Behavior of $\text{S}_2\text{O}_3^{2-}$ and $\text{SO}_3^{2-}$ in sulfur-bearing aqueous solution system for gold leaching

CHEN Xiang-yang(žཟဝ), LAN Xin-zhe(ধྍᅽ), ZHANG Qiu-li(ベン৬), ZHOU Jun(ᅛ), SONG Yong-hui(සႥpectives)

1. School of Metallurgical Engineering, Xi’an University of Architecture and Technology, Xi’an 710055, China; 2. Research Center of Metallurgical Engineering and Technology of Shaanxi Province, Xi’an University of Architecture and Technology, Xi’an 710055, China

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Abstract: The concentrations of $\text{S}_2\text{O}_3^{2-}$ and $\text{SO}_3^{2-}$ 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 $\text{S}_2\text{O}_3^{2-}$, $\text{SO}_3^{2-}$ and $\text{S}_2^2$ 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 $\text{SO}_3^{2-}$ reduce decomposition of $\text{S}_2\text{O}_3^{2-}$ and react with sulfur derived from the decomposition of $\text{S}_2^2$. So, $\text{SO}_3^{2-}$ 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 leaching gold reagent in the sulfur bearing system is $\text{S}_2\text{O}_3^{2-}$ and the important additive is $\text{SO}_3^{2-}$[8−12]. But, their functions are not clear. So, it is necessary to study the behaviors of $\text{S}_2\text{O}_3^{2-}$ and $\text{SO}_3^{2-}$ in the system. The principle of $\text{S}_2\text{O}_3^{2-}$ and $\text{SO}_3^{2-}$ has been discussed in many works. Some researchers discovered [4] that a little quantity of additive of Na$_2$SO$_3$ can decrease the decomposition of $\text{S}_2\text{O}_3^{2-}$. Therefore, it decreased the consumption $\text{S}_2\text{O}_3^{2-}$ of the sulfur bearing system[13−15]. The two new types of leaching gold reagents, LSSS and ML, are the systems bearing $\text{S}_2\text{O}_3^{2-}$ and $\text{S}_2^2$. But, the chemical reaction mechanism of the LSSS and ML is indefinite, especially the behaviors of $\text{S}_2\text{O}_3^{2-}$ and $\text{SO}_3^{2-}$ 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 $\text{S}_2\text{O}_3^{2-}$, $\text{SO}_3^{2-}$ and $\text{S}_2^2$ 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 °C with continuous stirring.

At last, the three-necked bottle was sealed, and after certain time, the concentrations of S₂O₃²⁻, SO₃²⁻ were measured using iodine titration.

The experimental conditions are listed in Tables 1–3.

Table 1 Experimental conditions in thiosulfate leaching system

<table>
<thead>
<tr>
<th>No.</th>
<th>c(SO₃²⁻)/(mol·L⁻¹)</th>
<th>c(S₂O₃²⁻)/(mol·L⁻¹)</th>
<th>Oxidation agent</th>
</tr>
</thead>
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<tr>
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<td>No</td>
</tr>
<tr>
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<td>0.1</td>
<td>0.5</td>
<td>No</td>
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<tr>
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<td>0.5</td>
<td>Air</td>
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<td>1-4</td>
<td>0.1</td>
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<td>Air</td>
</tr>
<tr>
<td>1-5</td>
<td>0</td>
<td>0.5</td>
<td>Oxygen</td>
</tr>
<tr>
<td>1-6</td>
<td>0.1</td>
<td>0.5</td>
<td>Oxygen</td>
</tr>
</tbody>
</table>

Table 2 Experimental conditions in polysulfide leaching system

<table>
<thead>
<tr>
<th>No.</th>
<th>c(SO₃²⁻)/(mol·L⁻¹)</th>
<th>c(Sₓ²⁻)/(mol·L⁻¹)</th>
<th>Oxidation agent</th>
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</thead>
<tbody>
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<td>0.01</td>
<td>No</td>
</tr>
<tr>
<td>2-3</td>
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<td>0</td>
<td>0.01</td>
<td>Oxygen</td>
</tr>
<tr>
<td>2-6</td>
<td>0.1</td>
<td>0.01</td>
<td>Oxygen</td>
</tr>
</tbody>
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Table 3 Experimental conditions in ML leaching system

<table>
<thead>
<tr>
<th>No.</th>
<th>c(SO₃²⁻)/(mol·L⁻¹)</th>
<th>c(S₂O₃²⁻)/(mol·L⁻¹)</th>
<th>c(Sₓ²⁻)/(mol·L⁻¹)</th>
<th>Oxidation agent</th>
</tr>
</thead>
<tbody>
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<td>0</td>
<td>0.5</td>
<td>0.01</td>
<td>Air</td>
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<tr>
<td>3-4</td>
<td>0.1</td>
<td>0.5</td>
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<td>Air</td>
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</tbody>
</table>

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 S₂O₃²⁻ decreased quickly in the thiosulfate system during the initial stage of reaction because S₂O₃²⁻ was oxidized by Cu(NH₃)₄²⁺. The chemical reaction equations were as follows:
2Cu(NH$_3$)$_2$$^+$+S$_2$O$_3$$^-$+2OH$^-$
= 2Cu(NH$_3$)$_2$$^+$+S$_2$O$_4$$^2$$-$+H$_2$O+4NH$_3$
$\Delta G^\Theta_{298}=-41.0$ kJ/mol (1)

4Cu(NH$_3$)$_2$$^+$+S$_2$O$_3$$^-$+6OH$^-$
= 4Cu(NH$_3$)$_2$$^+$+2SO$_4$$^2$$-$+3H$_2$O+8NH$_3$
$\Delta G^\Theta_{298}=-225.5$ kJ/mol (2)

It consumed more S$_2$O$_3$$^-$ ions with oxygen in the system at the beginning (see curves 1-5 and 1-6 in Fig.1). But the concentration of S$_2$O$_3$$^-$ decreased during the subsequent stage of reaction (See Fig.1). Therefore, the concentration of S$_2$O$_3$$^-$ kept invariable in the whole process and the system reached equilibrium in the ML system during the subsequent stage from Fig.3. It was also indicated that the concentration of S$_2$O$_3$$^-$ was higher than that without SO$_3$$^-$ in the system.

3.2 Behaviors of SO$_3$$^-$ in different sulfur bearing systems

The results are represented in Figs.4–6. The concentration of SO$_3$$^-$ decreased quickly in the thiosulfate system during the initial stage of reaction. It was caused by the chemical reactions (9) and (10).

$\Delta G^\Theta_{298}=-516.1$ kJ/mol (9)

2Cu(NH$_3$)$_2$$^+$+SO$_3$$^-$+2OH$^-$
= 2Cu(NH$_3$)$_2$$^+$+SO$_4$$^2$$-$+H$_2$O+4NH$_3$
$\Delta G^\Theta_{298}=-184.2$ kJ/mol (10)

A little SO$_3$$^-$ was produced in the polysulfide system during the initial stage. But the concentration of more S$_2$O$_3$$^-$:

SO$_3$$^-$+1/2 O$_2$=SO$_4$$^2$$-$
$\Delta G^\Theta_{298}=-199.2$ kJ/mol (5)

2S$_2$O$_3$$^-$+2OH$^-$=2SO$_4$$^2$$-$+2OH$^-$
$\Delta G^\Theta_{298}=-184.2$ kJ/mol (5)

The oxygen exited in the system promoted the previous reaction. Therefore, the concentration of S$_2$O$_3$$^-$ increased (Curve 2-4 in Fig.2). But, the superfluous oxygen accelerated the reaction (7), which induced the decrease of the S$_2$O$_3$$^-$ (Curve 2-6 in Fig.2):

S$_2$O$_3$$^-$+2O$_2$+H$_2$O=2SO$_4$$^2$$-$+H$_2$O
$\Delta G^\Theta_{298}=-889.2$ kJ/mol (7)

The concentration of S$_2$O$_3$$^-$ decreased slowly in the ML system during the initial stage (see Fig.3). The concentration of S$_2$O$_3$$^-$ was enhanced because SO$_3$$^-$ 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$_2$O$_3$$^-$+SO$_3$$^-$=2S$_2$O$_5$$^-$
$\Delta G^\Theta_{298}=-36.0$ kJ/mol (8)

The concentration of S$_2$O$_3$$^-$ 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$_2$O$_3$$^-$ was decreased during the subsequent stage in the polysulfide system from Fig.2. The concentration of S$_2$O$_3$$^-$ decreased obviously if the system was abundant in oxygen. Oxygen-enriched solution accelerated the chemical reactions (4) and (9), and then it consumed

Fig.4 Curves between concentration of SO$_3$$^-$ and time in thiosulfate system

Fig.5 Curves between consistence of SO$_3$$^-$ and time in polysulfide system
increased the concentration of SO$_3^{2-}$.

Fig.5).

(5), (8) and (10) occurred during the initial stage (See

added into the system at the beginning, for the reactions

system

process reactions and their Gibbs free energy.

of sulfur-bearing reagents is proposed to describe the

and ML system are discussed. The behavior mechanism

leaching

gold, including thiosulfate system, polysulfide system

portion of S$_2^{2-}$ was the same as that in the polysulfide system. The

reaction, and then the system equilibrium was attained

2S$_2^{2-}$+3O$_2$=2SO$_3^{2-}$

$\Delta G_{298}^{\Theta}$=-801.4 kJ/mol

The concentration of SO$_3^{2-}$ was unchanged in the

thiosulfate system during the subsequent stage of

reactions (4) and (11):

2SO$_3^{2-}$+3O$_2$=2SO$_4^{2-}$

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$\delta_2^{\delta-}$. So, SO$_3^{2-}$ ions have action to stabilize sulfur-bearing system and are favorable to leach gold.

References


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