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Behavior of $S_2O_3^{2-}$ and SO_3^{2-} in sulfur-bearing aqueous solution system for gold leaching

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Abstract: The concentrations of $S_2O_3^{2^-}$ and $SO_3^{2^-}$ were measured in gold leaching systems, including thiosulfate system, polysulfide system and the modified lime sulfur synthetic solution (ML) system in the process of chemical reaction. The interactions among $S_2O_3^{2^-}$, $SO_3^{2^-}$ and S^{2^-} were discussed. The behavior mechanism of sulfur-bearing reagents was proposed to describe the process reactions and their Gibbs free energy. The proper quantity oxygen and $SO_3^{2^-}$ reduce decomposition of $S_2O_3^{2^-}$ and react with sulfur derived from the decomposition of $S_X^{2^-}$. So, $SO_3^{2^-}$ ions have action to stabilize sulfur-bearing system and are favorable to leach gold. **Key words:** sulfur-bearing system; gold leaching; thermodynamics

1 Introduction

In the last few decades, many researchers investigated the non-cyanide or/and non-poisonous reagents leaching gold for the environmental issues. Up to now, the main non-cyanide processes include thiosulfate, polysulfide, LSSS (lime sulfur synthetic solution), ML (modified LSSS), thiocyanate, chloride, and bromide leaching processes etc[1–7].

Many processes and mechanisms of leaching gold system were studied in China. Research works on thermodynamics, dynamics and electrochemistry of thiosulfate leaching system indicated that thiosulfate dissolving gold was of an electrochemistry-catalytic mechanism[4]. Other investigators studied the mixed system of thiosulfate and polysulfide. Two new non-cyanide and non-poisonous leaching gold reagents, LSSS and ML, were prepared by ourselves[5]. The effective components of ML are $S_2O_3^{2-}$ and S_x^{2-} . Experiments of leaching gold with LSSS and ML have been carried out and the leaching ratio is above 85% [1, 6].

The effective leaching gold reagent in the sulfur bearing system is $S_2O_3^{2-}$ and the important additive is $SO_3^{2^-}[8-12]$. But, their functions are not clear. So, it is necessary to study the behaviors of $S_2O_3^{2-}$ and SO_3^{2-} in the system. The principle of $S_2O_3^{2^-}$ and $SO_3^{2^-}$ has been discussed in many works. Some researchers discovered [4] that a little quantity of additive of Na₂SO₃ can decrease the decomposition of $S_2O_3^{2-}$. Therefore, it decreased the consumption $S_2O_3^{2-}$ of the sulfur bearing system[13-15]. The two new types of leaching gold reagents, LSSS and ML, are the systems bearing $S_2O_3^{2-}$ and S_X^{2-} . But, the chemical reaction mechanism of the LSSS and ML is indefinite, especially the behaviors of $S_2O_3^{2-}$ and SO_3^{2-} in leaching gold systems[6–10]. And it prevented the application of the ML and LSSS. This work focused on the researches of consumption and transformation behavior of $S_2O_3^{2-}$, SO_3^{2-} and S_x^{2-} ions in the sulfur bearing reagents system of gold leaching, including thiosulfate system, polysulfide system and the ML system. The investigation was intended to find mechanism among the effective leaching gold agents and accelerated the application of bearing reagents in the gold leaching processes.

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2 Experimental

All the reagents used in our experiments were of analytical purity and were used without further purification. The starting solution was prepared by dissolving CuSO₄·5H₂O. After that, an appropriate amount of NH₃·H₂O was added in it. Then, other agents were put in the previous solution, and a final mixing solution containing S₂O₃²⁻ and/or SO₃²⁻ was obtained. The mixing solution was transferred into the three-necked bottle, and was kept in a water bath at 50 with continuous stirring.

At last, the three-necked bottle was sealed, and after certain time, the concentrations of $S_2O_3^{2-}$, SO_3^{2-} were measured using iodine titration.

The experimental conditions are listed in Tables 1-3.

Table 1 Experimental conditions in thiosulfate leaching system

No.	$c(\mathrm{SO_3}^{2-})/(\mathrm{mol}\cdot\mathrm{L}^{-1})$	$c(S_2O_3^{2-})/(mol \cdot L^{-1})$	Oxidation agent
1-1	0	0.5	No
1-2	0.1	0.5	No
1-3	0	0.5	Air
1-4	0.1	0.5	Air
1-5	0	0.5	Oxygen
1-6	0.1	0.5	Oxygen

 Table 2
 Experimental conditions in polysulfide leaching system

No.	$c(\mathrm{SO_3}^{2^-})/(\mathrm{mol}\cdot\mathrm{L}^{-1})$	$c(S_X^{2^-})/(\text{mol}\cdot L^{-1})$	Oxidation agent
2-1	0	0.01	No
2-2	0.1	0.01	No
2-3	0	0.01	Air
2-4	0.1	0.01	Air
2-5	0	0.01	Oxygen
2-6	0.1	0.01	Oxygen

Table 3 Experimental conditions in ML leaching system						
No.	$c(\mathrm{SO_3}^{2^-})/(\mathrm{mol}\cdot\mathrm{L}^{-1})$	$c(S_2O_3^{2^-})/(mol \cdot L^{-1})$	$c(S_X^{2^-})/(\text{mol}\cdot \text{L}^{-1})$	Oxidation agent		
3-1	0	0.5	0.01	No		
3-2	0.1	0.5	0.01	No		
3-3	0	0.5	0.01	Air		
3-4	0.1	0.5	0.01	Air		

3 Results and discussion

3.1 Behaviors of S₂O₃²⁻ in different sulfur bearing reagent systems

The experimental results are expressed in Figs.1–3. Fig.1 shows that concentration of $S_2O_3^{2-}$ decreased



Fig.1 Curves between concentration of $S_2O_3^{2-}$ and time in thiosulfate system



Fig.2 Curves between concentration of ${\rm S_2O_3}^{2^-}$ and time in polysulfide system



Fig.3 Curves between concentration of $S_2O_3^{2-}$ and time in ML system

quickly in the thiosulfate system during the initial stage of reaction because $S_2O_3^{2^-}$ was oxidized by $Cu(NH_3)_4^{2^+}$. The chemical reaction equations were as follows:

$$2Cu(NH_{3})_{4}^{2+}+S_{2}O_{3}^{2-}+2OH^{-} = 2Cu(NH_{3})_{2}^{+}+S_{2}O_{4}^{2-}+H_{2}O+4NH_{3}$$

$$\Delta G^{\Theta}_{298} = -41.0 \text{ kJ/mol}$$
(1)
$$4Cu(NH_{3})_{4}^{2+}+S_{2}O_{3}^{2-}+6OH^{-} = 4Cu(NH_{3})_{2}^{+}+2SO_{3}^{2-}+3H_{2}O+8NH_{3}$$

$$\Delta G^{\Theta}_{298} = -225.5 \text{ kJ/mol}$$
(2)

It consumed more $S_2O_3^{2-}$ ions with oxygen in the system at the beginning (see curves 1-5 and 1-6 in Fig.1). The following reactions happened:

$$2S_2O_3^{2^-}+O_2=2S_2O_4^{2^-}$$

$$\Delta G^{\Theta}_{298}=-155.6 \text{ kJ/mol}$$
(3)

$$S_{2}O_{3}^{2^{-}}+2OH^{-}+O_{2}=2SO_{3}^{2^{-}}+H_{2}O$$

$$\Delta G^{\Theta}_{298}=-373.1 \text{ kJ/mol}$$
(4)

The considerable a mount of $S_2O_3^{2-}$ was produced in the polysulfide system during the initial stage from Fig.2. The S_x^{2-} ions decomposed into S and S^{2-} ions. And the S^{2-} combined with SO_3^{2-} existing in the system, then was oxidized into $S_2O_3^{2-}$, which was the efficient component in the leaching gold process. The following reactions happened:

$$S^{2^{-}}+SO_{3}^{2^{-}}+H_{2}O+1/2 O_{2}=S_{2}O_{3}^{2^{-}}+2OH^{-} \Delta G^{\Theta}_{298}=-199.2 \text{ kJ/mol}$$
(5)

$$\Delta G^{\Theta}_{298} = -685.7 \text{ kJ/mol}$$
(6)

The oxygen exited in the system promoted the previous reaction. Therefore, the concentration of $S_2O_3^{2^-}$ increased (Curve 2-4 in Fig.2). But, the superfluous oxygen accelerated the reaction (7), which induced the decrease of the $S_2O_3^{2^-}$ (Curve 2-6 in Fig.2):

$$S_{2}O_{3}^{2^{-}}+2O_{2}+2OH^{-}=2SO_{4}^{2^{-}}+H_{2}O$$

$$\Delta G^{\Theta}_{298}=-889.2 \text{ kJ/mol}$$
(7)

The concentration of $S_2O_3^{2-}$ decreased slowly in the ML system during the initial stage (see Fig.3). The concentration of $S_2O_3^{2-}$ was enhanced because SO_3^{2-} ions were added in the system (Curves 3-2 and 3-4 in Fig.3). This accelerated the reaction (8). But when the oxygen was in existence, the reaction (3) was promoted.

$$S^{0}+SO_{3}^{2}=S_{2}O_{3}^{2}-\Delta G^{\Theta}_{298}=-36.0 \text{ kJ/mol}$$
 (8)

The concentration of $S_2O_3^{2-}$ almost had no change and got to reaction balance in the thiosulfate system during the subsequent stage of reaction (See Fig.1). But it would decrease slowly when the oxygen was filled into the system.

It was shown that the concentration of $S_2O_3^{2^-}$ was decreased during the subsequent stage in the polysulfide system from Fig.2. The concentration of $S_2O_3^{2^-}$ decreased obviously if the system was abundant in oxygen. Oxygen-enriched solution accelerated the chemical reactions (4) and (9), and then it consumed

more
$$S_2O_3^{2^-}$$
:
 $SO_3^{2^-}+1/2 O_2 = SO_4^{2^-}$
 $\Delta G^{\Theta}_{298} = -516.1 \text{ kJ/mol}$
(9)

The concentration of $S_2O_3^{2-}$ kept invariable in the whole process and the system reached equilibrium in the ML system during the subsequent stage from Fig.3. It was also indicated that the concentration of $S_2O_3^{2-}$ was higher than that without SO_3^{2-} in the system.

3.2 Behaviors of SO₃²⁻ in different sulfur bearing systems

The results are represented in Figs.4–6. The concentration of SO_3^{2-} decreased quickly in the thiosulfate system during the initial stage of reaction. It was caused by the chemical reactions (9) and (10).

$$2Cu(NH_{3})_{4}^{2+}+SO_{3}^{2-}+2OH^{-} = 2Cu(NH_{3})_{2}^{+}+SO_{4}^{2-}+H_{2}O+4NH_{3} \Delta G^{\Theta}_{298} = -184.2 \text{ kJ/mol}$$
(10)

A little SO_3^{2-} was produced in the polysulfide system during the initial stage. But the concentration of



Fig.4 Curves between concentration of SO_3^{2-} and time in thiosulfate system



Fig.5 Curves between consistence of SO_3^{2-} and time in polysulfide system

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Fig.6 Curves between concentration of SO_3^{2-} and time in ML system

 SO_3^{2-} decreased quickly when a quantity of SO_3^{2-} was added into the system at the beginning, for the reactions (5), (8) and (10) occurred during the initial stage (See Fig.5).

Fig.6 shows that the concentration of SO_3^{2-} decreased rapidly then increased to a certain value in the ML system during the initial stage of reaction. The reason was the same as that in the polysulfide system. The portion of S²⁻ reacted with the oxygen in the system, so it increased the concentration of SO_3^{2-} in the reactions (4) and (11):

$$2S^{2-}+3O_2 = 2SO_3^{2-} \Delta G^{\Theta}_{298} = -801.4 \text{ kJ/mol}$$
(11)

The concentration of SO_3^{2-} was unchanged in the thiosulfate system during the subsequent stage of reaction, and then the system equilibrium was attained from Fig.4. The concentration of SO_3^{2-} in the ML system was stable during the subsequent stage. The concentration of SO_3^{2-} increased when more oxygen was filled into the system.

4 Conclusions

(1) The behaviors of different sulfur-bearing reagents in the alkaline medium systems for leaching gold, including thiosulfate system, polysulfide system and ML system are discussed. The behavior mechanism of sulfur-bearing reagents is proposed to describe the process reactions and their Gibbs free energy.

(2) The proper quantities of oxygen and SO_3^{2-} reduce the decomposition of $S_2O_3^{2-}$ and react with sulfur

derived from the decomposition of $S_X^{2^-}$. So, $SO_3^{2^-}$ ions have action to stabilize sulfur-bearing system and are favorable to leach gold.

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