Effect of an additive TEA on thiosulfate leaching of low sulfur gold concentrate

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Abstract. The environmentally friendly and non-cyanide thiosulfate gold leaching technology was used to extract gold from a low-sulfur gold concentrate. The effect of TEA on leaching of pure gold under the condition of adding quartz indicated that TEA could significant increase the dissolution rates of gold and the mixed solution potentials and decrease the consumption of thiosulfate. Quartz has little effect on the gold leaching process. Moreover, the effect of additive Triethanolamine (TEA) on the gold extraction was further studied. The chemical analysis and process mineralogy analysis of the concentrate indicated that the concentrate contained 59 g/t Au, 64.49% SiO₂, 19.55% Al and 5.76% Fe. The concentrate was composed of quartz, muscovite and chlorite as major minerals. Quartz was the main gold-bearing mineral in concentrate. The gold particles of less than 20 μm in the concentrate reached 50.56%. Traditional thiosulfate leaching technology was used to extract gold from the concentrate, and the gold leaching rate was only 44.49% after 48 hours. When 0.024 M (M_TEA:M_copper =2:1) TEA was added in the thiosulfate leaching gold system, the thiosulfate consumption significantly reduced by about 32% and the leaching rate of gold increased to 73.40%.

1. Introduction

The extraction of gold from mineral sources is mainly performed using cyanide leaching. Among the advantages of this process are its chemical stability, high leaching rate and low cost for the extraction of gold. But in the meanwhile, a variety of non-cyanide gold leaching reagents has been extensively studied as the alternative methods for the traditional cyanidation technology due to the increasing concern regarding the hazardous character of cyanide [1-3]. Ammoniacal thiosulfate leaching is considered a suitable alternative reagent to cyanidation [4]. Because of its non-toxic nature, acceptable gold leaching rates, and ability to leach refractory minerals such as containing copper and carbonaceous materials [5,6].

Cu(II) is a major role in ammoniacal thiosulfate leaching gold system, which can catalyze and accelerate the gold dissolution during leaching process. Nevertheless, Cu(II) act as oxidant, promotes decomposition of thiosulfate, increases the consumption of reagents and the formation of passivation substances during the leaching process [6,7]. Thus, the HN₃-Cu(II)-S₂O₃²⁻ is a quite complicated leaching gold system that depending on the simultaneous presence of complexing agents (ammonia and thiosulfate), the Cu(II)/Cu(I) redox couple and the stability of thiosulfate in solution [8,9]. In order to
reduce the decomposition of thiosulfate, decrease the leaching passivation and increase gold leaching rate, several additives such as sulphite, ethylene diamine tetraacetic acid, orthophosphate, polyphosphate, carboxymethyl cellulose and humic acid additives were introduced into leaching process [3,10-14].

Triethanolamine (TEA) is an effective complexing agent which is commonly used as an accelerator for electroplating copper processes [15]. He Fei Zhao et al. [16] introduced TEA into ammoniacal thiosulfate leaching system and demonstrated the effect of the TEA on the decomposition of thiosulfate and the effect of leaching gold. The results indicate that in the case of a certain concentration of TEA, the dissolution rate of gold can be increased by approximately 50% and the thiosulfate consumption decreased by approximately 10%. It is consider that TEA reacts with the cupric-ammonia complex to produce an active and complex stereoscopic structure cupric-ammonia-TEA complex [Cu(NH$_3$)$_3$TEA]$^{2+}$.

In this paper, the HN$_3$-Cu(Ⅱ)-S$_2$O$_3^{2-}$ liquor was used in the leaching of a low sulfur gold concentrate. In order to improve the leaching effect, triethanolamine (TEA) was introduced as an additive in the leaching system. The addition of TEA would be able to improve the dissolution rate of gold and decrease the thiosulfate consumption. The effect of quartz on gold dissolution, mixed potential and thiosulfate consumption was comparatively studied with/without TEA.

2. Experimental work

2.1. Materials
Gold foils (99.99% Au, thickness 0.2 mm) with a surface area of approximately 1.00 cm$^2$ were used in this study. The gold foils were first polished with abrasive papers of 800, 2000, and 5000 grit sequentially, and then washed in turn with nitric acid and acetone, rinsed with distilled water and swept with lint-free paper. A new gold foil was used for each leaching test. Analytically pure sodium thiosulfate, ammonium sulfate, cupric sulfate pentahydrate, ammonia water (25% mass fraction), acetone, hydrogen peroxyde solution (30% mass fraction), nitric acid (50% volume fraction) and triethanolamine were provided by Tianjin Damao Chemical Reagent Factory, China. Deionized water was used in all experiments.

The low sulfur gold concentrate sample was obtained by Knelson concentrator of low sulfur gold ore originally from Hainan Region, China. The concentrate was milled in a laboratory ball mill. Subsequently, the as-received concentrate was dried at 60 °C for 24 h and then blended by rolling. The concentrate samples were then sampled for particle size analysis, chemical analysis and mineralogical characterization. Particle size analysis by laser particle size analyzer (Better BT-9300S) showed 90 wt% of the sample particles were smaller than 38 μm. The main chemical composition of the concentrate sample is shown in Table 1. The content of Au was determined by fire assaying method and was found to be 59 g/t (Table 1). The XRD pattern and SEM of the concentrate sample are shown in figure 1 and figure 2, respectively. The XRD pattern indicated that quartz, muscovite and chlorite were the major minerals present in the concentrate sample. Figure 2 shows the SEM image of the concentrate sample. Gold occurs mainly in shape of inclusion gold, fissure gold and single gold. The main carrying-gold minerals are quartz and muscovite. Part of gold located in the quartz and muscovite are seen in the figure 2(a) and (b). Process mineralogy analysis showed that the gold particles of less than 20 μm in the concentrate reached 50.56%.

| Table 1. Elemental composition of concentrate sample. |
|-----------------------------------------------|
| Element | Au (g·t$^{-1}$) | Al (%) | S (%) | TFe (%) | SiO$_2$ (%) |
| wt (%) | 59 | 19.55 | 0.60 | 5.76 | 64.49 |
Figure 1. XRD pattern of the concentrate sample.

Figure 2. SEM-EDS images of the concentrate sample.
a) Analytical techniques
Elemental concentrations in leaching solutions were determined by atomic absorption spectrophotometry (AAS; Hitachi Z-2300). Solutions were oxidized by hydrogen peroxide, acidified by aqua regia and boiled to ensure that all metal species were converted to chloride form. The thiosulfate concentration was analyzed by an iodometric method with the addition of EDTA (0.1 M) and methanol (20%) to eliminate the interference of the cupric tetra-amine complex and the sulfite, respectively. The mixed solution potential was determined with a platinum composite electrode and a reference electrode (Ag/AgCl, saturated KCl) (501, INESA) to avoid the interference of thiosulfate. All potentials were converted to standard hydrogen potentials (SHE).

b) Leaching tests
Pure gold leaching tests with or without the addition of TEA were performed in a 250-ml Erlenmeyer flask with a magnetic stirrer at a rotation speed of 350 r/min. 2.0g quartz was added for each experiment. A rubber stopper with an air hole (D = 5 mm) was used to stop the volatilization of NH₃. A leach solution of 200 ml with an initial pH of 9.83 (adjusted by ammonium hydroxide) was used for different experiment. The gold foils were suspended under the rubber stopper with a nylon thread, and ensured no contact with the Erlenmeyer flask wall during leaching. The leaching experiments were carried out in a 25 °C water bath for 24 h. Gold dissolution was calculated on the basis of the dissolved gold mass (mg) per cm² of the gold foil surface.

Leaching of the concentrate was conducted in a 1.0 L three-necked flask reactor using a mechanical stirrer at a rotation speed of 400 r/min. The reactors were closed through rubber stopper. Leach solution of 0.5 L was added to the concentrate of 100 g in the reactors. The leaching experiments were carried out in a 25 °C water bath for 48 h. The initial pH of the leaching solution was adjusted to 9.80 by sodium hydroxide or sulfuric acid. The samples were taken continuously at certain intervals from the solution during the 48 h leaching period. The samples were immediately measured by iodine titration for thiosulfate and oxidation for atomic absorption spectroscopy (AAS) analysis. The gold concentration was determined by atomic absorption spectroscopy (HITACHI, Z-2300). The morphologies and qualitative compositions of concentrate was determined by X-ray diffraction (RigakuD/max 2550VB+18kW) and scanning electron microscopy (SHIMADZU, CamScan SSX-550).

3. Results and discussion
3.1. Leaching pure gold with the addition of quartz
The XRD pattern and elemental composition of concentrate sample show that quartz is the main mineral (64.49%). Thus, quartz was selected as the main factor and added to the pure gold leaching experiment. The effect of TEA on gold dissolution, mixed potential and thiosulfate consumption was comparatively studied under quartz. Figure 3 shows gold dissolution in the presence of TEA at varied concentrations under 2.0 g quartz. As shown in figure 3, under 2.0 g quartz condition without TEA the gold dissolution rate slowed after about 6 h. This is similar to the standard leaching process without any additives, namely a passivation layer possibly formed with time. The formation of the passivation layer could hinder the diffusion of thiosulfate on the gold surface, thus reducing the dissolution rate of gold. This indicates that the kinetics of leaching pure gold remained unchanged by the addition of quartz.

As shown in figure 3, in the presence of 0.006 M, 0.012 M, and 0.024 M TEA the dissolution rate of gold is improved obviously compare to the standard condition without TEA in the 24 h leaching process. With 0.012 M TEA (M_{TEA}:M_{copper} = 1:1), the dissolution rate of gold reached the highest than other conditions. Meanwhile, an excessive concentration of TEA (0.048 M) decreased the gold dissolution. This is consistent with He Fei Zhao et al. [16] findings that the optimal concentration ratio of TEA to Cu²⁺ was 1:1 and that excessive TEA decreased the dissolution efficiency of gold. It is further proved that the effect of TEA on gold dissolution was not changed with addition of quartz.

As noted from figure 4, the mixed solution potentials increased in the presence of TEA. In the ammoniacal thiosulfate leaching system, the redox equilibrium potential of the cupric/cuprous couple
determines the mixed solution potential. When a certain amount of TEA was present in ammoniacal thiosulfate solutions, part or all of Cu(NH$_3$)$_2^{+}$ (the stability constant of Cu(NH$_3$)$_2^{+}$ was 10.87) will be converted to the stable [Cu(TEA)]$^+$ (the stability constant of [Cu(TEA)]$^+$ was 27.98). According to the Nernst equation, the stability of Cu(I) is much greater than that of Cu(II), which decreases the reduction ability of the Cu$^+$, and enhances cupric/cuprous complex equilibrium potential. When sufficient TEA (M$_{TEA}$:M$_{copper}$ = 4:1) was introduced into the leaching system, some or all of the Cu(NH$_3$)$_4^{2+}$ will be converted to [Cu(TEA)(OH)$_2$] and [Cu(TEA)$_2$(OH)$_2$] [16]. Therefore, the ability of Cu(II) catalytic oxidation is inhibited gradually. As a result, dissolution rate of gold decreased (Figure 3). Quartz is a stable mineral that cannot be dissolved and released ions during the ammoniacal thiosulfate leaching system.

**Figure 3.** Gold dissolution during thiosulfate leaching of pure gold in the presence of quartz and TEA. Solution: 0.1 M Na$_2$S$_2$O$_3$, 0.1 M (NH$_4$)$_2$SO$_4$, 0.012 M Cu$^{2+}$, and 2.0 g quartz; 0, 0.006, 0.012, 0.024, and 0.048 M TEA; pH = 9.83 adjusted with ammonium hydroxide at 25 °C.

**Figure 4.** Variation of mixed potential with time during the thiosulfate leaching of pure gold in the presence of quartz and TEA. Solution: 0.1 M Na$_2$S$_2$O$_3$, 0.1 M (NH$_4$)$_2$SO$_4$, 0.012 M Cu$^{2+}$, and 2.0 g quartz; 0, 0.006, 0.012, 0.024, and 0.048 M TEA; pH = 9.83 adjusted with ammonium hydroxide at 25 °C.

Figure 5 shows the effect of TEA on thiosulfate decomposition under the addition of 2.0 g quartz. The decompositions of thiosulfate was decreased with the addition of TEA, this beneficial effect became more pronounced an increase in the TEA concentration (figure 5). The introduction of TEA formed the stereoscopic structure [Cu(NH$_3$)$_x$(TEA)$_y$] with copper and ammonia. [Cu(NH$_3$)$_x$(TEA)$_y$] decreased the reactions between Cu(II) and thiosulfate [16]. Therefore, the thiosulfate decomposition caused by Cu(II) was decreased in the presence of TEA, as reflected in figure 5. Reduction of thiosulfate decomposition decreased the formation of passivation layers on the gold surface during leaching process. Thus, the dissolution of gold can be maintained at a high rate in the presence of 0.006 M, 0.012 M, and 0.024 M TEA. However, the sufficient TEA (M$_{TEA}$:M$_{copper}$ = 4:1) can convert part or all Cu(II) to [Cu(TEA)(OH)$_2$] and [Cu(TEA)$_2$(OH)$_2$] which decreased dissolution rate of gold, although the thiosulfate decomposition was extremely low in such cases. When 0.012 M TEA (M$_{TEA}$:M$_{copper}$ = 1:1)
presented in leaching solution, the highest gold dissolution was achieved and the decomposition of thiosulfate decreased by 10%.

Figure 5. Thiosulfate decomposition during thiosulfate leaching of pure gold in the presence of quartz and TEA.
Solution: 0.1 M Na₂S₂O₃, 0.1 M (NH₄)₂SO₄, 0.012 M Cu²⁺, and 2.0 g quartz; 0, 0.006, 0.012, 0.024, and 0.048 M TEA; pH = 9.83 adjusted with ammonium hydroxide at 25 °C.

c) Thiosulfate leaching of the low sulfur gold concentrate in the presence of TEA
Figure 6 shows the effect of TEA concentration on gold extraction in the process of leaching the low sulfur gold with ammoniacal thiosulfate. In all experiment conditions, the leaching rates of gold were very high in initial stage, and became slow with the time. This may be caused by single gold in concentrate. In initial stage, the concentrations of Cu(II) and S₂O₃²⁻ were high, which could access and dissolve the single gold readily. The leaching rates of gold gradually levelled off due to consumption of lixiviant and passivation on gold with time. As shown in figure 6, the leaching rate of gold decreased after 3 h in the absence of TEA. By comparison the leaching rates of gold decreased after 6 h in the presence of TEA. This indicated that the addition of TEA could reduce the passivation and delay formation of passivation. The final gold extraction was only 44.49% without TEA. In contrast, the final gold extraction increasing with TEA increased. When 0.024 M (M_{TEA}:M_{copper} =2:1) TEA was added in the leaching solution, the highest final gold extraction reached 73.40%. However, the sufficient TEA (M_{TEA}:M_{copper} = 4:1) decreased the final gold extraction, although the gold extraction was higher than that without TEA. In leaching pure gold, the highest gold dissolution can be obtained in the presence of 0.012 M (M_{TEA}:M_{copper} =1:1) TEA, while the gold dissolution was decreased with the increase in TEA concentration over this certain level (figure 3).The different effect of the TEA concentration on the leaching of pure gold and the low sulfur gold concentrate was possibly attributed to the dissolution of sulphide minerals in the concentrate and the release of heavy metal ions from the sulphide minerals [11].

Figure 6. Gold extraction during thiosulfate leaching of the low sulfur gold concentrate in the presence of TEA.
Solution: 0.1 M Na₂S₂O₃, 0.1 M (NH₄)₂SO₄, 0.5 M NH₃•H₂O, and 0.012 M Cu²⁺; 0, 0.006, 0.012, 0.024, and 0.048 M TEA; pH = 9.80 adjusted with sodium hydroxide or sulfuric acid at 25 °C.
The sulphide minerals of the low sulfur gold concentrate released heavy metal ions competed with the cupric ion for TEA complexation, and then usage amount of TEA increased. But, the low sulfur gold concentrate contained 0.6% S and the main mineral was quartz. Thus, when the sufficient 0.048 M (M_{TEA}:M_{copper} = 4:1) TEA present in the leaching solution, the concentrate cannot dissolve too much heavy metal ions and complex with TEA. As a result, sufficient TEA converted Cu(II) to [Cu(TEA)(OH)₂] and [Cu(TEA)₂(OH)₂] which decreased dissolution of gold. As shown in figure 6, 26.6% of the gold in the concentrate cannot be leached which may cause by inclusion gold.

The presence of TEA reduced the decomposition of thiosulfate in the leaching of the low sulfur gold concentrate (figure 7). The decomposition of thiosulfate gradually decreased with TEA concentration increasing. The consumption of thiosulfate reduced from 0.1 M to 0.025 M in the absence of TEA after 48 h leaching. The leaching of the low sulfur gold concentrate consumed more thiosulphate than that of leaching pure gold due to the effect of the semi-conductive minerals such as sulphide and iron minerals [11,17]. Meanwhile, part of the semi-conducting minerals and heavy metal ions could also enhance the decomposition of thiosulfate. The addition of TEA significant reduced the decomposition of thiosulfate. The highest gold extraction was achieved when 0.024 M TEA (M_{TEA}:M_{copper} = 2:1) was added, and the decomposition of thiosulfate decreased by approximately 32%, as shown in figure 6 and figure 7. TEA could complex with the dissolved heavy ion, thus decrease the decomposition of thiosulfate. On the other hand, the introduction of TEA formed the stereoscopic structure [Cu(NH₃)ₓ(TEA)ᵧ] with copper and ammonia. [Cu(NH₃)ₓ(TEA)ᵧ] increase the steric hindrance of the reactions between Cu(II) and thiosulfate. Therefore, the thiosulfate decomposition caused by Cu(II) was decreased in the presence of TEA.

Figure 7. Thiosulfate decomposition during thiosulfate leaching of the low sulfur gold concentrate in the presence of TEA. Solution: 0.1 M Na₂S₂O₃, 0.1 M (NH₄)₂SO₄, 0.5 M NH₃·H₂O, and 0.012 M Cu²⁺; 0, 0.006, 0.012, 0.024, and 0.048 M TEA; pH = 9.80 adjusted with sodium hydroxide or sulfuric acid at 25 °C.

4. Conclusion
The effect of TEA on leaching of pure gold (under the condition of adding quartz) and the low sulfur gold concentrate was investigated in NH₃-Cu-S₂O₃²⁻ leaching systems. In leaching of pure gold, a certain amount (0.006 M, 0.012 M and 0.024 M) of TEA could significant increase the dissolution rates of gold and the mixed solution potentials and decrease the consumption of thiosulfate. With 0.012 M TEA (M_{TEA}:M_{copper} = 1:1), the dissolution rate of gold reached the highest than other conditions. While, excessive TEA (0.048 M) dosage reduced the beneficial effect. In leaching of pure gold, the addition of quartz hardly changed the effect of TEA on the gold leaching process.

In leaching of the low sulfur gold concentrate, the consumption of thiosulfate reduced from 0.1 M to 0.025 M in the absence of TEA after 48 h leaching. The leaching of the low sulfur gold concentrate consumed more thiosulphate than that of leaching pure gold due to the effect of the semi-conductive minerals such as sulphide and iron minerals. The leaching kinetics and the final extractions of gold increased substantially and the thiosulphate consumption was decreased in the thiosulphate leaching of the low sulfur gold concentrate with the addition of TEA. These beneficial effects became more pronounced with the concentration of TEA increasing from 0.006 M to 0.024 M. With 0.024 M TEA
(M\textsubscript{TEA}:M\textsubscript{copper} = 2:1), the extraction of gold reached the highest (73.4%) than other conditions, while the decomposition of thiosulfate decreased by approximately 32%. The beneficial effect caused by TEA complexed with the dissolved heavy ion and decrease the decomposition of thiosulfate, thus reduce the passivation and delay formation of passivation. The sufficient TEA (M\textsubscript{TEA}:M\textsubscript{copper} = 4:1) decreased the final gold extraction, although the gold extraction was higher than that without TEA.

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