is a promising alternative for the hydrometallurgical treatment of gold ores. Degradation of thiosulfate before leaching and in the process of gold as well as the behaviours of tetrathionate and trithionate by electrochemical methods is investigated in this work. Results are reported for the analysis of gold thiosulfate leach solutions and it is shown that tetrathionate and pentathionate are the dominant reaction products from thiosulfate oxidation. Trithionate was the main reaction product within certain range of hydroxide concentrations (0.0001-0.01 M), tetrathionate concentration decreases as the hydroxide concentration increases when pH is greater than 13 which show tetrathionate can be readily decomposed to thiosulfate and trithionate by raising the pH. Degradation of thiosulfate in the process of gold leaching was carried out in the paper by electrochemical methods, The result shows that 43.57 % of thiosulfate in solution had consumed after 24 h.

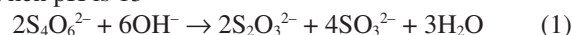
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INTRODUCTION

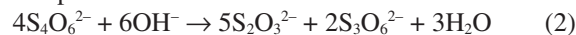
Cyanidation has been the commercial method of recovering gold from its ores due to many advantages over other extraction processes for the past 100 years, There has been a lot of attention given to the study of alternative lixivants in recent years due to the world wide environmental and public concerns over the discharge of cyanide. Thiosulfate is a promising and nontoxic lixiviant replacing cyanide for leaching gold and it is viewed as particularly attractive for the treatment of carbonaceous ores, since the gold thiosulfate complex does not adsorb onto carbon. One of the major problems in thiosulfate leaching is the high consumption of thiosulfate during gold leaching. High consumption of thiosulfate is mainly caused by its decomposition in solution. The understanding of the behaviour of thiosulfate is important in the process of leaching of gold by thiosulfate. The chemical interactions among thiosulfate, ammonia and copper(II) are incredibly complex¹, Ammonia and copper(II) lead to degradation of thiosulfate which have a negative effect on leaching gold with thiosulfate, it was found that tetrathionate and possibly trithionate as well, which were generated by copper(II) catalyzed oxidation of thiosulfate during the leaching, then, a significant challenge for thiosulfate gold leaching industrialization is

degradation of thiosulfate in the process of gold leaching. In an alkaline cupric-ammonia containing leach solution, thiosulfate oxidation will occur by either oxygen in solution or cupric, the reaction process is as follows²:

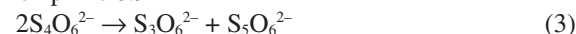
When pH is 13



When pH is 11.5



When pH is 8.9



From above reactions, It is concluded that tetrathionate ($S_4O_6^{2-}$) is primary oxidation product, other degradation products such as trithionate ($S_3O_6^{2-}$) and sulfite (SO_3^{2-}) can also be generated, thiosulfate and trithionate is formed by tetrathionate. Further research on thiosulfate degradation in cupric-ammonia leach solutions has been undertaken by numerous researchers³⁻⁶.

Some techniques such as ion chromatography have been developed for analyzing thiosulfate and polythionates in thiosulfate leach solutions. Study on degradation of thiosulfate in the process of gold leaching by electrochemical methods hardly be seen. This work was conducted to investigate the degradation of thiosulfate in the process of gold leaching by electrochemical methods.

EXPERIMENTAL

Electrochemical analysis was carried out using multifunctional microcomputer electrochemical analyzer (MEC-16, Jiangsu electroanalysis instrument Co., Ltd), All potentials were measured relative to the saturated calomel electrode, a three-electrode system including an Pt working electrode, a Pt counter electrode and a saturated calomel electrode (SCE) as reference electrode was applied.

The water used was deionized distilled water and all chemicals used were of analytical reagent grade. Tetrathionate was purchased from sigma, America. Trithionate was prepared using the methods outlined in the literature⁷.

Leach solutions: Open top reactors were filled with synthetic leach solution, ammonia water and copper(II) sulfate were mixed and added to the ammonium thiosulfate solution in leaching experiments, the solutions contained 0.1 M sodium thiosulfate, 1 M ammonia and 0.01 M copper(II) sulfate. the pH of the solution was adjusted with ammonia water, gold ore in Yunnan beiya gold mines was chosen as research object.

The leaching experiments performed were stirred at 300 rpm. A leaching solution of 200 mL with the desired quantity of reagent was used for each experiment. All experiments were performed at 25 °C.

RESULTS AND DISCUSSION

Conversion of thiosulfate to tetrathionate: Different electrodes such as glass carbon electrode, graphite electrode, *etc.* were compared under different conditions so that the best conditions and electrode were pointed out. Platinum electrode was selected as working electrode after repeated experiments due to good electrochemical characteristics, consequently, the square cyclic voltammetry that was measured at a Pt electrode in 0.006 M Na₂S₂O₃ + 0.2 M Na₂SO₄ solution within potential range from -0.4 to -1.0 V is shown in Fig. 1. As can be seen from Fig. 1, It is observed that the peak appears at -0.81 V for the analysis of thiosulfate. Fig. 1 shows that the electrochemical response of thiosulfate is notable with low detection limit under given specific conditions and which can be used for analyzing the thiosulfate.

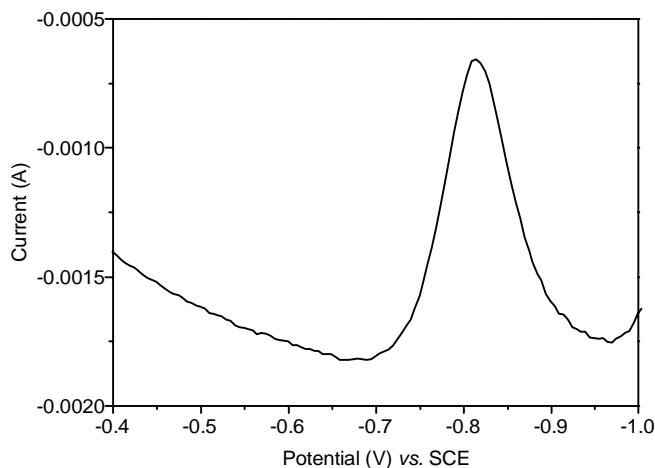


Fig. 1. Square cyclic voltammetry of thiosulfate, the thiosulfate concentration used is 0.006 M

When leaching reagent thiosulfate concentration is 0.01 M, the copper(II) ion concentration used is 0.01 M, the ammonia used is 1 M. The degradation of thiosulfate after 24 h was studied using square cyclic voltammetry based on a Pt electrode. There are four peaks in Fig. 2 when potential is scanned from 1 to -1 V essential role. It is evident that degradation of thiosulfate occurs within this potential range in presence of 0.01 M copper(II) ion and 1 M ammonia. As the degradation proceeds, the concentration of thiosulfate decreases. In most cases during the degradation, tetrathionate peak and trithionate peak can be observed in Fig. 2, This peak is accurately identified due to the formations of tetrathionate and trithionate as seen from in Figs. 3 and 5, the reaction was shown as (2) and (4):

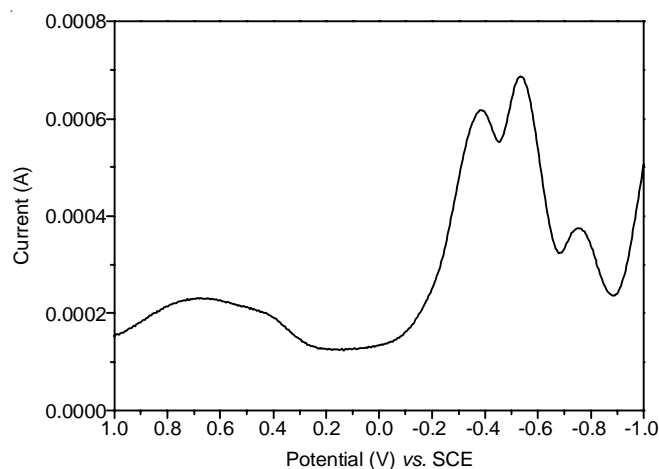
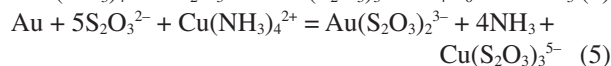
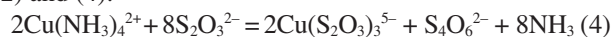


Fig. 2. Square cyclic voltammetry of degradation of thiosulfate in presence of copper(II) ion and ammonia. Thiosulfate concentration used is 0.01 M, copper(II) ion concentration used is 0.01 M, ammonia used is 1 M, time used is 24 h

Fig. 2 compared with Fig. 1 shows the clear variations in behaviours of thiosulfate in the leaching solution of gold. It is noted that degradation of thiosulfate occurred severely before gold leaching due to with high four ammoniations copper(II) concentration without reaction (5). All these show that the concentration of copper(II) ion present in solution is important for thiosulfate stability. Thiosulfate degradation is mainly caused by copper(II) ion and oxygen due to formation of polythionates such as tetrathionate and trithionate.

Conversion of tetrathionate to trithionate: Tetrathionate is one of the principal products of thiosulfate degradation during gold leaching with ammoniacal thiosulfate solution. It is known that under correct conditions, tetrathionate can be oxidized by copper(II)⁴. The changes in tetrathionate and trithionate under experimental conditions are illustrated in Fig. 3. As shown in Fig. 3, there is clear peak at -0.500 V which represents tetrathionate. Initially, the system contains tetrathionate only, after adding alkaline solution the new peak appears at -0.331 V. The new peak also appears at the same potential using standard solution under the same conditions (Fig. 5). Moreover, the new peak is increasing with the increase of pH value of solutions. It can be seen in Fig. 4 that the peak current shows

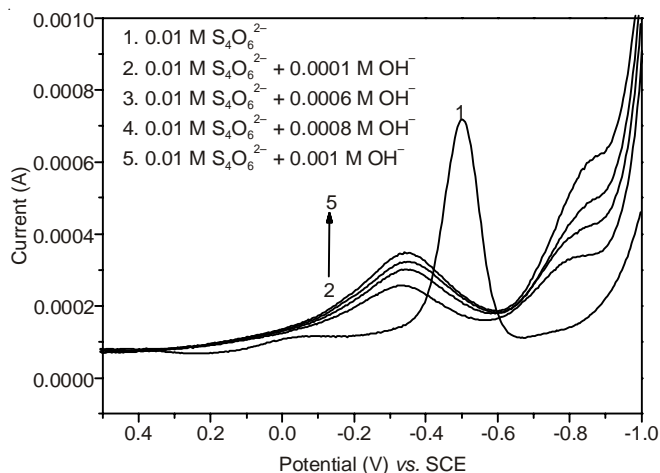


Fig. 3. Square cyclic voltammety of tetrathionate to trithionate

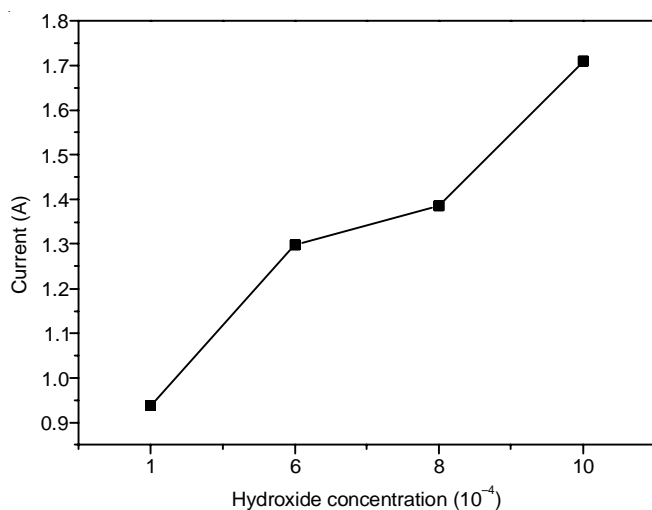


Fig. 4. Relationship between peak current and hydroxide concentration

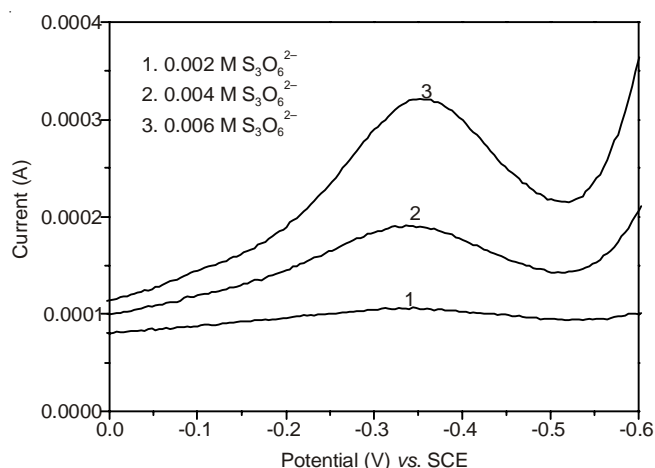


Fig. 5. Square cyclic voltammety of trithionate with various concentrations

the relationships with hydroxide concentration and obtain the fitted equation as follows:

$$Y = 0.4930 + 0.2399 \times X \quad (R = 0.9779)$$

The reaction conform to reaction (2), when pH greater than 13, the peak disappear. The effect of tetrathionate and trithionate on thiosulfate shows that both make the thiosulfate potential shift positive direction indicating thiosulfate is more difficult to oxidize in the presence of tetrathionate and trithionate.

It is evident from Fig. 3 that pH dramatically affect the thiosulfate in the process of gold leaching. Therefore, controlling pH of leaching solution is critical in the process of leaching of gold by thiosulfate since the leaching solution pH affect degradation of thiosulfate indirectly.

Fig. 3 also shows trithionate was the main reaction product within certain range of hydroxide concentrations (0.0001-0.01 M), with no tetrathionates being measured in solution which shows that tetrathionates are not stable under given conditions.

Conversion of tetrathionate having a pH greater than 13:

As shown in Fig. 3, by increasing the pH of leaching solution to greater than 13, the tetrathionate peak current decreases as the hydroxide concentration increases, with thiosulfate being measured, but no trithionate appeared in solution, The results are concordant with reaction (1). Fig. 6 shows that the rate of thiosulfate oxidation was higher when the pH is higher than 13. The reason is that the ammonium is converted to ammonia which improve the rate of thiosulfate oxidation when the pH was increased by adding more hydroxide, resulting in a higher rate of copper(I) oxidation by oxygen.

It is evident from Figs. 3 and 4 that $\text{pH} > 13$ also dramatically affect the thiosulfate degradation productions. Previous researchs have also shown that tetrathionate can be readily decomposed to thiosulfate and trithionate by raising the pH and trithionate is more stable than higher order polythionates, requiring higher pH or temperature to effect decomposition⁸. The result in this study is a close correspondence with previous researchs. Effects on thiosulfate oxidation rate was studied thoroughly⁹⁻¹¹, tetrathionate not always was the final product in thiosulfate oxidation, the final products of thiosulfate oxidation may be sulfate ions and elemental sulfur which lead to high consumption of thiosulfate.

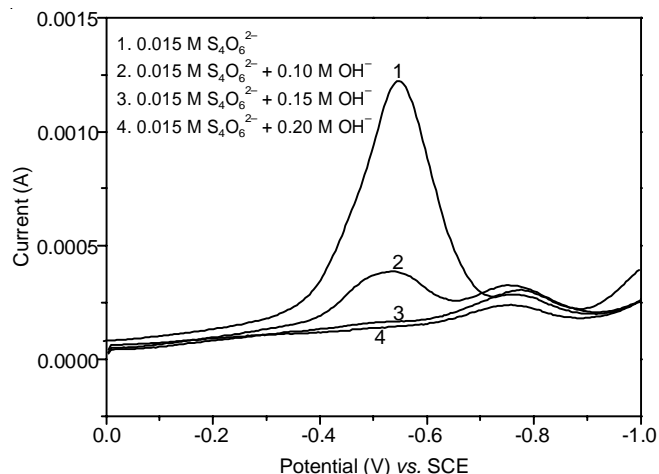


Fig. 6. Square cyclic voltammety of tetrathionate having a pH > 13

Tendency of thiosulfate concentration in the process of gold leaching:

In order to study the degradation of thiosulfate in the process of gold leaching, the peak current was measured within the potential range from 0.4 to -1 V in 24 h. The square cyclic voltammety when the leaching time is 2 is shown in Fig. 7. The thiosulfate response was at -0.6 V. The potential shifted to more positive compared with Fig. 1, the reason is due to the enhancement of exchange current density with thiosulfate concentration higher which lead to over

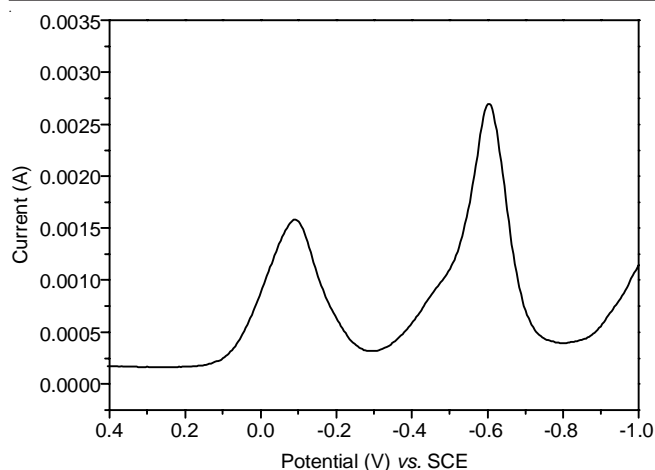
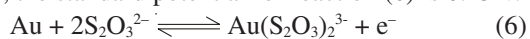


Fig. 7. Square cyclic voltammery in process of gold leaching in the solutions containing 0.1 M sodium thiosulfate, 1 M ammonia and 0.01 M copper(II) sulfate and pH 10.5 (leaching time is 2 h)

potential less. The response at -0.09 V may be attributed to reaction (6), the standard potential for reaction (6) is 0.15 V.



The change in thiosulfate concentration with time under the above leaching condition is illustrated in Fig. 8, thiosulfate degradation was very fast for this system in 2 h. After 8 h, the thiosulfate concentration was constant. After 24 h, 43.57 % of thiosulfate in solution had consumed. Then, the method was set up under optimized instrumental conditions to monitor thiosulfate concentration by using square cyclic voltammery at a Pt electrode, because of the instability of thiosulfate and the conversion to tetrathionate, trithionate and other sulfur compounds (elemental sulfur and polysulfide species). On-line measurement is difficult to perform at present, future studies will focus on the simultaneous determination of thiosulfate, tetrathionate, trithionate and fundamental studies on the kinetics of decomposition of tetrathionate, trithionate and thiosulfate in alkaline solution by electrochemical methods.

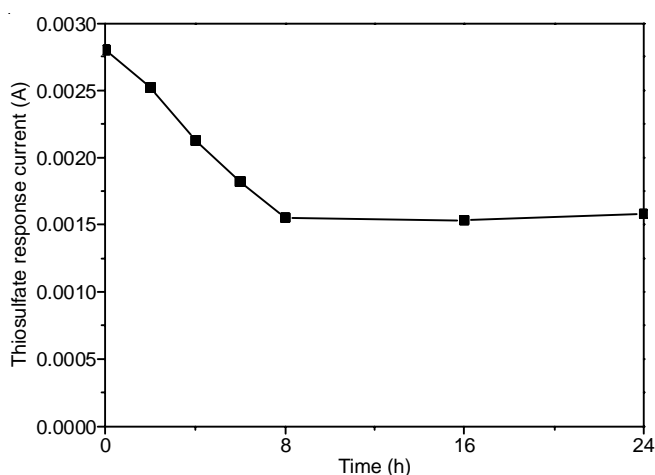


Fig. 8. Degradation of thiosulfate during ore leaching with time

Conclusions

On the basis of the results obtained for degradation of thiosulfate in the process of gold leaching the following could be concluded:

- An important factor in thiosulfate stability is the pH of the solution, since thiosulfate rapidly decomposes, degradation product was directly affected by hydroxide concentration and leaching time, tetrathionate is one of the principal products of thiosulfate degradation during gold leaching with ammoniacal thiosulfate solution. tetrathionate can be readily decomposed to thiosulfate and trithionate by raising the pH.

- Trithionate was the main reaction product within certain range of hydroxide concentrations (0.0001-0.01 M), with no tetrathionates being measured in solution. tetrathionate concentration decreases as the hydroxide concentration increases when pH is greater than 13, with thiosulfate being measured, but no trithionate appeared in solution.

- The thiosulfate concentration was monitored in the process of gold leaching in the solutions containing 0.1 M sodium thiosulfate, 1 M ammonia and 0.01 M copper(II) sulfate and pH 10.5, the result show that 43.57 % of thiosulfate in solution had consumed after 24 h.

Actually, there are many reversible reactions in which thiosulfate is either consumed or generated in the process of leaching which may cause significant degradation, then, the steady of thiosulfate is of great importance in the process of gold leaching.

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