

Effect of additives on thiosulfate leaching of a gold ore

S.J. Dai, P.C. Li, Q.Q. Wang*, D.W. Feng

University of Science and Technology, Liaoning, Anshan, China

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The effect of additives on gold leaching was investigated using ammonium thiosulfate or calcium thiosulfate. Thiosulfate stability was evaluated with additive dosage and thiosulfate type, usage, and ageing. The study results showed that ethylene diaminetetraacetic acid (EDTA) at its optimum concentration of 2 mM enhanced gold leaching and slightly improved the stability of gold thiosulfate species in solution while carboxy methyl cellulose (CMC) improved gold leaching, but gold was not stable in solution. There was an optimum CMC dosage, and beyond this, further addition of CMC hindered gold leaching. The surfactant sodium dodecyl sulfate (SDS) had a similar effect to CMC. At an agitation speed of 250 r/min, 100% leach recovery of gold was achieved with 0.03 M fresh ammonium thiosulfate, 2 mM EDTA after 11 h leach. In a resin-in-leach system, full gold recovery was also achievable with sufficient resin after 24 h leach with 0.06 M fresh ammonium thiosulfate and 2 mM EDTA at an agitation speed of 250 r/min.

Key words: Gold leaching, Thiosulfate, Additives, Leaching kinetics, Thiosulfate stability

INTRODUCTION

In recent years extensive research has focused on thiosulfate as a potential alternative lixiviant for gold due to the growing environmental and public concerns over the use of cyanide [1-4]. From an economic point of view, it is required that the leaching should be carried out under low reagent concentrations over extended periods where reagent consumption is low. In order to achieve this, stabilization of thiosulfate and gold thiosulfate in solution and reduction of passivation to allow gold leaching over extended periods are among the key issues to be concerned [5-7]. From previous experience, ore mineralogy is known to affect thiosulfate leaching of gold and the stability of thiosulfate and gold thiosulfate species. Specifically, sulfide minerals retard gold leaching and catalyse the degradation of thiosulfate and gold thiosulfate. Other reductants, e.g. carbonaceous matter, have also been found to affect the stability of thiosulfate and gold thiosulfate. Semi-conductive iron minerals, especially newly formed iron mineral phases generated in the leach system, were also reported to influence the stability of thiosulfate. Silica is not usually viewed as problematic in gold hydrometallurgy, but previous tests have shown that newly formed silica generated *via* acid or alkaline processing of silicate minerals and/or during calcination has a high adsorption capability, and strong reducing power for both Au(I) and Au(III) [8-11].

Thus, at low reagent concentrations the stability of thiosulfate and gold thiosulfate is a problem in

natural ores where amorphous silica and iron oxide are present. Because of this, the use of surfactants to manipulate the mineral particle surface properties to reduce the catalytic decomposition of thiosulfate and gold thiosulfate is necessary. In addition, the stabilization of thiosulfate and gold thiosulfate can be realised through manipulation of the solution chemistry using additives. Our previous studies have shown that the combination of solution and surface chemistry modification is able to stabilize the thiosulfate leaching system [12-15]. In this paper, the effect of selected additives on thiosulfate leaching of a gold ore, *i.e.* EDTA, carboxy methyl cellulose (CMC) and sodium dodecyl sulfate (SDS) was investigated.

EXPERIMENTAL

Materials

A milled gold ore sample with a solid content of 50% was provided by a gold mine and used in the leaching tests without further treatment. The gold ore sample was a refractory ore mainly containing 6 g Au/t, about 3% pyrite and 0.8% carbonaceous matter.

Laboratory reagent grade ammonium thiosulfate was purchased from Chem Supply (Australia). For comparison, an aged and consolidated ammonium thiosulfate from the same supplier was used as well. Calcium thiosulfate (30%) was used and the product has been stored in a sealed drum in the lab for over 6 years. Some precipitates appeared and some yellowish materials were present at the outlet. These materials, likely degradation products of calcium thiosulfate, may affect gold leaching. Hydrochloric and nitric acids were obtained from Merck. EDTA (disodium salt), CMC (sodium salt) and SDS were

*To whom all correspondence should be sent:
E-mail: wqq52526@126.com

provided by BDH Laboratory Supplies. MilliQ water was used in the tests. An anionic ion exchange resin was used in the resin-in-leach tests.

Analytical techniques

Elemental concentrations in solutions were determined by ICP-OES (Varian Instruments). Thiosulfate concentration was determined by the iodometric method. Fire assay was used to determine gold content in selected leach residues. Gold-loaded resins were ashed in a furnace at 640 °C for 1 h and the ash was digested in *aqua regia*. The elemental concentrations in the acidified solutions were determined by ICP-OES.

Leaching

Leaching of the ore samples was performed in 1.5 L baffled PVC reactors using overhead stirrers with flat-blade impellers. Slurry of 1.4 kg with a solid content of 35% was mixed with desired amounts of calcium or ammonium thiosulfate. All additives were mixed with the ore slurry and heated to 50 °C, followed by the addition of thiosulfate for leaching. A natural pH of about 8 was used in the leaching. Leaching was performed at 50 ± 1°C. Samples were taken regularly over 24 h. Samples were filtered, then immediately iodine titrated for thiosulfate determination and analysed by ICP-OES after dilution. Recovery of gold was defined as the percentage of dissolved gold in relation to the gold in the ore. Leach residues of 24 h were fire assayed for determination of gold contents. Mass balance calculations showed a good agreement.

RESULTS

Effect of additives on gold leaching with calcium thiosulfate

Fig. 1 shows the leaching results of the ore slurry with 0.03 M CaS₂O₃ at a stirring rate of 200 r/min. As shown in fig. 1, under the baseline condition, gold recovery reached its maximum at 7 h and dropped afterwards. However, the dissolved gold was not stable in solution, which is likely linked with the surface properties of the mineral particles in the ore. Thiosulfate and gold thiosulfate species interact with the mineral particles (especially sulfide minerals) as well as carbonaceous matter, causing instability of the gold thiosulfate species.

Addition of EDTA increased gold recovery but reduced the initial kinetics. This effect became more noticeable with increased EDTA concentration up to 2 mM. Gold recovery still decreased over time, but to a lesser extent in the presence of EDTA.

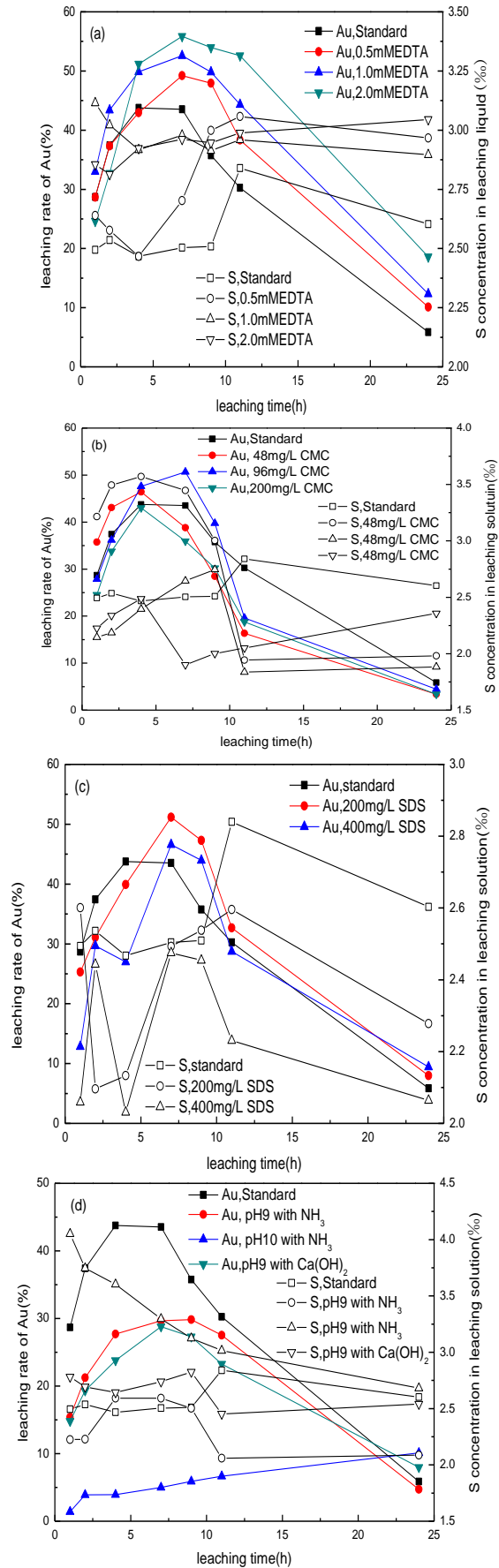


Fig. 1. Leaching results of the gold ore with different additives: (a) EDTA; (b) CMC; (c) SDS; (d) NH₃ and Ca(OH)₂

The leaching of sulfide minerals increased with the addition of EDTA, as reflected by the increased sulfur concentration in solution. CMC slightly increased gold recovery at low concentration but hindered gold leaching at a high concentration. At low CMC concentrations, the S concentration increased initially, but dropped substantially together with gold after prolonged leaching. The surfactant sodium dodecyl sulfate (SDS) slightly enhanced gold recovery at a lower concentration, but could not stabilise gold thiosulfate in solution. Gold recovery decreased at a higher pH with the addition of ammonia, despite the higher sulfide leaching. This is because the mixed solution potential substantially decreased at a higher pH level. At an elevated pH, ammonia was more beneficial for gold leaching than calcium hydroxide, due to the enhanced leaching of the sulfide minerals with ammonia.

Effect of stirring speed on gold leaching

Fig. 2 shows the leaching of the slurry feed with CaS_2O_3 and EDTA conducted at 200 and 250 r/min, respectively.

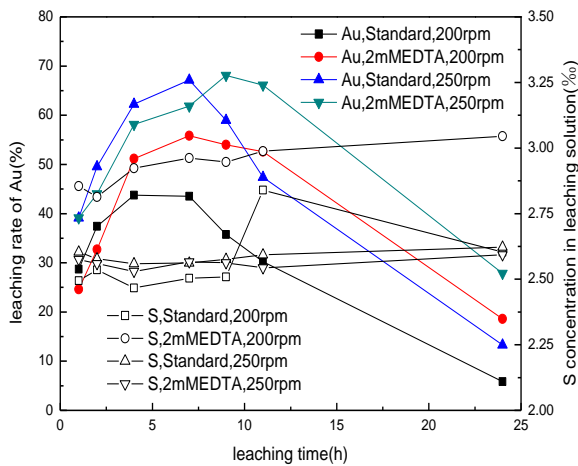


Fig. 2. Effect of stirring speed on gold leaching

In comparison with 200 r/min stirring speed, a higher stirring speed of 250 r/min gave a higher gold recovery at 0.03 M CaS_2O_3 . A higher stirring speed may cause slightly higher attrition among mineral particles and hence clean surface for gold leaching. In addition, a high stirring speed may lead to the absorption of more O_2 from the air into the solution. The dissolved oxygen concentration should thus be higher at a higher stirring speed.

The trends observed at higher stirring rates were consistent with those obtained at 200 r/min; EDTA again decreased initial leaching kinetics but stabilized gold thiosulfate to some extent.

Effect of dosage of EDTA on gold leaching with calcium thiosulfate

Leaching of the slurry feed with 0.03M CaS_2O_3 was conducted at 250 r/min, and the results are shown in Fig. 3.

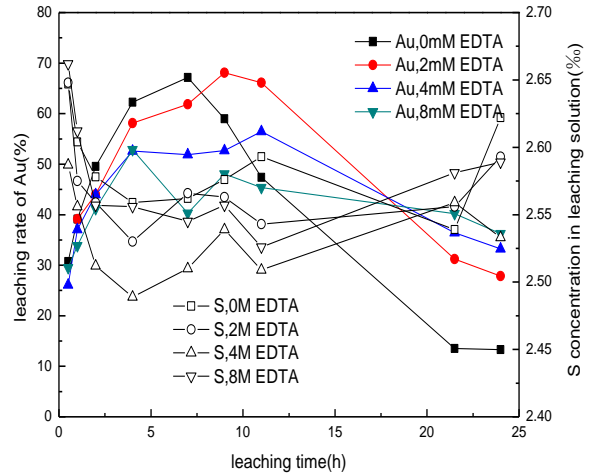


Fig. 3. Effect of dosage of EDTA on gold leaching

Fig. 3 shows that gold recovery reached its maximum at 7 h and dropped afterwards with no EDTA. The dissolved gold was not stable in solution, which is probably related to the surface properties of the mineral particles in the ore. Addition of EDTA increased gold recovery but reduced the initial kinetics. The gold recovery reached its maximum of 68.11% for 9 h and dropped afterwards with increased EDTA concentration up to 2 mM. A higher EDTA dosage caused a drop in gold recovery and reduced the initial kinetics with a concentration more than 2 mM. Gold recovery reached its maximum at 11 h and dropped afterwards with 4 or 8 mM EDTA. Gold recovery still decreased over time, but to a lesser extent in the presence of EDTA. The leaching of sulfide minerals increased with the addition of EDTA, as reflected by the increased sulfur concentration in solution. Thus, EDTA enhanced gold leaching and slightly improved the stability of gold thiosulfate species in solution, and its optimum concentration was 2 mM.

Effect of dosage of CaS_2O_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ on gold leaching

Fig. 4 shows the leaching of the slurry feed with CaS_2O_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ at 2 mM EDTA and 250 r/min.

Gold recovery increased at a higher thiosulfate concentration, and gold thiosulfate species became more stable in solution with time. When added at the same concentration, $(\text{NH}_4)_2\text{S}_2\text{O}_3$ gave a higher gold recovery than CaS_2O_3 . This is because the sulfide minerals were leached to a greater extent in the

presence of $(\text{NH}_4)_2\text{S}_2\text{O}_3$, as indicated by the higher sulfur content in solution. Leaching of the sulfide

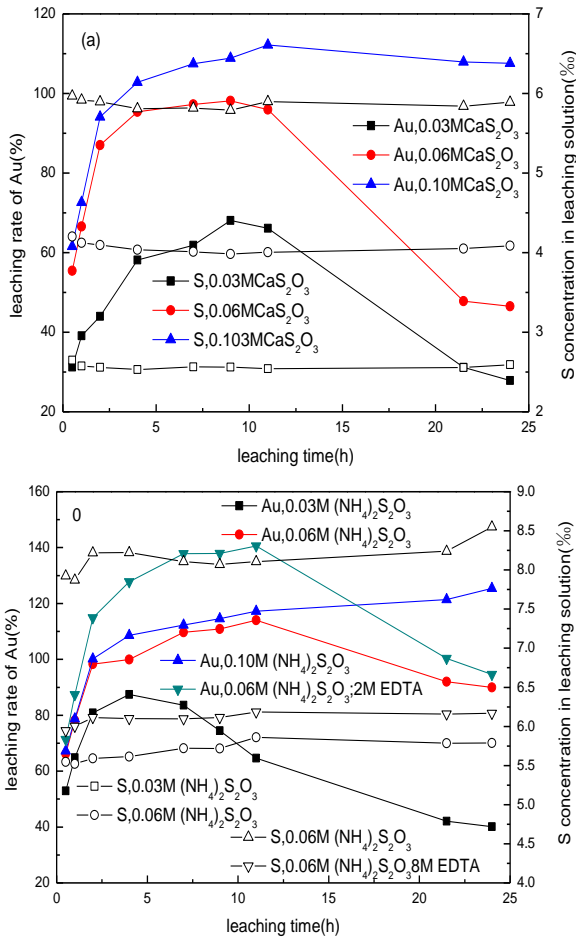


Fig. 4. Effect of dosage of (a) CaS_2O_3 and (b) $(\text{NH}_4)_2\text{S}_2\text{O}_3$ on gold leaching

minerals mainly occurred at the particle surfaces. Thus, higher leaching of the sulfide minerals appears to have reduced the interactions between thiosulfate/gold thiosulfate species and the sulfide mineral surfaces. EDTA enhanced gold leaching and slightly improved the stability of gold thiosulfate species in solution. EDTA enhanced gold leaching and slightly improved the stability of gold thiosulfate species in solution by using $(\text{NH}_4)_2\text{S}_2\text{O}_3$ as leaching agent. In some cases, the gold recovery was over 100% according to the dissolved gold concentration determined by ICP-OES. Analytical discrepancies resulting from the interference of other elements such as Fe may cause this phenomenon. However, the results do show that almost full gold recovery was achieved using $\geq 0.06 \text{ M CaS}_2\text{O}_3$ with 2 mM EDTA or $(\text{NH}_4)_2\text{S}_2\text{O}_3$.

The variation in thiosulfate concentration in leaching is shown in Fig. 5.

Fig. 5 presents the variation in thiosulfate concentration in leaching the slurry sample with CaS_2O_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_3$. In the CaS_2O_3 leaching systems, thiosulfate degraded, and this appeared to

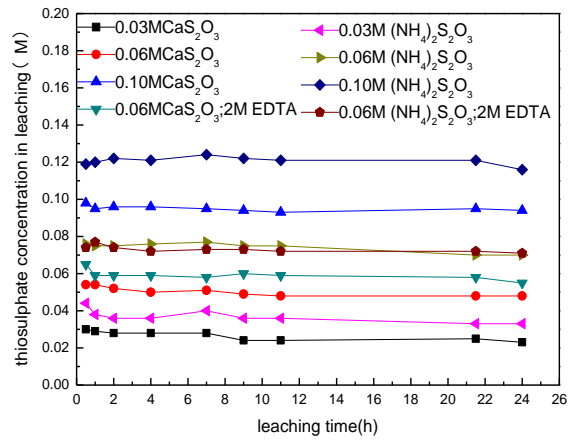


Fig. 5. Variation of $\text{S}_2\text{O}_3^{2-}$ concentration in leaching slurry feed with CaS_2O_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_3$. Stirring speed 250 r/min.

be more noticeable at a lower concentration. EDTA slightly enhanced the stability of thiosulfate. In contrast, thiosulfate degradation was limited in the $(\text{NH}_4)_2\text{S}_2\text{O}_3$ leaching system. The titrated thiosulfate concentrations after leaching were even higher than the initial thiosulfate concentrations. This is believed to be because some sulfide or oxysulfate species were generated in the leaching of the sulfide minerals due to ammonia. The formed intermediate sulfur species, e.g. S^{2-} and S_8 , were found to cause the loss of gold to leach residues, even in trace concentrations. The presence of dissolved S^{2-} may result in gold precipitation, and S_8 has high affinity for gold species.

Resin-in-leach

For each resin-in-leach test, 5 ml of anionic resin was added into the leach slurries to enable sorption, and then separated from the slurries after 7 h or 24 h using a 300 μm sieve. The loaded resins were washed with deionised water, dried and ashed for acid digestion. To reduce the breakdown of resin in the leaching tanks, the stirring speed was reduced to 200 r/min. The resin-in-leach results are displayed in Table 1.

In the presence of 5 ml of resin, the gold recovery dropped slightly at 0.06 M CaS_2O_3 between 7 h and 24 h. In all other cases, the gold recovery increased from 7 h to 24 h.

There was still some gold remaining in solution with the addition of 5 mL of resin, which indicates either that the ion exchange capacity of 5 mL of resin was insufficient for uptake of all gold, or that other metal species present saturated the resin. EDTA showed no impact on gold adsorption on the resin, and gold recovery increased in the presence of EDTA with resin. At 0.06 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, the gold recovery approached 100% with the addition of 2 mM EDTA.

Table 1. Resin-in-leach tests. Stirring speed 200 r/min

Conditions	Solution	Resin	Overall	Residue
0.06 M CaS ₂ O ₃ , 7 h	7.57	72.74	80.31	23.1
0.06 M CaS ₂ O ₃ , 24 h	3.93	74.56	78.49	14.2
0.06 M CaS ₂ O ₃ , 12 mM EDTA, 7 h	7.94	69.57	77.51	24.6
0.06 M CaS ₂ O ₃ , 12 mM EDTA, 24 h	8.14	87.90	96.04	5.70
0.06 M (NH ₄) ₂ S ₂ O ₃ , 7 h	4.58	69.7	74.32	27.5
0.06 M (NH ₄) ₂ S ₂ O ₃ , 24 h	12.81	78.55	91.36	10.1
0.06 M (NH ₄) ₂ S ₂ O ₃ , 2 mM EDTA, 7 h	8.22	83.75	91.97	11.3
0.06 M (NH ₄) ₂ S ₂ O ₃ , 2 mM EDTA, 24 h	12.94	89.36	102.3	3.2

Effect of ageing of (NH₄)₂S₂O₃ on gold leaching

Fig. 6 shows the leaching results with fresh and aged 0.06 M (NH₄)₂S₂O₃ at a stirring speed of 250 r/min.

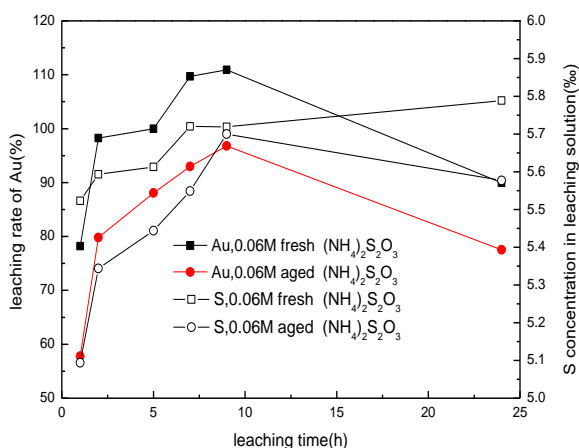


Fig. 6. Influence of ageing of (NH₄)₂S₂O₃ on gold leaching

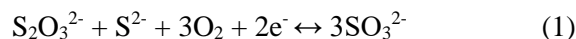
The aged (NH₄)₂S₂O₃ was stored in the laboratory for over a couple of years, and the crystals were consolidated. Also, thiosulfate probably degraded to some extent after ageing. The aged (NH₄)₂S₂O₃ provided a relatively lower gold recovery. The degradation of thiosulfate may form intermediate sulfur species such as elemental sulfur, which may cause the loss of gold.

DISCUSSION AND CONCLUSIONS

Ammonium thiosulfate showed better leaching performance than calcium thiosulfate at the same concentration, at least in part because ammonium thiosulfate leached more sulfide minerals than calcium thiosulfate. This will reduce the galvanic interactions among sulfide minerals and the interactions between thiosulfate/gold thiosulfate species and the sulfide minerals, hence reducing leaching passivation, as well as precipitation of gold.

Gold recovery increased and gold became more stable in solution over time at a higher thiosulfate concentration. A higher stirring speed was beneficial for gold recovery and stability. At a relatively low solids content of 35%, the attrition among the mineral particles is expected to be low. At 50 °C, the dissolved oxygen content will be low in the leaching

solution. A higher oxygen intake at a higher stirring speed is assumed to be a significant factor in the observed higher gold recovery. In sulfide mineral-containing systems, intermediate sulfur-containing reaction products including S²⁻ and S₈ are present. S²⁻ and S₈ can cause gold loss when present even in trace amounts. In the presence of oxygen, S²⁻ can react with S₂O₃²⁻ to form SO₃²⁻ according to (1):



The S²⁻ concentration should remain lower at higher dissolved oxygen content, and S₈ should be also lower. However, this needs to be further investigated to be proven.

EDTA increased gold recovery and gold stability, and this beneficial effect became more pronounced at a higher concentration. Gold recovery from the slurry sample approached 100% after 24 h at 0.06 M calcium or ammonium thiosulfate with the addition of EDTA. CMC improved gold leaching, but gold was not stable in solution. There was an optimum CMC dosage, and beyond this, further addition of CMC hindered gold leaching. The surfactant SDS had a similar effect to CMC. EDTA has complexing abilities, which enhance the leaching of sulfide surfaces and reduce the interference of heavy metals. This will reduce the galvanic interactions among sulfides, as well as the catalytic interactions between thiosulfate/gold thiosulfate and the sulfide minerals. Surfactants such as SDS and CMC mainly act to modify particle surfaces, minimising the leaching passivation. In an ammonia-copper-thiosulfate system, S²⁻ and S₈ are unlikely to be present in solution, because Cu²⁺ ions could efficiently precipitate S²⁻. The mixed solution potential is also higher, reducing the possibility of S₈ formation. Thus, additives should be used to remove the S²⁻ and S₈ species, and/or operating conditions should be changed to minimise the formation of S²⁻ and S₈ species. Therefore, a combination of various additives should be used to improve gold leaching and to keep gold stable in solution.

Aged thiosulfate gave a lower gold recovery than the freshly purchased batch. Polythionates and S₈

may be present in the aged thiosulfate. Polythionates cause lower gold leaching and S₈ adsorbs gold.

EDTA had little impact on adsorption of gold thiosulfate on resin. In the resin-in-leach process, almost full gold recovery was achieved at 0.06 M thiosulfate with the addition of EDTA. It should be noted that not all variables were optimised, e.g. resin usage, thiosulfate and EDTA concentrations. In the resin-in-leach process using ammonium thiosulfate and EDTA, gold recovery reached over 90% after 7 h. With process optimisation, it was expected that full gold recovery can be achieved in shorter time in resin-in-leach using ammonium thiosulfate and EDTA.

Thiosulfate consumption was higher for calcium thiosulfate at lower concentrations. In contrast, thiosulfate consumption was negligible for ammonium thiosulfate leaching. The titrated thiosulfate concentration after leaching was even higher than its original concentration in the case of ammonium thiosulfate. Ammonium thiosulfate enhanced the leaching of the sulfide minerals in the ore, generating various sulfur species to stabilise thiosulfate. Even for calcium thiosulfate, the thiosulfate consumption was relatively low. Thus, the stability of gold thiosulfate species was not directly linked to the stability of thiosulfate. This further indicates that traces of S²⁻ and S₈ should be blamed for gold drop with time.

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