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Invited Review

A review of gold extraction using noncyanide lixiviants: Fundamentals, advancements, and challenges toward alkaline sulfur-containing leaching agents

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Abstract: Alkaline sulfur-containing lixiviants, including thiosulfate, polysulfides, and alkaline sulfide solutions, stand out as a promising class of alternatives to cyanide because of their low toxicity, high efficiency, and strong adaptability. In this paper, we summarized the research progress and remaining challenges in gold extraction using these noncyanide reagents. After a brief introduction to the preparation method, the transformation process of various sulfur-containing species in alkaline solutions was discussed. Thereafter, some insights into the mechanism of gold leaching in alkaline sulfur-containing solutions were presented from different aspects, including thermodynamics analysis, electrochemical dissolution, and leaching kinetics. Moreover, recent progress in *in-situ* generation of sulfur-containing anions from gold-bearing sulfide minerals was outlined as well. Gold passivation caused by sulfur species was discussed in particular because it is considered the greatest challenge facing sulfur-containing leaching systems. Alkaline sulfur-containing lixiviants are expected to serve as alternatives in industrial applications of gold extraction, particularly for refractory gold ores containing copper and carbonaceous matter.

Keywords: gold extraction; sulfur-containing lixiviants; degradation; *in-situ* generation; passivation

1. Introduction

For more than a century, cyanidation has dominated the gold extraction industry because of its effectiveness, chemical stability, low cost, and mature process technology [1–2]. However, cyanidation often offers a poor extraction efficiency for refractory gold ores containing copper, arsenic, stibnite, and carbonaceous matter [3–4]. In addition, the use of cyanide involves substantial risk to the environment and human health because of its high toxicity [5]. Against such a background, extensive research has been devoted to the exploration of environmentally friendly and economically viable techniques for gold extraction [6–7]. As a result, numerous different types of noncyanide lixiviants have been proposed as cyanide alternatives, including thiourea [8], bromine [9], chloride [10], iodine–iodide [11], alkaline amino acids [12–13], polysulfides [14], and thiosulfate [15–17]. In recent studies, thiosulfate and polysulfides, which are sulfur-containing agents, have been found useful for gold leaching under alkaline conditions.

Thiosulfate was identified in the 1900s as a lixiviant for the extraction of precious metals in the presence of appropriate additives [18]. The ammoniacal thiosulfate leaching process has been used for the extraction of gold and silver from leached residues of sulfide copper concentrates [19]. In oxygenated alkaline solutions, thiosulfate can form stable complexes with gold(I) ions, as presented in Eq. (1):

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O = 4[Au(S_2O_3)_2]^{3-} + 4OH^- \quad (1)$$

Compared with the cyanidation process, thiosulfate leaching not only reduces environmental hazards and reagent costs but also offers high selectivity and acceptable

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leaching characteristics [16,20–21]. Moreover, this cyanide-free leaching technique offers substantial potential for the processing of refractory gold ores containing copper or carbonaceous minerals [22–24]. Several mining companies have put great effort into extracting gold from carbonaceous gold ores using thiosulfate on a semicommercial or commercial scale [25–26]. Barrick Gold Corporation has developed a process that combines an alkaline pressure oxidation pretreatment with ammonia-free thiosulfate leaching; this process is being successfully conducted at Goldstrike, Nevada, USA [27–28]. Given the environmental hazards posed by ammonia and the high consumption of thiosulfate, researchers are devoting increasing effort to exploring ammonia-free thiosulfate leaching. Although researchers have extensively investigated the fundamentals of thiosulfate leaching, progress toward its commercial application remains slow because of several main obstacles, which include high thiosulfate consumption, gold passivation, and immature subsequent processing of gold recovered from leached solutions [29–30].

In addition, polysulfide has been introduced as another alternative in the class of sulfur-containing lixiviants. Polysulfide anions (S_n^{2-}, $2 \le n \le 5$) can be obtained via the reaction of elemental sulfur and sulfide ions in alkaline solutions in which gold has been dissolved to form gold–sulfur complexes [31–33]. The general reaction for gold dissolution in polysulfide solutions is described as:

$$Au + S_n^{2-} = [AuS_n]^- + e^- \quad (2)$$

Ammoniacal polysulfide solutions can dissolve gold at elevated temperatures and pressures, and the dissolution rate depends on the temperature and composition of sulfur species in the leach solution [34]. The recovery of gold reached 90% at 50°C in a polysulfide/thiosulfate solution with cupric ammonium as a catalyst, even though the gold concentrate contained 5wt% arsenic [35]. Yang *et al.* [36] also reported that 93% of gold was leached in a hot polysulfide solution containing antimony. Recently, tetrasulfide and pentasulfide have been found to play important roles in gold leaching using alkaline polysulfide solutions that offer good leaching performance for gold-bearing antimony ores [14]. According to these previous studies, polysulfide leaching is applicable to certain gold ores containing arsenic and antimony.

Alkaline sulfide lixiviation is also used as a noncyanide technique for gold extraction. The dissolution of elemental sulfur in alkaline solutions creates a range of metastable sulfur-containing anions that can be used to dissolve gold. This hydrometallurgical system operates essentially on the combined function of sulfide (S^{2-}), polysulfides (S_n^{2-}), and thiosulfate ($S_2O_3^{2-}$). It offers an alternative approach to the selective leaching of gold, silver, antimony, tin, arsenic, and tellurium [37–38]. Some authors have reported that gold and copper were effectively recovered from gold-bearing enargite concentrates in parallel with the removal of arsenic and antimony using this leaching technique [39–40]. This hydrometallurgical system has been used industrially for the production of antimony in some countries.

Currently, the ammoniacal leaching and nonammoniacal thiosulfate leaching of gold are being extensively studied, and several studies on the leaching of gold using polysulfide solutions have also been published. However, no specialized review for sulfur-containing leaching agents has been reported in which such agents are regarded as a whole. In the present paper, we systematically summarize the research progress and the challenges facing the use of sulfur-containing lixiviants for gold leaching under alkaline conditions. First, the preparation of alkaline sulfur-containing solutions is introduced in brief, after which the transformation process of various sulfur species is described. Fundamental research on the mechanisms of gold leaching using sulfur-containing lixiviants is then reviewed, including thermodynamics analysis, electrochemical dissolution, and leaching kinetics. Furthermore, it is discussed that the *in-situ* generation of sulfur-containing reagents from gold-bearing sulfide minerals during gold leaching. Finally, research progress on gold passivation caused by sulfur species and the identification of passivated species are summarized in detail.

2. Preparation and transformation of sulfur-containing lixiviants

2.1. Preparation of alkaline sulfur-containing solutions

Sulfur is a common polyvalent element in nature, with a wide range of accessible oxidation states from S^{2-} to S^{6+} [41]. Depending on the leaching potential of the solutions, the oxidation states of sulfur in different sulfur-containing species can vary, as listed in Table 1. Zero-valent sulfur (S^0) is a central intermediate in the sulfur cycle and commonly exists in the form of elemental sulfur (S_8).

In general, alkaline sulfur-containing systems are prepared using a traditional liquid-phase method involving the dissolution of elemental sulfur or sulfide in an alkaline solution [42]. Sodium hydroxide is the alkali agent most commonly used to prepare alkaline sulfur-containing solutions [43–44]. Calcium hydroxide has been introduced as an alternative to sodium hydroxide, resulting in the so-called lime–sulfur synthetic solution (LSSS) [45–46]. Fig. 1 presents a schematic of the preparation of alkaline sulfur-containing solutions.

Table 1. Oxidation states of sulfur in several main sulfur species

Name	Sulfur specie	Charge	Oxidation state
Sulfide	S	−2	−2
Polysulfide	S_2	−2	−1
Polysulfide	S_3	−2	−2/3
Polysulfide	S_4	−2	−1/2
Polysulfide	S_5	−2	−2/5
Sulfur	S_8	0	0
Thiosulfate	S_2O_3	−2	+2
Pentathionate	S_5O_6	−2	+2
Tetrathionate	S_4O_6	−2	+5/2
Trithionate	S_3O_6	−2	+10/3
Sulfite	SO_3	−2	+4
Sulfate	SO_4	−2	+6

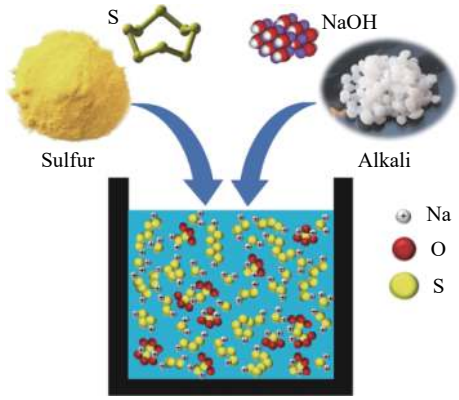

Fig. 1. Schematic of the preparation of alkaline sulfur-containing system.

As demonstrated in Fig. 1, sulfur undergoes a complex series of disproportionation and oxidation reactions to generate large amounts of metastable sulfur species such as sulfide (S^{2-}), polysulfides (S_n^{2-}), thiosulfate ($S_2O_3^{2-}$), and even polythionates ($S_nO_6^{2-}$, $2 \le n \le 6$). The formation of the predominant sulfur-containing anions, such as thiosulfate and polysulfides, is illustrated in Eqs. (3) and (4). Several important species in the metastable sulfur-containing system and their geometrical structures are demonstrated in Fig. 2.

$$4S + 6OH^- = 2S^{2-} + S_2O_3^{2-} + 3H_2O \quad (3)$$

$$(n-1)S + S^{2-} = S_n^{2-} \ (2 \le n \le 5) \quad (4)$$

As presented in Table 1, a metastable polysulfide molecule with different chain lengths will be generated first, followed by the formation of thiosulfate and polythionate ions when sulfide begins to oxidize to sulfate. Hojjatie *et al.* [47] patented an efficient process for the continuous preparation of calcium thiosulfate from lime–sulfur through further oxidation of calcium polysulfide. The calcium thiosulfate produced by this process can be used in certain

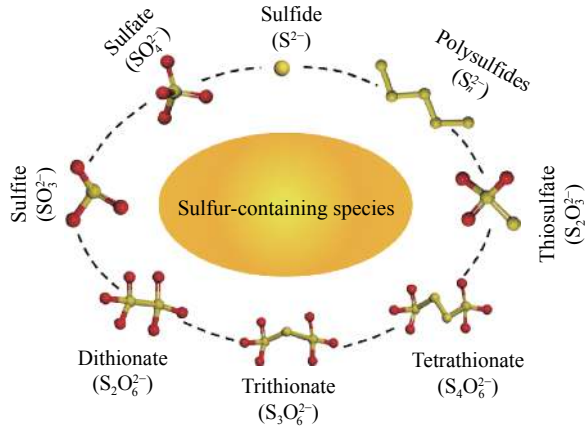

Fig. 2. Various sulfur-containing species prepared by the disproportionation and oxidation of sulfur.

leaching processes for precious metals. Zhou *et al.* [48] prepared a mixed solution containing sodium thiosulfate and sodium polysulfide. The leaching efficiency of gold using such a sulfur-containing solution is highly dependent on the temperature and oxygen pressure. Zhao *et al.* [49] investigated the effects of several key factors on the transformation of sulfur during the preparation process. They found that sulfur-to-lime mass ratio and reaction time strongly influenced the pH of the LSSS. Wen *et al.* [14] prepared sodium polysulfides by adding elemental sulfur and sodium sulfide in sodium hydroxide solutions and used them to leach gold from antimony ore. Nitrogen served as the shielding gas for the preparation of polysulfides, avoiding their further oxidation. In alkaline solutions, sulfide is easily oxidized to polysulfide and thiosulfate, which can solubilize gold [50].

2.2. Transformation of sulfur-containing species

2.2.1. Polysulfides

Polysulfides are known as metastable intermediates containing chains of sulfur atoms, which tend to undergo oxidation and degradation into other species. As early as 1914, polysulfides were obtained by the addition of sulfur to a solution containing sulfide ions [51]. The precise preparation and identification of polysulfide species are substantial challenges because the number of sulfur atoms varies depending on the different preparation conditions [52]. The concentration of sodium sulfide and temperature clearly affects the average polysulfide chain length. The degradation of individual polysulfides to thiosulfate and sulfide was due to a nucleophilic attack by OH^- ion [53]. Irrespective of various factors, polysulfide species, including S_1^{2-}, S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, and S_6^{2-}, were detected in alkaline media. Among these anions, the disulfide and trisulfide ions were found to be the predominant species. With increasing acidity of the

solution, disulfide ions (S_2^{2-}) transformed first to trisulfide (S_3^{2-}) and then to tetrasulfide (S_4^{2-}) ions, which were further converted to pentasulfide ions (S_5^{2-}) [54]. As reported by Hiskey and Atluri [32], the overall equilibrium for unstable polysulfides in aqueous solution is represented as:

$$nS^{2-} \rightleftharpoons S_n^{2-} + (2n-2)e^- \quad (5)$$

Under alkaline conditions, thiosulfate can be transformed from polysulfide anions with the further dissolution of elemental sulfur [55]. Argyropoulos *et al.* [56] pointed out that thiosulfate and elemental sulfur were the auto-oxidation products of polysulfides. Kleinjan *et al.* [57] investigated the transformation of polysulfide ions in aqueous solution, focusing on the oxidation kinetics. Their results showed that the dissolution of sulfur in hydrogen sulfide solutions produced polysulfide ions, which were further oxidized to elemental sulfur and thiosulfate. Compared with crystalline inorganic sulfur or colloidal sulfur, the hydrolysis of newly generated elemental sulfur was relatively faster. In addition, they found that the oxidation of polysulfide was more rapid than that of sulfide and that more thiosulfate was generated at pH values greater than 9.

2.2.2. Thiosulfate

Thiosulfate is a class of sulfur–oxygen compound containing the $S_2O_3^{2-}$ radical, in which the two sulfur atoms are in different chemical environments. The sulfide-like sulfur atom is the predominant contributor to its unique chemical properties. Thiosulfate solutions are stable if they are prepared and stored in oxygen-free water [58]. Without the catalytic effect of copper ions, the degradation of thiosulfate in alkaline solutions is extremely slow under normal pressure and temperature. The potential–pH diagram for the S–H_2O system indicates that thiosulfate only exists in a narrow, elongated region, whereas its metal complexes are stable over a relatively wide potential/pH range [59]. As a metastable sulfur species, thiosulfate tends to easily undergo disproportionation reactions in aqueous solution. Several studies on the disproportionation of thiosulfate were published in the middle of the last century; these studies focused on reaction kinetics and identification of the reaction products. For example, Pryor [60] proposed a kinetic model for thiosulfate disproportionation in an alkaline solution at 250–280°C. The products were mainly sulfide and sulfate but also contained small amounts of elemental sulfur, polysulfide, and sulfite. Xu and Chang [61], using X-ray photoelectron spectroscopy (XPS), found that sodium sulfite and elemental sulfur were generated from the disproportionation of sodium thiosulfate at elevated temperatures.

Depending on the various conditions, thiosulfate can be decomposed to generate several sulfur species such as sulfide, sulfite, sulfate, polythionates, polysulfides, and elemental sulfur. The transformation of thiosulfate to other sulfur species is inevitable in gold leaching solutions. Substantial research has been carried out to demonstrate the degradation or oxidation of thiosulfate during gold leaching. In alkaline solutions, thiosulfate reacts with oxygen to generate intermediate species such as polythionates and sulfite, which are subsequently oxidized to sulfate. The presence of copper and ammonia accelerates the oxidation of thiosulfate, with tetrathionate being generated as the initial product [62]. According to the literature [63–64], the following main reactions are involved in the degradation of thiosulfate (Eqs. (6)–(11)):

$$2S_2O_3^{2-} + 0.5O_2 + H_2O = S_4O_6^{2-} + 2OH^- \quad (6)$$

$$S_3O_6^{2-} + 0.5O_2 + 2H_2O = 3SO_3^{2-} + 4H^+ \quad (7)$$

$$2SO_3^{2-} + O_2 = 2SO_4^{2-} \quad (8)$$

$$S_2O_3^{2-} + 2O_2 + H_2O = 2SO_4^{2-} + 2H^+ \quad (9)$$

$$2S_2O_3^{2-} + 2O_2 = S_3O_6^{2-} + SO_4^{2-} \quad (10)$$

$$3S_2O_3^{2-} + 2O_2 + H_2O = 2S_3O_6^{2-} + 2OH^- \quad (11)$$

Thiosulfate can be regenerated from intermediate sulfur species such as sulfide, sulfite, and polythionates [64]. As presented in Eq. (12), the rearrangement of tetrathionate results in the formation of trithionate and pentathionate in near-neutral solutions [65]. With increasing alkalinity, pentathionate and trithionate further decompose to form thiosulfate and sulfite. The two intermediates have exhibited the ability to accelerate the degradation of tetrathionate [66–67]. In addition to thiosulfate and sulfite, a small amount of sulfide is also generated during the degradation process. The reaction between sulfite and sulfide not only regenerates thiosulfate but also promotes the re-dissolution of metal sulfide precipitates; thus, sulfite functions as a stabilizer for the thiosulfate leaching system (Eq. (17)) [22,68]. The overall reactions for the regeneration are presented as:

$$2S_4O_6^{2-} = S_3O_6^{2-} + S_5O_6^{2-} \quad (12)$$

$$2S_4O_6^{2-} + 6OH^- = 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (13)$$

$$4S_4O_6^{2-} + 10OH^- = 7S_2O_3^{2-} + 2SO_4^{2-} + 5H_2O \quad (14)$$

$$S_4O_6^{2-} + S_2O_3^{2-} \rightleftharpoons S_5O_6^{2-} + SO_3^{2-} \quad (15)$$

$$S_4O_6^{2-} + SO_3^{2-} = S_3O_6^{2-} + S_2O_3^{2-} \quad (16)$$

$$4SO_3^{2-} + 2S^{2-} + 3H_2O \rightleftharpoons 3S_2O_3^{2-} + 6OH^- \quad (17)$$

$$S_5O_6^{2-} + 3OH^- = 2.5S_2O_3^{2-} + 1.5H_2O \quad (18)$$

$$2S_3O_6^{2-} + 6OH^- = S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \quad (19)$$

Ji *et al.* [69] developed a novel thiosulfate leaching process for gold extraction without any additive, which effectively reduced the thiosulfate consumption. In their work, the additional sulfite reacted with tetrathionate to generate thiosulfate and sulfate. Sulfite treatment is an effective solution for the reduction of tetrathionate; however, it is ineffective at reducing trithionate because the transformation of tetrathionate to thiosulfate is much easier than that to trithionate and because the latter requires a relatively higher temperature. Pan *et al.* [70] used high-performance liquid chromatography to analyze the stability and reactivity of polythionates in alkaline solutions. They found that hexathionate was decomposed to pentathionate, tetrathionate, thiosulfate, and heptathionate. Unlike tetrathionate and pentathionate, a vast amount of sulfur was deposited as a major final product of this process.

In summary, various sulfur-containing species are in equilibrium with each other and the mutual transformation process is driven by a series of redox reactions. The disproportionation of elemental sulfur (S_8) results in the formation of sulfide and polysulfide, some of which can be further oxidized to various oxysulfur species such as thiosulfate and polythionates. In alkaline media, the ultimate oxidation product of these sulfur species is sulfate. During the transformation process, thiosulfate can be regenerated as a result of degradation of pentathionate and trithionate or the reaction between sulfite and sulfide (Eqs. (18) and (19)). On the basis of the previous discussion, the simplified route of transformation of these sulfur-containing species is presented in Fig. 3.

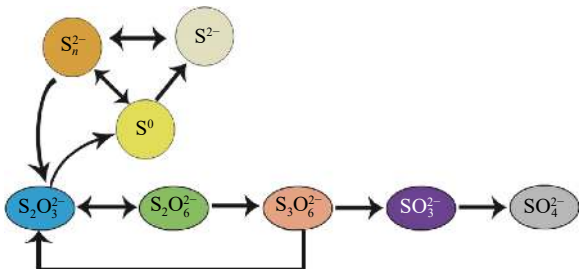

Fig. 3. Illustration of the oxidation and degradation processes of sulfur.

3. Dissolution of gold in sulfur-containing leaching systems

3.1. Fundamental thermodynamics of gold leaching

The dissolution of elemental sulfur in alkaline solutions results in the formation of a metastable sulfur-containing system that contains various sulfur species, including sulfide, polysulfide, and sulfur–oxygen species such as thiosulfate and polythionates. Alkaline sulfur-containing lixiviation has been introduced as an alternative approach for gold extraction because these sulfur species can form stable complexes with gold(I) cations under alkaline conditions. The stability constants and standard reduction potentials of the main sulfur–gold complexes [71–73] are given in Table 2. The stability of the gold(I)–sulfide complex is relatively greater than that of the complex formed with bisulfide or thiosulfate. Zia *et al.* [71] calculated the interaction energy between the gold surface with different sulfur species using the density function theory (DFT) method. Their results showed that the interaction energy of −302.29 kJ·mol^{-1} between sulfide and the gold surface was greater than the interaction energies between gold and the other sulfur species, indicating that the adsorption of sulfide ions was more likely to occur. The interaction energy between thiosulfate and gold was −142.77 kJ·mol^{-1}; thus, it exhibited a lower tendency than sulfide to bind to the gold surface.

As previously mentioned, the disproportionation of elemental sulfur in alkaline solutions generates not only sulfide but also polysulfide and thiosulfate. To investigate the composition of complex sulfur-containing systems, Pourbaix developed an electrochemical equilibrium diagram for sulfur in aqueous solution [74]. According to the published literature [72–73], a metastable potential–pH diagram for alkaline sulfur-containing system has been established using the StabCal thermochemistry package.

Fig. 4(a) describes the sulfide/polysulfide system containing only sulfur, sulfide, bisulfide, and polysulfide. On the basis of the calculation results, polysulfide is considered as a potential oxidant for gold leaching because polysulfide species have a relatively higher oxidation state than sulfide and can be reduced to sulfide, with a concomitant decrease in molecular weight. Fig. 4(b) clearly illustrates that poly-

Table 2. Stability constants and standard reduction potentials for main sulfur–gold complexes

Complex	Reaction	Standard potential / mV	Stability constant (β)	Ref. No.
$Au(S_2O_3)_2^{3-}$	$Au(S_2O_3)_2^{3-} + e^- \rightarrow Au + 2(S_2O_3)_3^{2-}$	150	10^{26}	[72]
AuS^-	$AuS^- + e^- \rightarrow Au + S^{2-}$	−460	2×10^{36}	[73]
$Au(HS)_2^-$	$Au(HS)_2^- + e^- \rightarrow Au + 2HS^-$	−90	1.3×10^{30}	[73]

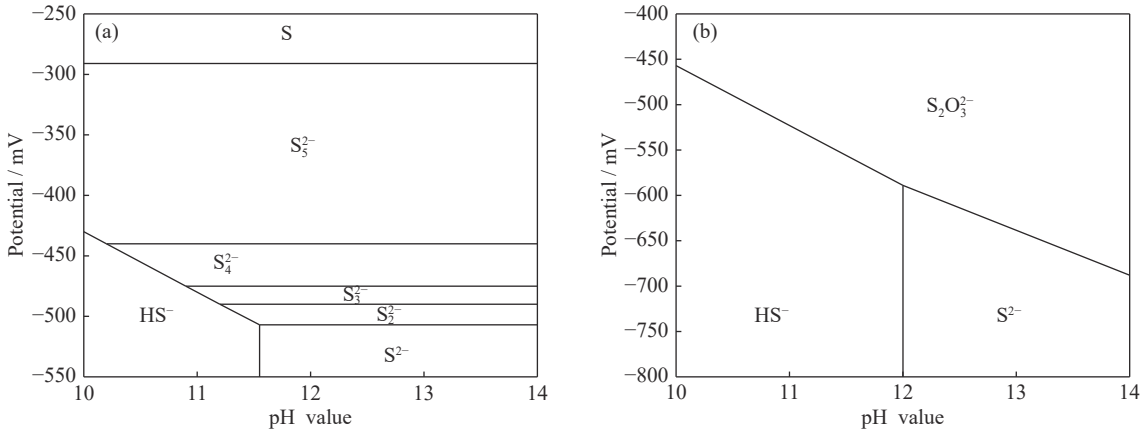

Fig. 4. Potential–pH diagrams generated for the S–H_2O system at 60°C: (a) for the sulfide/polysulfide system; (b) for the sulfide system with sulfur–oxygen species.

sulfide ions disappear at high pH regions when thiosulfate is introduced as a species for the thermodynamic calculation. Jeffrey and Anderson [72] pointed out that the mixed potential of the leaching system was −515 mV which was similar to the potential for the reduction of S_2^{2-} to S^{2-} (−507 mV). Hence, they speculated that sulfide was the effective lixiviant rather than thiosulfate and that the polysulfides acted as oxidants during gold leaching. Anderson [73] reported similar observations, where the gold leaching kinetics in alkaline sulfide solutions were investigated using an *in-situ* electrochemical technique. Wen *et al.* [14] claimed that the tetrasulfide (S_4^{2-}) and pentasulfide (S_5^{2-}) were the main active components for gold leaching in sodium pentasulfide solutions. Anderson *et al.* [33] explored the effect of temperature on the stability of the AuS^- complex in an alkaline sulfide system. The potential–pH diagram shows that the stability region of gold sulfide was relatively larger at high temperatures. Therefore, as expected, an increase in temperature is beneficial to gold leaching in alkaline sulfide solutions.

Thiosulfate is another sulfur-containing leaching agent and can be generated from the oxidation of polysulfides. The dissolution of gold in thiosulfate solutions is slow, but this process is accelerated 18–20 times by the presence of copper and ammonia [26]. The potential–pH diagrams for S–H_2O, Au–S–H_2O, and Au–NH_3–S systems have been reported in several studies involving the thiosulfate leaching of gold [59,75–76]. In these works, metastable sulfur species such as sulfite, thiosulfate, polythionates, and polysulfides were considered, along with a wide potential/pH range. The results suggest that the thiosulfate ion exhibits a narrow range of stability in the alkalescent pH region. The major complex of gold is $[Au(S_2O_3)_2]^{3-}$ at pH values less than 9 but is $[Au(NH_3)_2]^+$ when the pH value is greater than 9. However, in general, the sole predominant gold-bearing complex is $[Au(S_2O_3)_2]^{3-}$ in thiosulfate solutions [77–78]. The aforementioned contradictory results are attributable to different free energy values for thiosulfate species generation being used in the thermodynamic calculations. Furthermore, the feasibility of using thiosulfate for gold leaching at elevated temperatures and pressures in the absence of copper and ammonia was confirmed using the potential–pH diagram of the Au–S–H_2O system [79].

3.2. Electrochemistry and kinetics of gold leaching

3.2.1. Electrochemical dissolution of gold

The dissolution of gold is an essential electrochemical process that involves a complex series of oxidation–reduction reactions. The results of electrochemical studies have been used to explain the mechanism of gold leaching in alkaline sulfur-containing solutions. For example, Yu and Zhang [80] studied the electrochemical process of gold leaching in LSSS. The activation energy of gold oxidation was determined to be 16.835 $kJ \cdot mol^{-1}$. Using spectroelectrochemical techniques, Parker *et al.* [81] observed that the reduction of sulfide species on the gold surface occurred at −0.68 and −0.94 V. The peak at the higher potential was assigned to the conversions of zero-valent sulfur to polysulfide ions and polysulfide ions to sulfide. In alkaline thiourea solutions, the passivation of the gold electrode surface occurred at potentials more positive than 0.42 V and the presence of Na_2SiO_3 could promote the electrochemical dissolution of gold [82]. In addition, several authors have reported the successful application of electrochemical leaching of gold using leaching reagents generated at the anode [83–84]. Nadirov *et al.* [85] prepared a special sulfur–graphite electrode that they subsequently used to generate sulfur-containing agents for gold extraction in alkaline solutions. The recovery of gold reached 93% with a leaching rate of 33 ×

10^{-6} mol·L^{-1}·min^{-1} when the cathodic current density was fixed at 80 mA·cm^{-2}.

In terms of thiosulfate leaching, the electrochemical dissolution of gold is divided into two processes: the anodic oxidation of gold and the cathodic reduction of oxygen or other additives. The reduction of Cu(II) is the cathode half-reaction coupled with the oxidation of gold to gold–thiosulfate complexes in the leaching potential region. The presence of ammonia alleviates the adverse effect of various sulfur species on gold leaching due to the formation of a gold–amine complex intermediate [86]. Zhang and Nicol [87–88] reported that the anodic dissolution of gold was enhanced by copper ions, which was likely related to the formation of a copper–thiosulfate–oxygen intermediate. They observed that the anodic current efficiency during thiosulfate leaching process was much lower in the absence of an oxidant. Oraby *et al.* [89] investigated the electrochemical dissolution of gold and gold–silver alloys using alkaline thiosulfate leaching. They claimed that both gold and silver could be dissolved in thiosulfate solutions and that the leaching rate of pure silver was approximately 6.89 times greater than that of pure gold. For the dissolution of gold–silver alloys, the leaching rate of gold greatly improves with an increase in the proportion of silver. The leaching of gold in ammoniacal thiosulfate solutions conforms to the electrochemical catalytic mechanism [30]. In anodic areas, ammonia complexes with gold(I) ions first form an intermediate product of $[Au(NH_3)_2]^+$. The NH_3 in the gold complex is then replaced by thiosulfate anion ($S_2O_3^{2-}$), which results in the formation of a more stable complex of $[Au(S_2O_3)_2]^{3-}$. In cathodic areas, copper(II) is reduced to copper(I), and the reduction product of $[Cu(S_2O_3)_3]^{5-}$ is quickly oxidized to $[Cu(NH_3)_4]^{2+}$ by dissolved oxygen in the solution. Notably, $[Cu(NH_3)_4]^{2+}$ is used as a catalyzer to improve the leaching rate of gold but also accelerates the degradation of thiosulfate because of its strong oxidizing ability [90–91].

3.2.2. Kinetics behavior of gold leaching

The kinetics of gold leaching using alkaline sulfur-containing lixiviants has received extensive attention because these materials are potential alternatives to cyanide. Jeffrey and Anderson [72] speculated that the dissolution of gold in alkaline sulfide solutions was chemically controlled rather than diffusion controlled and was highly dependent on temperature. The electrochemical quartz crystal microbalance (EQCM) offers a sensitive approach to determine the mass changes during gold leaching in parallel with electrochemical behavior [92]. Joshi and Asselin [93] studied the leaching of pure gold in 1 mol·L^{-1} Na_2S solution using the EQCM technique. A substantial mass loss was observed at a potential interval of −0.40 to −0.06 V with a leaching rate of 6.4×10^{-5} mg·s^{-1}·cm^{-2}. Anderson [73] reported that the leaching rate of gold in an alkaline polysulfide/sulfide system was 1.9×10^{-5} mol·m^{-2}·s^{-1} with an activation energy of 41.6 kJ·mol^{-1}.

The leaching kinetics of gold in thiosulfate solutions containing copper and ammonia follows a chemical control model, and the passivation of the gold surface is the major contributor to the decrease of the leaching rate [94–95]. An EQCM study of gold leaching in ammoniacal thiosulfate solutions showed that thiosulfate decomposition produced a sulfur-rich layer, which passivated the gold electrode and lowered the leaching rate of gold [96]. Porvali *et al.* [97] found that the temperature strongly affected the extraction of gold from pressure oxidized concentrate using thiosulfate–copper–ammonia leaching. The optimum leaching efficiency reached 89% after 6 h, with the leaching rate of gold being 2.987 mg·cm^{-2}·h^{-1}. Senanayake [77] found that the overall dissolution of gold was consistent with the shrinking-core model, which confirmed the formation of surface adsorption layers. The average leaching rate of gold in an alkaline solution containing 1 mol·L^{-1} thiosulfate and 0.1 mol·L^{-1} sodium hydroxide was less than 10^{-11} mol·cm^{-2}·s^{-1} in the potential range of 0.20 to 0.35 V, which was relatively lower than that in aerated cyanide solutions (5×10^{-9} mol·cm^{-2}·s^{-1}) [88,98]. These results implied that gold could be oxidized in alkaline thiosulfate solutions, although the leaching rate was low. This conclusion is in agreement with those of other authors, where the dissolution rate of gold in 1 mol·L^{-1} ammonia–thiosulfate solution containing copper ions was 4×10^{-9} mol·cm^{-2}·s^{-1} [95]. An investigation of the kinetics of gold dissolution in non-ammoniacal thiosulfate solutions was conducted using a rotating electrochemical quartz crystal microbalance [99]. The results showed that gold oxidation was chemically controlled, which could be enhanced by an increase in temperature or the thiosulfate concentration. The leaching rate of gold was two orders of magnitude lower than a typical cyanidation rate. However, the use of several improvement measures, including elevated temperature, increased the oxygen concentration, in addition, copper addition and the galvanic effect of sulfide minerals could increase the gold leaching rate to the same order of magnitude as a typical cyanidation rate.

4. *In-situ* generation of sulfur-containing agents

Sulfide minerals are well known to be an important source of sulfur, which is an indispensable element for pre-

paring sulfur-containing lixiviants. Some metal sulfides always contain a considerable amount of gold, particularly pyrite and arsenopyrite. For refractory gold ores, the gold is locked in the sulfide matrix, which requires the structure of the host minerals to be destroyed through various pretreatment processes before leaching. Most of gold tends to accumulate in the elemental sulfur generated during the partial oxidation of sulfide minerals [72–73]. This finding provides powerful support for using sulfur-containing species for gold leaching. Therefore, a unique advantage of the sulfur-containing leaching agents is that they can be generated *in situ* from gold-bearing sulfide minerals during the leaching process.

A comprehensive review of the mechanisms of pyrite dissolution and oxidation in aqueous solution was published by Chandra and Gerson [100]. Except for iron-bearing species, the oxidation products consist of polysulfides, elemental sulfur, thiosulfate, and polythionates as well as sulfite. This finding is consistent with a report by Huai *et al.* [101], who focused on the surface oxidation of pyrite coupled with gold. In addition to pyrite, other sulfide minerals such as pyrrhotite and arsenopyrite also can be oxidized to various sulfur-containing anions in the leaching process. In oxygenated alkaline solutions, the pyrrhotite oxidation can generate several sulfur species, including polysulfide, elemental sulfur, and thiosulfate [102]. The oxidation of gold-bearing arsenopyrite in alkaline solutions is an electrochemical process, where thiosulfate, monothioarsenate, arsenate, and sulfate are formed in parallel with gold leaching [79].

As reported by Fang *et al.* [103], 90% of gold was extracted from an acid-leached residue that contained 17.4wt% of elemental sulfur and 4.32wt% arsenic using thiosulfate generated from the oxidation of elemental sulfur at 85°C under oxygen at a pressure of 0.1–0.3 MPa. Choi *et al.* [68] patented a process for the preparation of thiosulfate-based lixiviants using elemental sulfur generated form the partial oxidation of pyrite and pyrrhotite during acidic pressure oxidation pretreatment. Melashlvili *et al.* [104–105] studied the dissolution of gold with thiosulfate formed *in situ* during pyrite oxidation in alkaline media. The sulfide sulfur in the pyrite lattice was first oxidized to elemental sulfur and further converted to thiosulfate and other sulfur oxyanions. At $8.3 \leq pH \leq 9.2$, a rapid degradation of thiosulphate was observed with polythionates, sulfite, and sulfate being produced in the potential range 22–141 mV. A maximum recovery of gold as high as 96% was achieved at $pH < 12$.

Xu *et al.* [106] explored the feasibility of gold leaching using generated thiosulfate from sulfur oxidation during oxygen pressure pretreatment. The recovery of gold reached 83.6% with humic acid as an additive, and thiosulfate consumption was distinctly reduced. Furthermore, our group proposed a similar idea that elemental sulfur generated from gold-bearing sulfides during microwave pyrolysis could be used to extract gold from itself [107]. Microwave pretreatment in the absence of oxygen not only produced elemental sulfur that was used to synthesize a leaching agent but also liberated the gold encapsulated within sulfide minerals. Nadirov *et al.* [85] developed a sulfur–graphite electrode (SGE) equipped with a polyvinyl chloride (PVC) separator, which was used as source of sulfur-containing agents for gold leaching. Under optimized conditions, the recovery of gold reached 93% when this electrochemical leaching technique was used. According to a review published by Sitando *et al.* [64], thiosulfate can be generated *in situ* from both the oxidation of sulfide minerals and degradation of other sulfur-containing reagents during gold leaching. Currently, a challenging issue for the extensive commercial application of thiosulfate leaching is how to effectively reduce thiosulfate consumption, especially for the copper–ammonia thiosulfate system. On the basis of the previous discussion, the *in-situ* generation of sulfur-containing agents through the full utilization of sulfur in gold-bearing sulfide minerals is a potential approach to this problem.

5. Gold passivation caused by sulfur species

5.1. Effect of sulfur species on gold leaching

Gold is commonly associated with or encapsulated within carrier minerals such as pyrite, arsenopyrite, pyrrhotite, chalcopyrite, and gangue minerals [108–109]. A large number of studies have reported the effect of sulfide minerals on the electrochemical behavior of gold dissolution and the formation of passivation layers during cyanidation [110–113]. For example, Jeffrey and Breuer [114] studied the effect of sulfide ions on the electrochemistry of gold leaching in alkaline cyanide solutions. They found the soluble sulfide generated from sulfide minerals produced a passivating layer of sulfur. Sulfide minerals have inhibiting effects on gold leaching, and pre-oxidation is an effective approach to improve the recovery of gold from a sulfide-rich industrial gold ore [115]. The passivation of gold caused by the dissolved sulfur species was likely responsible for the poor leaching performance. The dissolution of metal sulfides in alkaline solutions generates some sulfur-containing anions that passivate the gold surface and retard the leaching process. Therefore, the passivation of gold is more likely to occur in sulfur-containing leaching systems.

Much attention has been devoted to the passivation ef-

fect of sulfur species on gold leaching and the interface behavior of sulfur species on the gold surface. Zia *et al.* [71] investigated the passivation of gold by sulfur species in cyanide and thiosulfate solutions. They calculated the interaction energy between various sulfur species and gold surfaces using DFT. Their results showed that the formation of the passivation film was mainly attributable to the interaction of sulfide, polysulfides, tetrathionate, and sulfite species with the gold surface. Several early studies suggested that the deposition of sulfur on the gold electrode resulted from the oxidation of sulfide-containing ions [116–118]. Wierse *et al.* [119] revealed the formation mechanism of sulfur layers adsorbed onto gold electrodes using electrochemical techniques. They reported that sulfide ions were discharged to form a sulfur adsorption layer in polysulfide solutions as a result of sulfur bond cleavage and adsorption of single sulfur atoms. Zelinsky [120] used the rotating-disk electrode technique to gain insight into thiosulfate oxidation during gold dissolution and observed that the passivating layer hindered the transmission of current at the electrode–solution interface, resulting in a decrease of current at potentials close to 0.8 V.

5.2. Identification of the passivating species

Identifying sulfur species that hinder the dissolution of gold by forming a passive layer is a challenging task. With the development of surface characterization techniques, the mechanism of passivation and the effect of various sulfur species on gold dissolution behavior have been gradually elucidated. The aforementioned studies related to the characterization of gold-passivating species are summarized in Table 3.

Electrochemical studies have shown that an isolating layer that consists of copper sulfide, elemental sulfur, and colloid sulfur hindered the dissolution of gold in thiosulfate solutions containing copper ions [121–123]. Zhang and Nicol [88] observed the current efficiency for gold leaching was very low in alkaline thiosulfate solutions, implying that a sulfur-like surface film was formed from thiosulfate oxidation and inhibited the dissolution of gold. Some researchers have speculated that the passivation of gold in a thiosulfate leaching system is mainly attributable to the formation of elemental sulfur derived from the oxidation of sulfur species [124–125]. In addition to elemental sulfur and gold–sulfur compounds, some oxygen-containing sulfur species were generated on the gold surface during the leaching process. For example, Baron *et al.* [126] reported that the decomposition of thiosulfate produced several intermediates such as tetrathionate, trithionate, elemental sulfur, and sulfide. The adsorption of polythionates and elemental sulfur were the main contributors to gold passivation, and tetrathionate further degraded into trithionate and thiosulfate at a longer exposure time. Zelinsky and Novgorodtseva [96] also pointed out the degradation products of thiosulfate, such as tetrathionate, sulfate, and elemental sulfur, are likely responsible for the passivation of gold.

Some researchers [127–128] focused on characterizing the surface products and the interaction of gold and sulfur-containing ligands. In the surface-enhanced Raman spectroscopy (SERS) spectra, peaks attributed to sulfur–sulfur and sulfur–oxygen bonds were assigned to tetrathionate and a gold(I) thiosulfate complex, respectively. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and XPS analysis results confirmed that ammonia and copper were adsorbed onto the gold surface, with copper sulfide being formed. They concluded that the adsorbed species were cyclo-octasulfur (cyclo-S_8), tetrathionate-like species, and gold or copper sulfides. Using electrochemical and SERS techniques, Jeffrey *et al.* [124] investigated the composition of passivating species that hindered the dissolution of gold in thiosulfate solutions. The results showed that the oxidation of thiosulfate resulted in the formation of sulfur, polysulfides, and adsorbed polythionate on the gold surface. This conclusion is consistent with the report by Nicol *et al.* [129]. In addition, they found that the formation of ammonia copper(I) polysulfide was conducive to the anodic dissolution of gold because the ability of polysulfide to inhibit gold dissolution was weaker than that of elemental sulfur alone and that of elemental sulfur with polythionate. Parker *et al.* [81] explored the mechanism of interaction between sulfide species and the gold surface using SERS. They observed the appearance of an Au–S stretching band in the spectrum corresponding to a low leaching potential; however, more sulfur was adsorbed to form polymeric sulfur as the leaching potential was increased. The appearance of peaks assigned to sulfur–sulfur bonds at 471, 210, and 157 cm^{-1} confirmed the formation of cyclo-S_8. Nie *et al.* [130] claimed that the passivation film formed in thiosulfate solutions consisted of elemental sulfur, polysulfide, and trithionate. The addition of ammonia was found to promote the dissolution of gold by removing the sulfur layer.

Recently, Smith *et al.* [131] presented a quantitative analysis of the constituents of a passive layer during gold leaching in oxygenated thiosulfate solutions using shell-isolated gold nanoparticles (SHINs). The inhibition of gold dissolution was attributed to the generation of various sulfur allotropes such as elemental sulfur, cyclo-S_8, and polymeric

sulfur chains. Whereas elemental sulfur and cyclo-S_8 originated from the decomposition of tetrathionate, polymeric and monoatomic sulfur were the main degradation products of trithionate [132]. Huergo *et al.* [133] synthesized gold nanostructures by reducing gold(III) with sodium sulfide solutions. Their results suggested that the passivation layer mainly consisted of monomeric sulfur, polysulfides, and some elemental sulfur; however, neither Au_2S nor other oxidized gold species was present in the reduction products in detectable amounts. Lustemberg *et al.* [134] also speculated that the sulfur coating was a mixture of monomeric and polymeric chemisorbed sulfur rather than Au–S compounds. Nevertheless, Woods *et al.* [135] observed the absorption of a gold sulfide monolayer with an S/Au molar ratio of 1:3 in the leaching potential region. X-ray absorption spectroscopy (XAS) and XPS characterizations of nanoscale Au–S products obtained through the reaction of aqueous gold(III) and sulfide ions indicated that the gold sulfide precipitate decomposed to polysulfide species [136]. For sulfide-containing solutions, similar behavior of the S/Au(III) interface was reported by Rodriguez *et al.* [137]. This contradictory observation could be due to more sulfur being deposited to form sulfur–sulfur linkages instead of sulfur–gold bonds at higher potentials.

On the basis of the aforementioned works, we concluded that gold passivation is more likely to occur in such an alkaline sulfur-enriched leaching system. As a result, the issue of how to inhibit the passivation of gold is a pressing problem for the applications of sulfur-containing leaching agents. Although the mechanism of gold passivation by sulfur species still remains controversial, the adsorption of different sulfur-containing compounds is generally considered to passivate the gold surface and hinder the access of the lixiviants required for gold leaching. Furthermore, little is understood about the effects of sulfur species and their interaction with gold. Therefore, the formation mechanisms of the passivating layers and effective solutions require further study and development.

Table 3. Summary of possible gold passivating species in different studies

Characterization technique	Gold passivating species	Ref. No.
Electrochemical	Sulfur and CuS_2	[121]
Electrochemical	Colloid sulfur	[122]
Electrochemical	Sulfur and sulfides	[118,123]
Electrochemical	Sulfur and sulfur–oxygen species	[125]
Electrochemical	Sulfur-like surface film	[88]
Electrochemical	Tetrathionate, sulfate, and elemental sulfur	[96]
SERS	Sulfur, polysulfides, polythionate, and copper sulfide compounds	[124]
SERS	Sulfur, sulfide-like species, trithionate, and tetrathionate	[129]
SERS	Elemental sulfur, gold sulfide, polythionates	[135]
SERS	Cyclo-S_8, polymeric and monoatomic sulfur	[81,132]
SERS, XPS, and Scanning tunneling microscopy	Polysulfides, monomeric sulfur, and some elemental sulfur	[134]
SERS using shell-isolated gold nanoparticles	Cyclo-S_8, elemental sulfur, polymeric sulfur chains	[131]
Electrochemical and SERS	Sulfide, elemental sulfur, tetrathionate, and trithionate	[126]
SERS, ATR-FTIR, and XPS	Cyclo-S_8, tetrathionate-like species, gold and copper sulfides	[127–128]
Electrochemical and Raman spectroscopy	Elemental sulfur, polysulfide, and trithionate	[130]

6. Summary and conclusions

Over the past several decades, researchers have devoted great attention to fundamentals and applications of gold leaching using thiosulfate, polysulfide, and alkaline sulfide lixiviation; the related materials essentially belong to a class of alkaline sulfur-containing lixiviants. This paper summarizes the research progress and challenges facing the use of sulfur-containing agents for gold leaching.

The dissolution of elemental sulfur in alkaline solutions forms a metastable sulfur-containing system that can be applied to extract gold from the raw material. Elemental sulfur undergoes disproportionation and oxidation to generate various sulfur-containing anions such as sulfide, polysulfide, and thiosulfate, which can form stable complexes with auric ions. Notably, the alkaline sulfur-containing solution is a thermodynamically metastable system. A transformation process occurs among the various sulfur species, in which the sulfur is in different oxidation states depending on the potential of leaching solution. As sulfide begins to oxidize toward sulfate, it will first generate polysulfides with different chain lengths and then oxysulfide species such as thiosulfate and polythionates. The alkaline degradation of thiosulfate produces tetrathionate, pentathionate, trithionate, and sulfite, with sulfate being the ultimate oxidation product. Moreover, thiosulfate can be regenerated from the decom-

position of polythionates or the reaction between sulfide and sulfite.

For the sulfide/polysulfide system, the dominant ligand of gold(I) ions is sulfide, whereas polysulfide serves as the oxidant rather than the lixiviant because of its high oxidation state. At a relatively high potential, thiosulfate also can form stable complexes with gold(I) ions. Electrochemical and kinetics studies on gold leaching using sulfur-containing agents mainly focus on thiosulfate leaching systems. The mechanism of electrochemical catalytic oxidation plays an essential role in the dissolution of gold. The rate of gold leaching is chemically controlled rather than diffusion controlled and is thus highly dependent on temperature.

A unique advantage of sulfur-containing leaching agents is that they can be generated *in situ* from gold-bearing sulfide minerals, which offers a potential solution to the pressing problem of high thiosulfate consumption while simultaneously enabling the comprehensive utilization of sulfur resources. The passivation of gold by sulfur species is regarded as the greatest challenge facing alkaline sulfur-containing leaching systems. Sulfur-containing anions undergo oxidation or decomposition to produce a passivation layer, which mainly consists of various sulfur allotropes, sulfides, and polythionates. Elucidating the mechanism of passivation requires further fundamental research on the contribution of different sulfur species and their interaction with the gold surface. Such noncyanide leaching lixiviants offer substantial advantages over the processing of refractory gold ores containing copper and carbonaceous matter. Given the increasing research interests in gold leaching using sulfur-containing leaching agents, we expect the industrial application of these noncyanide leaching reagents will be realized in the near future.

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