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Thiourea leaching of gold in presence of jarosite and role of oxalate

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Abstract: The effect of jarosite generated from bio-oxidation on gold leaching in acidic thiourea solution was studied, and the role of the oxalate additive was also investigated. The biogenetic jarosite was found to markedly raise the thiourea consumption and hinder the gold dissolution. The dominant cause for the detrimental effect of jarosite is likely that iron ions were released from jarosite dissolution in the acidic solution and thus increased the solution potential, resulting in the accelerated decomposition of thiourea and the aggravated passivation of gold surface by the passivating species from thiourea decomposition. However, the addition of oxalate to solution was shown to be effective in weakening the adverse effect of jarosite manifested as much reduced thiourea consumption and enhanced gold dissolution. The possible acting mechanisms of oxalate were revealed by the analyses of solution potential, Zeta potential and XPS. Oxalate could not only weaken the interaction between Fe^{3+} and thiourea via complexing with Fe^{3+} but also prevent the passivation species from coating on gold surface through indiscriminate adsorption and electrostatic repulsion.

Key words: biogenetic jarosite; gold leaching; thiourea consumption; oxalate

1 Introduction

In the gold industry, bio-oxidation, oxidative roasting, and pressure oxidation are the most commonly used pretreatment methods for refractory sulfide gold ores/concentrates [1], which generally yield less than 80% gold extraction by direct cyanidation. Mostly, the low gold extraction is ascribed to gold particles being locked in the non-porous sulfide matrix of associated minerals such as pyrite, chalcopyrite, and arsenopyrite [2]. Bio-oxidation is an alternative cost-effective treatment method for metal production particularly from low-grade ores, giving its moderate capital expenditure and low operating costs [3−6]. Compared with oxidative roasting and pressure oxidation, bio-oxidation of gold-bearing sulfide minerals has much lower environmental impact and production cost [7,8].

The bacteria commonly employed in the bio-oxidation of gold concentrates are *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans* [9,10]. The metal dissolution by bacteria oxidation can occur through a direct or indirect mechanism [11]. In the direct mechanism, metal sulfides can be directly oxidized into water-soluble sulfate by these acidophilic bacteria. In the indirect mechanism, H_2SO_4 is generated from the oxidation of elemental sulfur or reductive sulfur compounds by bacteria, and the formed H_2SO_4 can in turn be used as a strong leaching agent for metal dissolution from ores [12,13]. The ferrous ions produced from bioleaching are further oxidized to ferric ions by the bacterial population, providing energy for bacterial growth and the Fe^{3+} oxidant for bio-oxidation process. It is widely acknowledged that various iron-, arsenic- and sulfur-containing impurities, such as jarosite, orpiment, and realgar can be formed

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during bio-oxidation of gold sulfide ores [14,15]. Among them, the amount of jarosite is the most, which could reach up to 70% [16].

Cyanidation has been the dominant technique for gold leaching from its ores or concentrates because of its low cost, simple process and mature technology [17,18]. However, this technique is potentially harmful to the environment due to the high toxicity of cyanide. In the view of the increasing requirement for the environmental protection worldwide, the non-cyanide techniques have been developed in the past few decades [19−24]. The acidic thiourea (TU) leaching technique has been regarded as a promising substitute for cyanidation due to its much lower toxicity and faster kinetics [25−28]. Furthermore, no need of acid-base neutralization between the process of thiourea leaching and bio-oxidation makes this technique more suitable than cyanidation for gold extraction from refractory sulfide gold ores/concentrates pretreated by bio-oxidation [29−32]. Previous studies have indicated that the excessive ferric ions in bio-oxidation process and some impurities left in the bio-oxidized residues tend to destabilize the thiourea, leading to higher consumption of thiourea [33,34]. Jarosite is an impurity with the most quantity that remains in the residue after bio-oxidation, but its effect on gold dissolution in acidic thiourea solutions and thiourea stability has less been reported.

In this work, the effect of jarosite from the reproduction process of *Acidithiobacillus ferrooxidans* in 9K culture medium on thiourea leaching of gold using the oxidant of Fe^{3+} was reported, and the relevant acting mechanisms were explored. In addition, oxalate, a common ligand that can effectively complex with Fe^{3+} to improve the thiourea stability, was used as an additive. The role of oxalate in thiourea leaching in the presence of biogenetic jarosite was investigated, and the possible mechanism was also proposed. These issues were studied and discussed by leaching experiments of gold foil or ores and a series of analyses of mineralogical phase, morphology, composition of surface species, Zeta or solution potential, etc. The experimental and analytical results obtained may be conductive to promote the commercial application of bio-oxidation pretreatment followed by thiourea leaching for gold extraction from its refractory ores or concentrates.

2 Experimental

2.1 Strain and culture medium

The strain *Acidithiobacillus ferroosidans* (*A. ferrooxidans*) was used for the generation of jarosite and the bioleaching pretreatment of gold ore, which was preserved at the Key Laboratory of Biometallurgy of Ministry of Education, Changsha, China. The 9K medium for cell cultivation was composed of 3 g/L $(NH_4)_2SO_4$, 0.1 g/L KCl, 0.5 g/L K_2HPO_4, 0.5 g/L $MgSO_4\cdot7H_2O$, 0.01 g/L $Ca(NO_3)_2$ and 44.7 g/L $FeSO_4\cdot7H_2O$.

2.2 Materials and reagents

Gold foils (Au purity >99.99%, thickness of 0.2 mm) were used in the leaching experiments with a surface area of about 0.25 cm^2. The gold foils were polished with an abrasive paper of 2000 grit, dipped in ~5 mol/L H_2SO_4 solution for 30 min and rinsed with deionized water; a gold foil with fresh surface was prepared for each leaching experiment. The refractory gold ore was obtained from Shandong province, China, and it was ground to a particle size of 80% <0.034 mm before its leaching and analyses. The refractory gold ore consisted mainly of pyrite and quartz, and the contents of Au, Fe, S and SiO_2 were 48 g/t, 18.02%, 17.31% and 19.06%, respectively.

The chemical reagents, such as thiourea, ferric sulfate, sulfuric acid, ammonium sulfate, potassium chloride, dipotassium hydrogen phosphate, magnesium sulfate, calcium nitrate, ferrous sulfate, and sodium oxalate used here were all of analytical reagent grade. Deionized water prepared by water purification system (UPR-I-5/10/15T) was used to prepare solutions, and the solutions were used immediately.

2.3 Preparation of jarosite and bio-oxidation of refractory gold ore

The jarosite used in this study was biosynthesized from the growth process of *A. ferrooxidans* in 9K culture medium in flasks [35]. Each flask was inoculated with 15% (volume fraction) inoculum with cell concentration of 2.0×10^8 cells/mL. The initial pH of the medium was adjusted to be 1.8 with the addition of ~3 mol/L H_2SO_4. The reaction system was incubated at

160 r/min and 30 °C in an incubator shaker for 7 d. After reaction finished, the precipitates (i.e., biogenetic jarosite) were collected after filtration with a 0.45 μm filter paper, dried under vacuum overnight, and subsequently characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). The bio-oxidation experiment for the refractory gold ore was carried out under the same conditions as the preparation of jarosite with a pulp density of 10 g/L gold ore. After 28 d, the bioleached residue was filtered, washed and dried for subsequent gold leaching.

2.4 Leaching tests

Leaching tests of the suspended gold foil, biogenetic jarosite, as-received gold ore, and bioleached residue were carried out in 250 mL beakers each using a magnetic stirrer at a rotating speed of 180 r/min for gold foil and jarosite and 300 r/min for gold ore/residue. The pulp densities of jarosite, as-received gold ore, and bioleaching residue in thiourea solution were 6, 200 and 200 g/L, respectively. Unless otherwise stated, all the tests were conducted under the conditions of [TU] 2 g/L, [Fe^{3+}] 1.35 g/L, temperature (25±0.5) °C, and leaching time 4.0 h. The pH value of solution was maintained at 1.5 by adding ~3 mol/L H_2SO_4 per 0.5 h. During the leaching of gold foil or jarosite, 5 mL of solution sample was withdrawn every 1 h for subsequent chemical analysis. After the leaching was complete, the gold foil was taken out of the solution, while the pulp was directly filtered through a 0.45 μm filter paper; the leached gold foil and residue obtained were rinsed with deionized water, dried under vacuum overnight, and subsequently subjected to the characterization analysis. After 4 h leaching of as-received gold ore and bioleached residue was finished, the pulp was filtrated, and the filtrate was collected for the analyses of gold concentration and thiourea concentration.

2.5 Analytical methods

The concentrations of Au and total Fe, i.e., Fe(T) in leachates were determined with an inductively coupled plasma-atomic emission spectrometry (PS−6, Baird). The concentration of Fe^{2+} was measured by the 1,10-phenanthroline analytical method at 510 nm using a UV−Vis spectrophotometer. The concentration of Fe^{3+} was calculated from the difference between Fe(T) and Fe^{2+} [36]. Thiourea concentration was analyzed by a potassium iodate titration with starch as an indicator [37]. The pH value of solution was measured with a pH meter (PHSJ−4A). The potential was determined with a platinum electrode and a reference electrode (Ag/AgCl, saturated KCl); all potentials were reported relative to the standard hydrogen electrode (SHE). The mineralogical phase of the jarosite before and after leaching was determined by XRD (RIGAKU, D/Max 2500, Japan). The morphological studies of leached gold foil surface and leached residue were carried out by SEM−EDS (MIRA3 LMH, TESCAN). X-ray photon spectroscopy (XPS) (ESCALAB 250Xi, Thermo Fisher) was used to identify the surface species on gold foil surface. The Zeta potential was determined with micro-electrophoretic method using a Zeta potential analyzer (ZEN3690, Malvern).

3 Results and discussion

3.1 Biosynthesis and characterization of jarosite

Figure 1 shows the variation of solution parameters including pH, solution potential (φ_h), Fe^{2+} concentration and Fe^{3+} concentration during the growth of *A. ferrooxidans* grown in 9K culture medium. As shown in Fig. 1(a), the pH of solution increased for the first two days, and then decreased in the following five days. The increase of pH may be caused by the bio-oxidation of Fe^{2+} catalyzed by *A. ferrooxidans*, according to the reaction given in Reaction (1). The reason for the decrease of pH may be that the hydrolysis of Fe^{3+} to jarosite produces acid, according to Reaction (2). Figure 1(a) also indicates the variation of φ_h as a function of time. Over the first two days, the oxidation of Fe^{2+} to Fe^{3+} contributed to the increase of φ_h. According to the Nernst equation [38], φ_h value is related to the ratio of Fe^{3+}/Fe^{2+} in the solution. As seen in Fig. 1(b), the Fe^{3+} concentration rapidly decreased over the first two days, and then remained basically unchanged. The Fe^{3+} concentration increased obviously firstly, and then decreased slightly, likely due to the formation of the iron-containing precipitate (i.e. jarosite).

$$4Fe^{2+}+O_2+4H^+\rightarrow 4Fe^{3+}+2H_2O \quad (1)$$

$$3Fe^{3+}+K^{+}+6H_2O+2SO_4^{2-}\rightarrow KFe_3(SO_4)_2(OH)_6+6H^{+} \quad (2)$$

The iron-containing precipitate generated during the bioleaching was characterized by XRD and SEM−EDS, and the results are shown in Fig. 2. The XRD pattern in Fig. 2(a) indicates that the mineralogical phase for the precipitate was jarosite. The SEM−EDS image (Fig. 2(b)) shows that the jarosite existed with irregular shape and was composed of smooth polyhedral particles, consistent with the finding from ZHANG et al [35]. In addition, the elemental compositions (mainly O, Fe, S and K) presented from the EDS spectrum and element mapping images further confirmed the biosynthesis jarosite.

3.2 Thiourea leaching of gold in presence of jarosite

3.2.1 Dissolution of jarosite in acidic thiourea solution

Figure 3 shows the dissolution behavior of jarosite (6 g/L) in acidic thiourea solution with the change of total Fe concentration as an indicator. As can be seen, the Fe concentration decreased slightly over time in the thiourea solution without jarosite. In contrast, the Fe concentration increased with the addition of jarosite. This is likely because the decomposition of jarosite took place in acidic solution, and the decomposition reaction is shown in Reaction (3) [39]. The jarosite decomposition was shown to be strongly dependent upon temperature [40,41], which explains why only a small amount of jarosite was dissolved at the ambient temperature of 30 °C. However, the small amount of Fe released from jarosite has a significant effect on the thiourea stability and gold dissolution.

$$KFe_3(SO_4)_2(OH)_6+6H^{+}\rightarrow 3Fe^{3+}+K^{+}+2SO_4^{2-}+6H_2O,\quad \lg K=-12.50 \quad (3)$$

3.2.2 Effect on thiourea consumption

The thiourea consumption without and with the addition of jarosite is presented in Fig. 4(a). As can be seen, without adding jarosite, about 34.46% of thiourea was oxidized after leaching for 4 h. However, the addition of jarosite had a negative

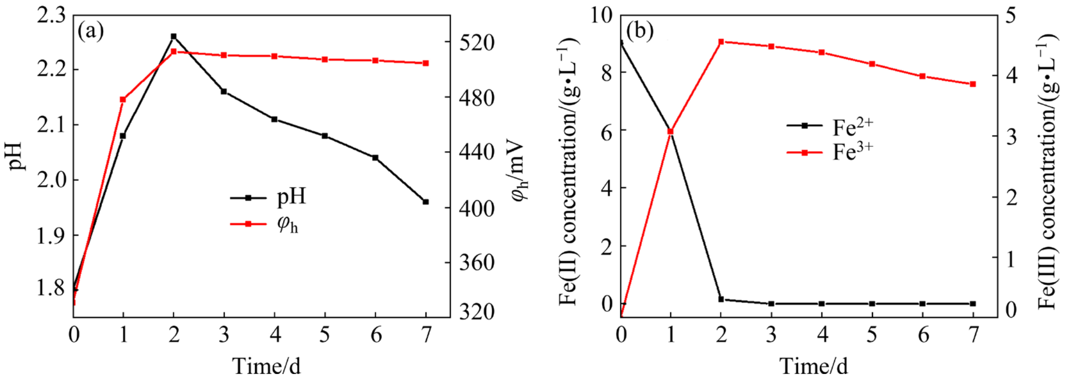

Fig. 1 Change in solution parameters of pH, φ_h, Fe^{2+} concentration and Fe^{3+} concentration with growth of *A. ferrooxidans* in 9K culture medium

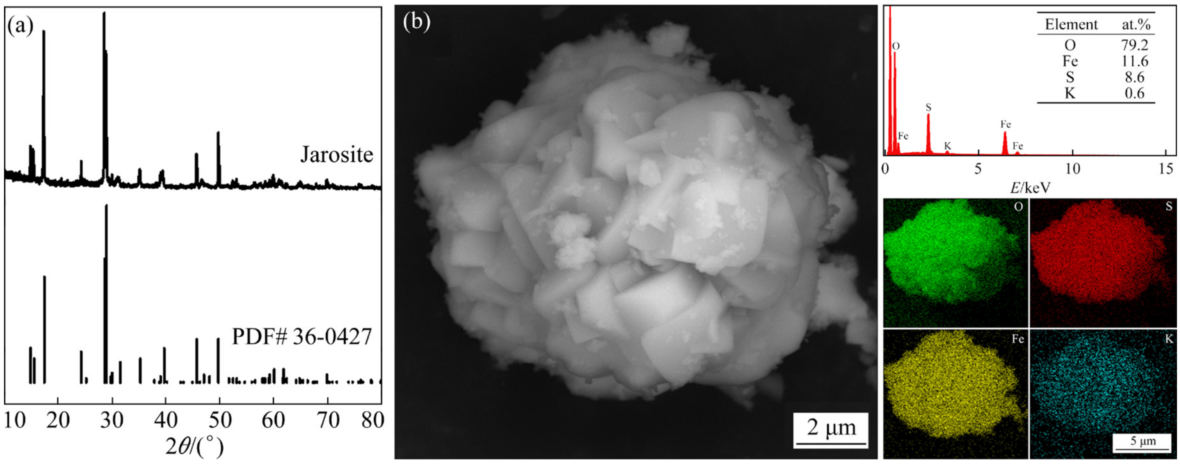

Fig. 2 XRD pattern (a) and SEM image and element mappings with EDS spectrum (b) for biogenetic jarosite

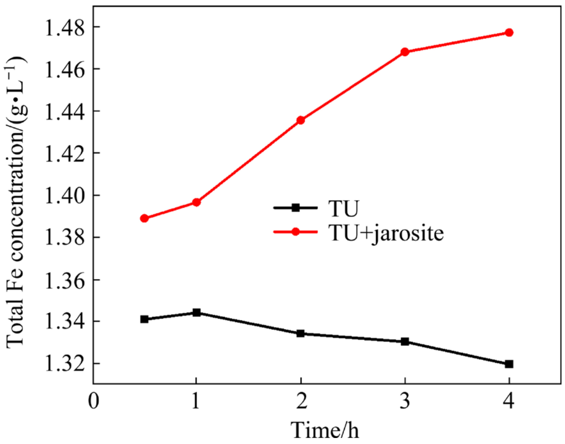

Fig. 3 Variation of total Fe concentration from dissolution of jarosite in acidic thiourea solution

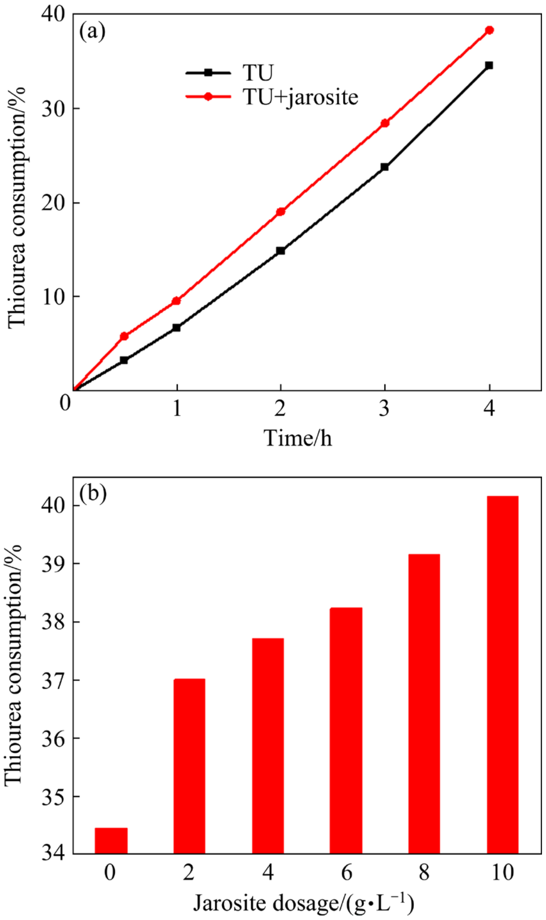

Fig. 4 Variation of thiourea consumption: (a) With time in presence of 6 g/L jarosite; (b) With different jarosite dosages after 4 h leaching

effect on the thiourea stability, which accelerated the decomposition of thiourea, increasing the thiourea consumption to 38.24% at 4 h. This is possibly because ferric ions derived from jarosite decomposition increased the Fe^{3+} concentration of the solution, and thus enhanced the oxidation of thiourea by Fe^{3+}, as shown in Reaction (4). In addition, the increase of jarosite dosage further promoted the decomposition of thiourea, as indicated in Fig. 4(b). With increasing the addition of jarosite from 2 to 10 g/L, the thiourea consumption at 4 h rose from 37.02% to 40.16%.

$$2CS(NH_2)_2+2Fe^{3+}\rightarrow 2Fe^{2+}+[CS(NH_2)(NH_2)]_2^{2+},\quad \lg K=11.83 \qquad (4)$$

In the acidic thiourea leaching system, the oxidative decomposition of thiourea is closely linked to the solution potential, which was also measured. The variation of solution potential during the leaching in the presence of 6 g/L jarosite without and with the addition of 2 g/L oxalate is presented in Fig. 5. Only the situation without oxalate was discussed in this section. As indicated, the solution potential without the addition of jarosite decreased with time, whilst with the addition of jarosite the solution potential increased. As reported in the literature [38], the mixed pulp potential is determined by the Fe^{3+}/Fe^{2+} redox equilibrium potential. So, the reason for the decrease of solution potential may be that the rate of consumption of ferric ion mainly due to the oxidation of thiourea was faster than that of its generation. When the jarosite was added to the acidic thiourea solution, the release of ferric ion from jarosite increased the concentration of ferric ion, and thus improved the solution potential.

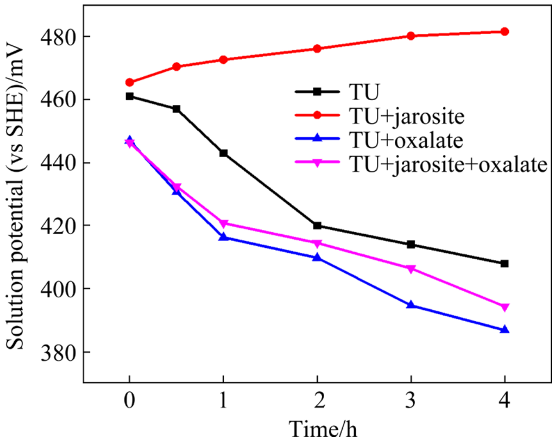

Fig. 5 Variation of solution potential with leaching time in presence of 6 g/L jarosite without and with addition of 2 g/L oxalate

3.2.3 Effect on gold dissolution

Figure 6(a) indicates the variation of gold dissolution as function of time in the absence and presence of jarosite. The gold dissolution in thiourea solution with no jarosite added was 37.71 mg/cm^2 after 4 h leaching. It is clear that the presence of jarosite had a negative impact on gold dissolution in thiourea solution; with the addition of 6 g/L jarosite, the gold dissolution reduced from 37.71 to 32.74 mg/cm^2. When the dosage of jarosite increased from 2 to 10 g/L, the gold dissolution decreased constantly from 36.21 to 28.42 mg/cm^2 after 4 h leaching, as shown in Fig. 6(b). As such, appropriate measure appears necessary to eliminate or reduce the detrimental impact of jarosite on thiourea leaching of gold especially from the refractory gold ores/concentrates pretreated by bio-oxidation, where large amounts of jarosite remain.

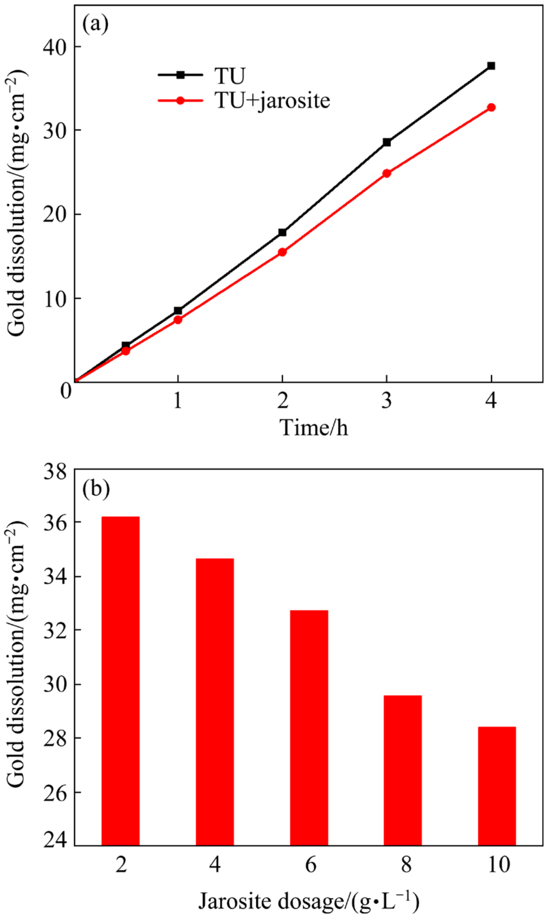

Fig. 6 Variation of gold dissolution: (a) With time in presence of 6 g/L; (b) With different jarosite dosages after 4 h leaching

3.3 Role of oxalate in thiourea leaching of gold in presence of jarosite

As mentioned in Section 3.2.2, the release of ferric ion increased the solution potential, which caused the increase in the rate of thiourea oxidation. Therefore, using a ligand that can form complexes with ferric ion is an effective strategy to improve the stability of thiourea in the acidic solution. In this sense, oxalate ($C_2O_4^{2-}$) can form stable complexes with ferric ions and the relative reactions are shown in Reactions (5) and (6). In addition, the reduction of both $Fe(C_2O_4)_3^{3-}$ and $Fe(C_2O_4)_2^-$ to form $Fe(C_2O_4)_2^{2-}$ can be promoted, as shown in Reactions (7) and (8) [42,43]. Medusa−Hydra chemical equilibrium software was adopted to construct the φ_h−lg[$C_2O_4^{2-}$] diagram for the Fe species in the Fe−$C_2O_4^{2-}$−H_2O system, as presented in Fig. 7. Clearly, with the increase of oxalate dosage, the Fe^{3+}/Fe^{2+} redox couple converts to the couples of $Fe(C_2O_4)^+/Fe^{2+}$ and $Fe(C_2O_4)_2^-/Fe^{2+}$, and the equilibrium potential decreases from 0.771 to 0.625 V. The complexation of oxalate with Fe^{3+} reduces the reduction potential of the Fe^{3+}/Fe^{2+} couple, which therefore is beneficial to improving the thiourea stability.

$$Fe^{3+}+2ox^{2-}\rightarrow Fe(ox)_2^-,\ \lg K=13.81 \quad (5)$$

$$Fe^{3+}+3ox^{2-}\rightarrow Fe(ox)_3^{3-},\ \lg K=18.6 \quad (6)$$

$$Fe(ox)_3^{3-}+e\rightarrow Fe(ox)_2^{2-}+ox^{2-},\ \varphi^0=-0.025\ V \quad (7)$$

$$Fe^{3+}+2ox^{-}+e\rightarrow Fe(ox)_2^{2-},\ \lg K=16.25 \quad (8)$$

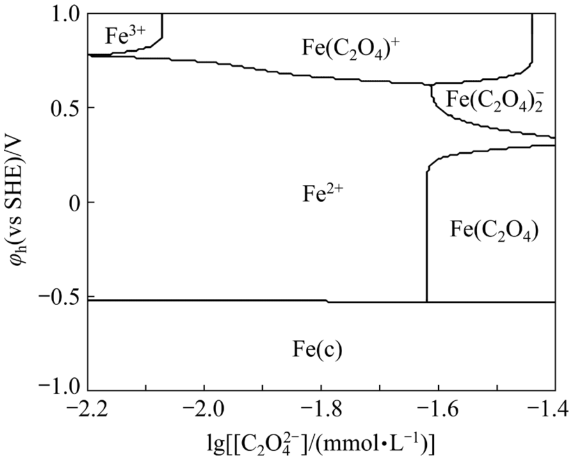

Fig. 7 φ_h−lg [$C_2O_4^{2-}$] diagram of Fe species in Fe−$C_2O_4^{2-}$−H_2O system at 25 °C and 1.01×10^5 Pa

3.3.1 Effect on jarosite decomposition

The dissolution of iron from jarosite with the presence of oxalate is indicated in Fig. 8. Apparently, the dissolution of iron from jarosite in acidic thiourea solution was increased when the oxalate was presented in the time range studied here since oxalate could act as a leaching agent for iron. Moreover, the increase of oxalate dosage improved the dissolution of jarosite manifested as the increased Fe concentration. Oxalate can form stable complexes with ferric ion to reduce its oxidizability, thus improving the stability of thiourea, which is beneficial to preventing passivation species derived from thiourea decomposition from coating on the jarosite surface. Therefore, the concentration of iron derived from jarosite dissolution increased after the addition of oxalate.

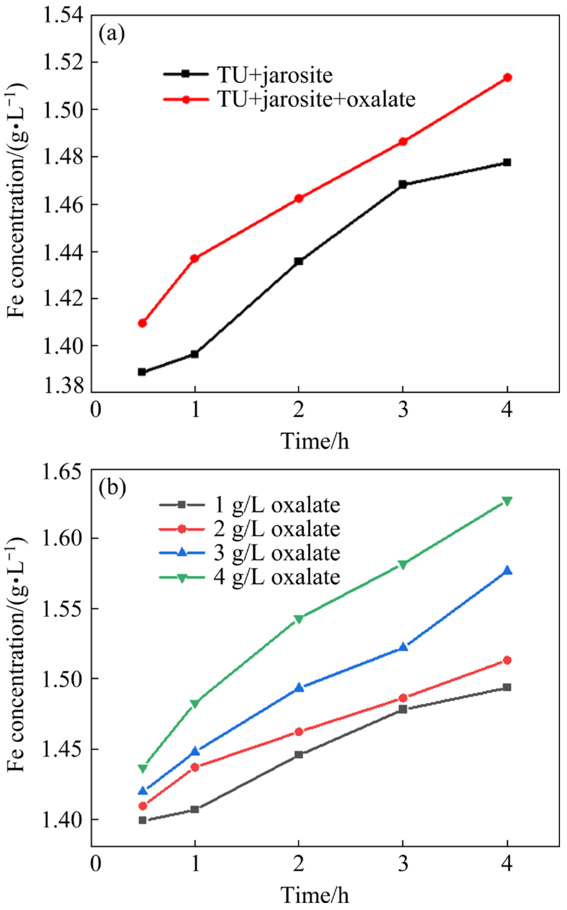

Fig. 8 Variation of concentration of Fe derived from jarosite (6 g/L) dissolution: (a) With time in presence of 2 g/L oxalate; (b) With oxalate dosage

3.3.2 Effect on thiourea consumption

The variation of thiourea consumption as a function of time in the presence of 2 g/L oxalate is presented in Fig. 9(a). As can be seen, when oxalate was presented, the thiourea consumption in the presence of 6 g/L jarosite decreased from 38.24% to 28.30% after 4 h leaching. Besides, the thiourea consumption was lower than that of thiourea leaching without jarosite and oxalate (38.24%) but was higher than of thiourea leaching in the presence of only oxalate (24.76%). The effect of oxalate dosage on thiourea consumption was further studied, as shown in Fig. 9(b). The thiourea consumption was found to decrease with the increase of oxalate dosage. The solution potential decreased in the presence of oxalate, as presented in Fig. 5, which is in favor of the improvement in the stability of thiourea. Therefore, the consumption of thiourea reduced when oxalate was added in the presence of jarosite.

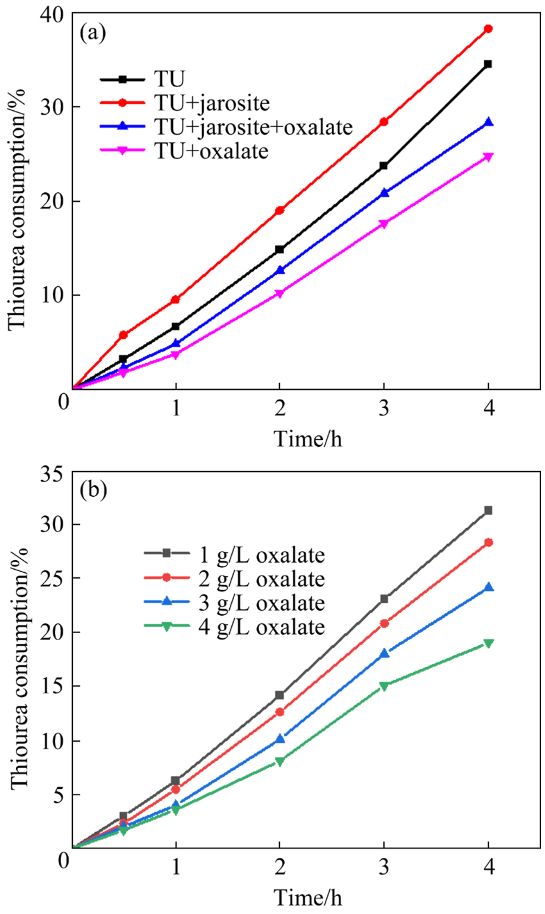

Fig. 9 Variation of thiourea consumption: (a) With time; (b) With oxalate dosage during thiourea leaching

As indicated in Fig. 5, the potential level declined evidently when oxalate was added. Because the redox equilibrium potential of Fe^{3+}/Fe^{2+} determines the mixed potential, the decline of potentials is likely attributed to the coordination of oxalate with Fe^{3+} [38]. As a result of the coordination, the oxidizability of Fe^{3+} is reduced. Thus, this also demonstrates that oxalate can weaken the interaction between thiourea and Fe^{3+}.

3.3.3 Effect on gold dissolution

Figure 10(a) indicates the variation of gold dissolution as a function of time in the presence of 2 g/L oxalate. The gold dissolution in thiourea solution with the addition of 6 g/L jarosite was

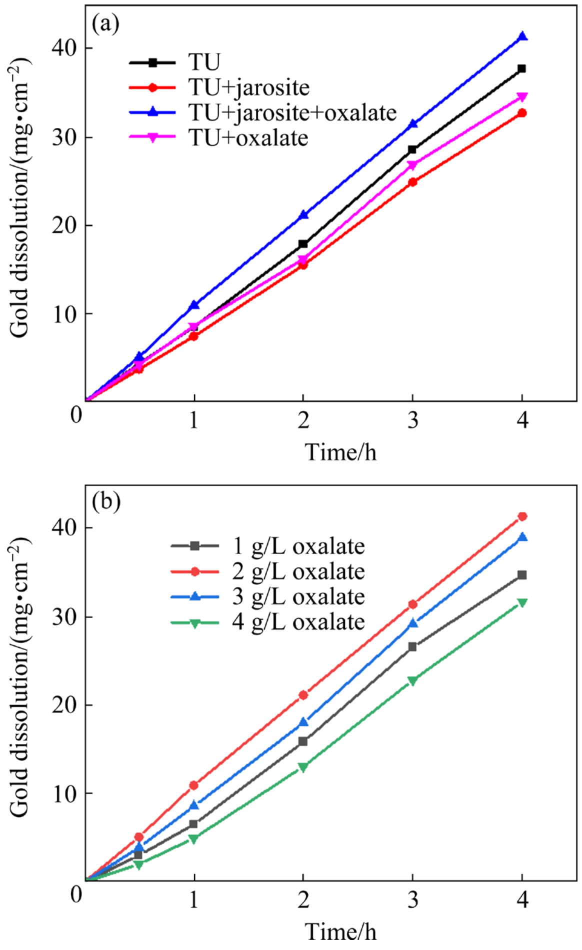

Fig. 10 Variation of gold dissolution: (a) With time in presence of 2 g/L oxalate; (b) With oxalate dosage during thiourea leaching

around 32.74 mg/cm^2 after 4 h leaching. It is apparent that the presence of oxalate had a positive impact on gold dissolution in thiourea solution, and the gold dissolution increased to 41.36 mg/cm^2, which was higher than that of leaching in thiourea solutions without jarosite/oxalate. The dissolution of gold in the thiourea solution containing only oxalate was 34.62 mg/cm^2, and it was lower than that of thiourea leaching without jarosite and oxalate. As presented in Fig. 10(b), the increase of oxalate in the range of 1−2 g/L could augment gold dissolution, and then it began to drop beyond 2 g/L oxalate. As indicated in Fig. 7, with rising the oxalate concentration from 1 to 2 g/L, the Fe^{3+}/Fe^{2+} couple transforms to $Fe(C_2O_4)^+/Fe^{2+}$, and the equilibrium potential decreases slightly. With further increasing the oxalate dosage, $Fe(C_2O_4)_2^-/Fe^{2+}$ couple is formed, but its equilibrium potential decreases evidently, which is likely to slow the gold dissolution kinetics. This explains why the gold dissolution decreased when the oxalate dosage was higher than 2 g/L.

The Zeta potentials of jarosite as a function of pH in the absence and presence of 2 g/L oxalate are shown in Fig. 11, and the results show that the isoelectric point of jarosite was approximately 3.75. The Zeta potentials of jarosite became obviously more negative when oxalate was presented, which was likely attributed to the adsorption of electronegative oxalate on jarosite surface. Oxalate rendered the surface of gold and passivation species in the solution both negatively charged, and thus the electrostatic repulsion prevented passivation species from coating on gold surface. The gold surface was still hydrophilic and easily accessible for leaching solution, because the negatively charged functional groups of carboxyl in the ion were also highly hydrophilic [44,45]. So, the gold dissolution was improved during the leaching by the addition of oxalate.

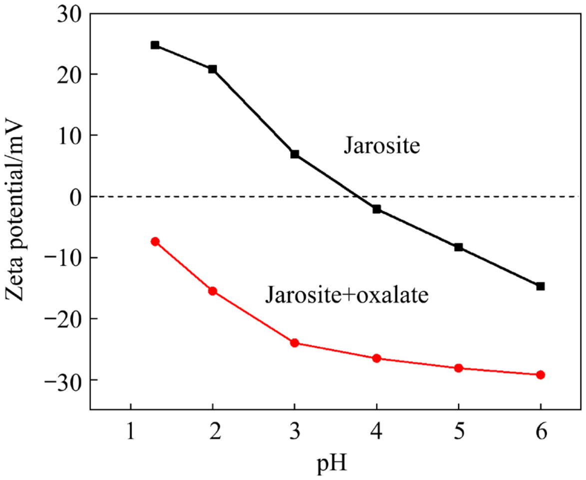

Fig. 11 Zeta potential versus pH for jarosite in absence and presence of 2 g/L oxalate

3.4 Morphology and phase composition of jarosite before and after leaching

3.4.1 SEM−EDS analysis

The surface morphology and element composition of the leached residue in the absence and presence of oxalate were characterized by SEM−EDS, and the results are shown in Fig. 12. Leached residues in the absence and presence of oxalate had irregular shape and were composed of smooth polyhedral particles. Compared with Fig. 2(b), it can be inferred that the surface morphologies of jarosite before and after leaching with and without the addition of oxalate had no

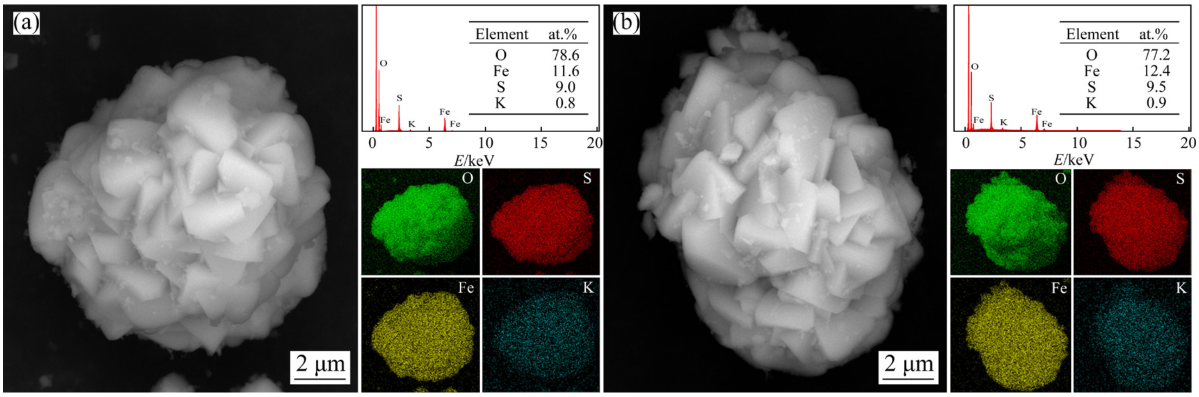

Fig. 12 SEM images and element mappings with EDS spectra for jarosite after 4 h leaching in absence (a) and presence (b) of 2 g/L oxalate

significant changes, and the element composition was also almost not changed.

3.4.2 XRD analysis

To further investigate the change of mineralogical phase for the leached residue of jarosite, XRD analysis was carried out, and the results are presented in Fig. 13. Clearly, the leached residues had the same phase (i.e., jarosite), whether there was the addition of oxalate or not. This demonstrates that the phase of leached residue was scarcely changed after the thiourea leaching.

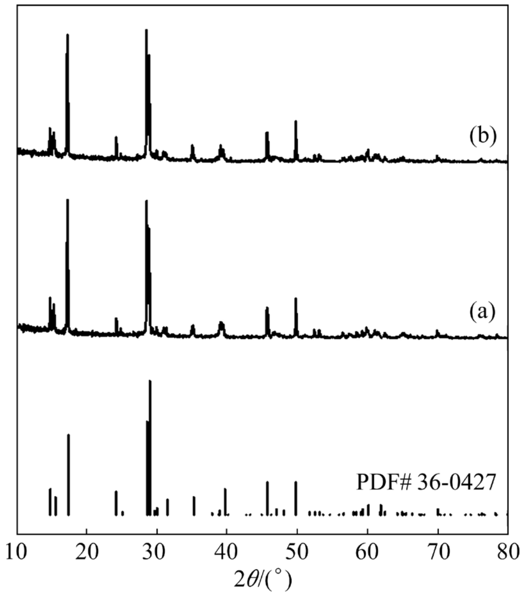

Fig. 13 XRD patterns of leached residue in absence (a) and presence (b) of 2 g/L oxalate

3.5 Change in morphology and composition of gold foil surface

3.5.1 SEM analysis

After leaching, a light brown tarnished film seemed to appear on the gold foil surface. Thus, the surface morphology of leached gold foil was subjected to the SEM analysis (see Fig. 14). The different morphological characteristics of gold foil before and after thiourea leaching in the presence of jarosite without and with the addition of oxalate were found. The leached gold foil surfaces in the absence and presence of jarosite and oxalate were corroded in different degrees, and appeared to be covered with a wrinkled membrane, as shown in Fig. 14(b). EDS analysis was carried out to identify the chemical composition of the film, but almost only Au was detected in the spectra (not shown). The composition of the film could not be identified by EDS analysis likely due to its extremely low amount on gold surface. According to Ref. [46], the film was likely to be mainly composed of sulfur-containing species derived from the decomposition of thiourea.

3.5.2 XPS analysis

Leached gold foils were subjected to XPS analysis for the purpose of identifying their surface species in different leaching systems. The results of XPS analysis are shown in Figs. 15(a−c), in which the spectra of S 2p were recorded. It is indicated that all of the S 2p spectra appeared at 161.8−168.7 eV. The peak in the range of 160.0−164.0 eV could be converted into three peaks. Namely, the S $2p_{3/2}$ peaks centered at 161.5, 162.6 and 164.4 eV, which were assigned to monosulfide S^{2-} [46], disulfide S_2^{2-} [47,48] and elemental sulfur S^0 [49], respectively. The peak centering at around 168.1 eV was likely derived from SO_4^{2-} [50,51]. Thus, it was found that the sulfur species on gold surface included S^{2-}, S_2^{2-}, S^0 and SO_4^{2-}. The peaks area and contents of sulfur species in different

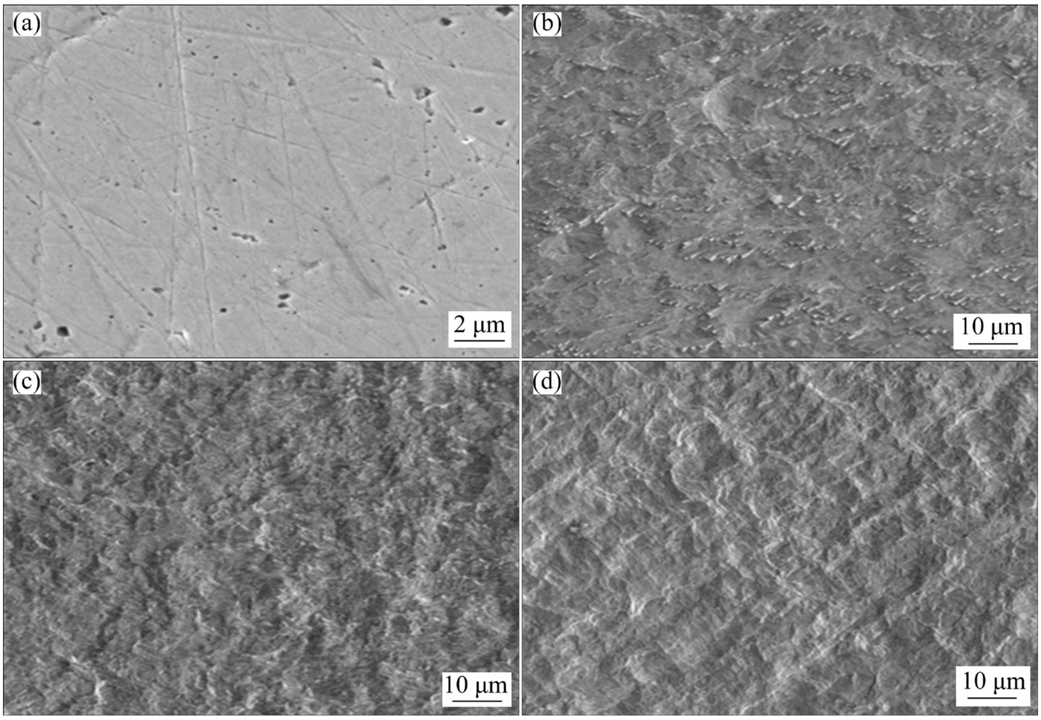

Fig. 14 Typical SEM images: (a) Original gold surface; (b) Leached gold surface; (c) Leached gold surface with 6 g/L jarosite; (d) Leached gold surface with 6 g/L jarosite and 2 g/L oxalate

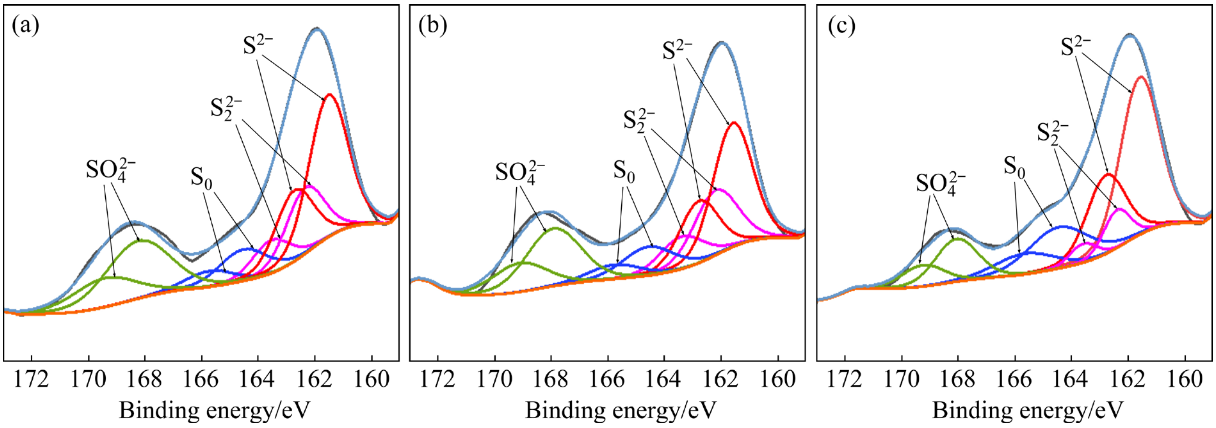

Fig. 15 XPS spectra of S 2p: (a) Leached gold surface without jarosite and oxalate; (b) Leached gold surface with jarosite; (c) Leached gold surface with jarosite and oxalate

leaching systems are presented in Table 1. It is clear that the peak area followed the order of thiourea leaching in the presence of jarosite > thiourea leaching in the absence of jarosite > thiourea leaching with the addition of jarosite and oxalate. Besides, the content of S^{2-} and S^0 in the presence of oxalate was obviously higher, but the content of S_2^{2-} and SO_4^{2-} was evidently lower. This may be related to the decomposition process of thiourea in the presence of oxalate.

3.6 Gold leaching from refractory gold ore

The gold leaching from a refractory gold ore consisting mainly arsenopyrite and pyrite was performed to investigated and confirm the beneficial effects of bio-oxidation pretreatment and oxalate additives (2 g/L). After bio-oxidation, most of arsenic (>90%) and iron (>90%) were extracted from the concentrate, but large amount of jarosite was also formed and remained in the bioleached residue. The results of gold extraction and thiourea consumption in different leaching systems are given in Table 2. The gold extraction was only 24.6% for the refractory gold ore without bio-oxidation pretreatment, and the thiourea consumption reached up to 9.8 kg/t (ore). After bio-oxidation, the gold extraction without the addition of oxalate was significantly increased to 82.7%, whilst thiourea consumption decreased to 6.4 kg/t (ore). In the presence of oxalate (2 g/L), the gold extraction was further improved to be 87.4%, and thiourea consumption was also reduced to 3.7 kg/t (ore). It can be concluded that the addition of oxalate is conducive to improve the gold leaching and maintain the thiourea stability, making bio-oxidation pretreatment and oxalate assisted thiourea leaching a promising technology to achieve environmentally friendly and economical extraction of gold from its refractory sulfide ores.

Table 1 Peak parameters and chemical states of S 2p in different leaching systems

Leaching system	Chemical state	Peak area/ (cps·eV)	Content/%
TU	S^{2-}	3268.89	41.60
	S_2^{2-}	1506.785	19.18
	S^0	904.635	11.51
	SO_4^{2-}	2177.845	27.71
TU+ jarosite	S^{2-}	3551.95	41.62
	S_2^{2-}	1787.28	20.94
	S^0	1030.525	12.07
	SO_4^{2-}	2165.055	25.37
TU+ jarosite+ oxalate	S^{2-}	3955.66	53.61
	S_2^{2-}	666.165	9.03
	S^0	1576.455	21.36
	SO_4^{2-}	1180.59	16.00

Table 2 Gold extraction and thiourea consumption in different leaching systems

Leaching system	Gold extraction/%	Thiourea consumption/ ($kg·t^{-1}$(ore))
Thiourea leaching without pretreatment	24.6	9.8
Thiourea leaching after bio-oxidation	82.7	6.4
Thiourea leaching with oxalate addition after bio-oxidation	87.4	3.7

In conclusion, the presence of jarosite could accelerate the thiourea decomposition and hinder the gold dissolution. When oxalate was added to thiourea solution, the harmful effect of jarosite on thiourea stability and gold dissolution could be effectually reduced. The influencing mechanisms of jarosite and oxalate for thiourea leaching of gold are proposed in Fig. 16. Namely, in the presence of jarosite, the thiourea consumption increased, and the amount of passivating sulfur species on gold surface also increased, leading to the impediment on gold leaching. With the addition of oxalate, the oxidizability of Fe^{3+} was reduced because oxalate could complex with Fe^{3+} to form stable complexes, which is beneficial to improving the stability of thiourea. Moreover, oxalate could prevent passivation species from coating on gold surface through electrostatic repulsion. The gold surface was still hydrophilic and easily accessible for leaching solution, because the negatively-charged functional groups of carboxyl in the ion were also highly hydrophilic. Therefore, the presence of oxalate can contribute to the improvement in gold dissolution and the reduction of thiourea consumption during the leaching.

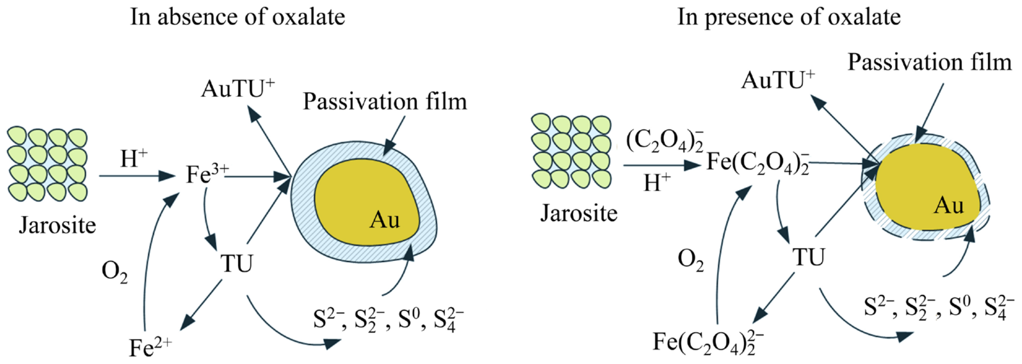

Fig. 16 Possible mechanisms involved in thiourea leaching of gold in presence of jarosite

4 Conclusions

(1) Dissolution of biogenetic jarosite could occur in acidic thiourea solution, releasing the Fe^{3+} oxidant to solution and thus increasing the solution potential. Addition of oxalate to the thiourea solution increased the release of iron ions from the jarosite but decreased the solution potential due to the complexation of oxalate with iron ions.

(2) The presence of jarosite in the thiourea solution had an adverse effect on both thiourea stability and gold dissolution manifested as the increased thiourea consumption and declined gold dissolution. With the increasing of jarosite dosage from 2 to 10 g/L, the thiourea stability and gold dissolution continually decreased. The addition of oxalate to the thiourea solution could effectually relieve the harmful effect of jarosite on thiourea leaching of gold. As the oxalate dosage increased from 1 to 4 g/L, the thiourea stability constantly increased while the gold dissolution was improved at <3 g/L oxalate dosage and decreased at >3 g/L oxalate dosage mainly due to too low solution potentials.

(3) The adverse effect of jarosite was largely attributed to the fact that the iron ions released by jarosite dissolution increased solution potential, and thus accelerated the oxidative decomposition of thiourea, leading to the deterioration of the oxidative dissolution of gold. In addition, some passivating sulfur-containing species including S^{2-}, S_2^{2-}, S^0 and SO_4^{2-} derived from thiourea decomposition could coat on the surface of gold, impeding gold leaching. The beneficial effect of the oxalate additive was likely due to the fact that oxalate could complex with Fe^{3+} to form stable Fe^{3+} complexes, which decreased the solution potential, and thus much reduced the deriving force of the oxidation of Fe^{3+} towards thiourea. Moreover, oxalate was likely to prevent the passivation species from coating on gold surface through indiscriminate adsorption and electrostatic repulsion.

(4) The leaching results from a refractory gold ore showed that the bio-oxidation pretreatment and oxalate-assisted thiourea leaching process could achieve a significant gold extraction from 24.6% to 87.7% with much reduced thiourea consumption from 9.8 to 3.7 kg/t (ore). Therefore, a promising technology of bio-oxidation and oxalate-assisted thiourea leaching was provided for eco-friendly and economical extraction of gold from its refractory sulfide ores. Besides, it can be inferred that the use of some ligands that can form complexes with Fe^{3+} as additives may be an effectively strategy to improve the thiourea leaching of gold from its ores pretreated by bio-oxidation.

CRediT authorship contribution statement

Ke LI: Investigation, Validation, Writing − Original draft; **Qian LI:** Conceptualization, Methodology, Funding acquisition. Writing − Review & editing; **Tao JIANG:** Supervision, Resources; **Yong-bin YANG:** Supervision, Resources; **Bin XU:** Investigation, Writing − Review & editing; **Rui XU:** Writing − Review & editing; **Yan ZHANG:** Resources, Writing − Review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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黄钾铁矾对硫脲浸金的影响及草酸盐的作用机理

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摘　要：研究生物氧化产生的黄钾铁矾对酸性硫脲浸金的影响，并探讨草酸添加剂的作用机制。结果表明，黄钾铁矾会增加硫脲的消耗和阻碍金的溶解。黄钾铁矾能显著提高硫脲的分解，阻碍金的溶解。黄钾铁矾造成不利影响的主要原因可能是酸性溶液中黄钾铁矾释放的铁离子使溶液浆电位增加，从而加速硫脲的分解，并加剧硫脲分解产生的钝化物种对金表面的钝化作用。添加草酸盐可以有效削弱黄钾铁矾的不利影响，表现为明显降低硫脲的消耗和促进金的溶解。通过溶液电位、Zeta 电位和 XPS 分析，揭示草酸的可能作用机理。草酸盐不仅可以通过与 Fe^{3+}配位减弱 Fe^{3+}与硫脲之间的相互作用，还可以通过无差别吸附和静电斥力阻止钝化产物在金表面包裹。

关键词：生物黄钾铁矾；金浸出；硫脲消耗；草酸盐

(Edited by Bing YANG)