Color of Oxidative Pressure Leaching Liquor: A Case of Sphalerite

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Abstract: In lab-scale experiments of oxidative pressure leaching of sphalerite, an interesting phenomenon is that the leaching liquor looks three main colors: black, red and green. In on-going work, semi-quantitative study is carried out to investigate such phenomenon, including drawing of predominance area color diagram, effect of sulfur surfactant on color of leaching liquor, color and stability of oxidation of leaching liquor. Experimental results show that color of the leaching liquor depends on leaching condition mainly including temperature, dissolved oxygen concentration, that experimental results show sulfur surfactant has no effect on the color of leaching liquor, that, with increased molar ratio of elemental sulfur and sodium sulfide, $S_{x}^{2-}, x = 1 \sim 8$ is more stable, and that in oxidation of aqueous sulfide anion, to achieve reasonable fast oxidation kinetic, temperature of 150 °C and oxygen pressure of $2 \times 10^5$ Pa is the minimum required conditions, which is coincide with such conditions to achieve reasonable fast oxidation kinetic in oxidation of aqueous ferrous iron. In this paper, different reaction mechanisms in given leaching condition were discussed.

1. Introduction

Many studies[1-6] prove that polysulfide is produced in oxidative pressure leaching, that with increasing value of $x$, $S_{x}^{2-}, x = 1 \sim 8$ is of less possibility of hydrolyzation, and its color become deeper, from yellow, to orange and red. But quantitative study of relationship between color and leaching condition is not documented.

In oxidative pressure leaching liquor, there may exist high concentration of zinc and ferrous ion, and non-neglectable concentration of sulfur. It is documented[7] ferrous sulfide is black, zinc sulfide, white, and that solubility product of zinc sulfide and ferrous sulfide is $2 \times 10^{-25}$ and $6 \times 10^{-19}$,
respectively, at 25 ℃. By comparing the two mentioned above, sulfide occurs as polysulfide rather than monosulfide.

Oxidative pressure leaching in industrial practice involves treating a finely ground concentrates, using pressure autoclaves, in an acidic sulfate media under an oxygen atmosphere at around 150 ℃. Leaching kinetics are more favorable above the melting point of sulfur (119 ℃), however, it has been found that molten elemental sulfur has a tendency to occlude unreacted minerals and inhibit the diffusion of dissolved oxygen to the mineral surface, halting the reaction. Surfactants, such as ligninsulphonates, have found use in dispersing molten sulfur and allowing for higher metal recoveries in similar technologies such as the oxidative pressure leaching of zinc sulphide concentrates[8]. But in present study, the leaching liquor looks the same color, with or without sodium sulfide, and more and less quantity of such sulfur surfactant.

2. Methodology

2.1 Experimental material and equipment
The chemical and mineralogical composition is described as Table 1 and Fig.1.

| Element | Zn   | S    | Fe   | Cu   | Pb   | Ge   | Others |
|---------|------|------|------|------|------|------|--------|
| Mass Content, wt.% | 51.22 | 29.88 | 5.62 | 0.11 | 2.7  | 0.0075 | 10.4625 |

To achieve concentrate available for experiment, grind and screen it, then dry it in 40℃, and at last leach it in a 2-liter pressure autoclave. To investigate the nature of polysulfide anion, sodium polysulfide was prepared with chemical grade reagent. In the stirring sodium sulfide aqueous solution, elemental sulfur was added.

Sodium is tending to absorb water in the air, which cause it very difficult to be measured accurately. An alternative method is to take it from its aqueous solution, and with this method much experimental error can be eliminated since sodium lignosite is not a pure chemical reagent, its molecular weight ranging from 10,000~100,000. Concentration of the prepared sodium lignosite is 0.005 g·l⁻¹.

2.2 Analytic methods
Determination and analysis of content and concentration of zinc, polysulfide anion \((S_x^{2-}, x = 1 \sim 8)\) and aqueous ferrous and ferric iron is done.
3. experimental results and discussion

3.1 Drawing of predominance area color diagram

A great number of oxidative pressure leaching experiments were carried out to definite the predominance area color diagram. Leaching conditions: sphalerite concentrate, 100 g; stirring speed, 500 rpm; sodium lignosite, 15ml; leaching duration, 1hr; zinc and acid molar ratio, 1.2:1; liquid and solid ratio, 6:1(ml:g).

Experimental results show initial acidity hasn’t effect on the color of leaching liquor. The predominance area color diagram is drawn as Fig.2

In the black-color predominance area diagram (seen as Fig.2), there may exist many reversible reactions as follows.

\[
\begin{align*}
MS_x & \rightleftharpoons M^{2+} + xS^{2-} \quad (M=\text{Fe}^{2+}, \text{Zn}^{2+}; x=1\text{~to~}9) \quad (1) \\
S_x^{2-} + 2H^+ & \rightleftharpoons S_{x-1} + H_2S \quad (2) \\
H_2S & \rightleftharpoons H^+ + HS^- \quad (3) \\
HS^- & \rightleftharpoons H^+ + S^{2-} \quad (4)
\end{align*}
\]

From the fact that hydrolyzation of metal (poly) sulfide (Reaction 1), hydrolyzation of \(S_x^{2-}\) (Reaction 2), and ionization of \(H_2S\) (Reaction 3 and 4), it is concluded with increased value of \(x\) solubility of \(MS_x\) become bigger. Analysis results proved it. In those leaching liquor with conditions within red predominance area, there exist substantially concentration of aqueous zinc, ferrous and sulfide, which small solubility of sulfide fails to explain that.

3.2 Effect of sulfur surfactant on color of leaching liquor

To investigate effect of sulfur surfactant on the color of leaching liquor oxidative pressure leaching experiments with different quantity of sodium lignosite were carried out. The leaching conditions are taken randomly within red predominance area.

Leaching conditions: sphalerite concentrate, 100 g; agitation speed, 500 rpm; sodium lignosite, 15ml, 10ml and 0 ml; leaching duration, 1hr; zinc and acid molar ratio, 1.2:1; liquid and solid ratio, 6:1(ml:g); leaching temperature, 130 °C; Oxygen partial pressure, 0.4 MPa.

Experimental results show sulfur surfactant has no effect on the color of leaching liquor. The comparison results are described as Fig.3.

As seen as Fig.3, there doesn’t exist substitute difference between them, though the concentration of total sulfur deceases with reduced quantity of sodium lignosite, which may be analysis error because of presence of sulfur-containing sodium lignosite and oxy-sulfur species\(^{[9,11]}\). Polysulfide anion \(S_x^{2-}, x>1\) may cause from the incomplete oxidation of sulfide (HS\(^-\), \(H_2S\)) in the catalyst Fe(III).
presence.

In general, HS\(^{-}\) is oxidized to elemental sulfur, but elemental sulfur can also react with HS\(^{-}\) to form polysulfide. The transformation of sulfur oxoanions (S\(_2\)O\(_5\)\(^{2-}\), S\(_2\)O\(_4\)\(^{2-}\), SO\(_3\)\(^{2-}\)) and sulfide (HS\(^{-}\), S\(^{-}\)) is interesting to workers in chemical engineering, and concerns the sulfur cycle. The oxidation state of sulfur, polysulfides and sulfur oxoanions in order of oxidation state from lower to higher is as follows:

\[
\text{HS}^{-}\rightarrow\text{S}^{0}\rightarrow\text{S}^{1+}\rightarrow\text{S}^{2}\rightarrow\text{S}_{2}\text{O}_{3}^{2-}\rightarrow\text{S}_{2}\text{O}_{4}^{2-}\rightarrow\text{SO}_{3}^{2-}\rightarrow\text{SO}_{4}^{2-} \quad \text{(end product)}
\]

Different mechanism of formation of polysulfide anion has been present. For example, polysulfide anion (S\(_x\)\(^{2-}\)) could be formed from reaction of elemental sulfur with dissolved hydrogen sulfide:

\[
\text{HS}^{-}+(x-1)\text{S}^{0}\rightleftharpoons S_x^{2-}+\text{H}^{+}
\]

Formation of disulfide could be the result of the coupled reduction of ferric iron and oxidation of sulfide ions. i.e:

\[
2\text{Fe}^{3+}+2\text{e}^{-}\rightarrow 2\text{Fe}^{2+} \quad \text{(6)}
\]

\[
2\text{S}^{2-}\rightarrow 2\text{S}^{0}+2\text{e}^{-} \quad \text{(7)}
\]

Another mechanism is reaction of oxy-sulfur species with aqueous sulfide anion:

\[
(x-1)\text{S}_{2}\text{O}_{3}^{2-}+\text{S}^{2-} \rightleftharpoons S_x^{2-}+(x-1)\text{SO}_{3}^{2-} \quad \text{(8)}
\]

Therefore, under a given leaching condition, polysulfide anion (S\(_x\)\(^{2-}\)) is easy to form, in spite of presence of sodium lignosite or not.

### 3.3 Color and stability of \(S_x^{2-}\)

To investigate the color and stability of \(S_x^{2-}\), \(x = 1 \sim 8\), sodium polysulfide with different elemental sulfur and sodium sulfide molar ratio ranging 0 to 3.5 is prepared, in 500 ml sodium sulfide (30 g·l\(^{-1}\))By comparing the color of the prepared solution, all of them are red and their color become deeper with increased elemental sulfur and sodium sulfide molar ratio.Add the same molar acetic acid to the sodium polysulfide aqueous solution. Reaction condition: reaction temperature, 80 \(^\circ\)C; Reaction duration, 1 hr.; Agitation speed, 100 rpm. The relationship between aqueous sulfide with different ratio of elemental sulfur and sodium sulfide and oxidation rate is described as Fig.4.The prepared sodium sulfide was oxidized in a 2-liter pressure autoclave with industrial pure oxygen with 1.1×10\(^6\) Pa, and for an hour. The relationship between aqueous sulfide with different ratio of elemental sulfur and sodium sulfide and oxidation rate is also describe as Fig.4.

Reaction of aqueous sulfide ion with hydrogen ion and Oxidation of aqueous sulfide processes in the following step.

\[
\text{S}^{2-}+2\text{H}^{+}\rightarrow\text{H}_2\text{S}+(x-1)\text{S} \quad \text{(11)}
\]

\[
\text{S}^{2-}+1.5\text{O}_2\rightarrow\text{S}_x\text{O}_{3}^{2-}+(x-2)\text{S}^{0} \quad \text{(12)}
\]

As seen as Fig.4, oxidation of polysulfide anion (Reaction 12) by dissolved oxygen has much faster kinetics than its acidification (Reaction 11). With increased molar ratio of elemental sulfur and sodium sulfide, \(S_x^{2-}\), \(x = 1 \sim 8\) is more stable.

### 3.4 Oxidation of leaching liquor.

Add sulfuric acid into polysulfide anion-containing leaching liquor to check its stability. It is found that red color stayed unchanged, which means such polysulfide anion, is thermodynamically stable. From the result discussed in 3.3, in the red predominance area, possibility is that value \(x\) of \(S_x^{2-}\), \(x = 1 \sim 8\) is very big. Add aqueous ferrous iron and ferric iron into the polysulfide anion-containing leaching liquor to check its stability. When aqueous ferrous iron was added, the red liquor stays unchanged, but when aqueous ferric iron is added, black precipitation looked in the red liquor. Oxidation of aqueous sulfide anion maybe process as follows.

\[
\text{S}_x^{2-}+2\text{Fe}^{3+}\rightleftharpoons \text{S}_{x+1}^{2-}+\text{S}+2\text{Fe}^{2+} \quad \text{(13)}
\]

From oxidation of polysulfide, color of leaching liquor depend on concentration of aqueous ferric iron, analysis results proves it. The polysulfide anion-containing leaching liquor was oxidized in a
2-liter pressure autoclave with industrial pure oxygen to investigate effect oxygen pressure and temperature on the oxidation rate of aqueous polysulfide anion. To investigate the effect of oxygen pressure, oxidation experiments were done as following conditions: temperature, 150 °C; Initial sulfuric acid concentration, 50 g/l; Stirring speed, 500 rpm; Oxygen flow rate, 0. The relationship between oxygen pressure and oxidation rate of aqueous sulfide anion was described as Fig. 5.

As seen as Fig. 5 and 6, in oxidation of aqueous sulfide anion, to achieve reasonable fast oxidation kinetic, temperature of 150 °C and oxygen pressure of 2 × 10⁵ Pa is the minimum required conditions, which is coincide with such conditions to achieve reasonable fast oxidation kinetic in oxidation of aqueous ferrous iron. That means in such polysulfide anion-containing leaching liquor, oxidation of aqueous sulfide anion is completed by aqueous ferric iron. Therefore, there exist different reaction mechanisms between red- and green- predominance color area.

Analysis results show within red predominance color area, the concentration of aqueous ferrous iron and that of aqueous ferric iron is 1.41 g·l⁻¹ and below 0.1 g·l⁻¹, respectively, while within green predominance color area, 1.03 and 1.60 g·l⁻¹, respectively.

In red predominance color area, the possible main mechanism is as follows.

\[
\begin{align*}
\text{ZnS} & + \text{H}^+ \rightleftharpoons [\text{ZnSH}]_0^+ \quad (14) \\
[\text{ZnSH}]_0^+ + \text{H}^+ & \rightleftharpoons [\text{ZnSH}_2]_0^{2+} \quad (15) \\
[\text{ZnSH}_2]_0^{2+} + 0.5 \text{O}_2 & \rightleftharpoons \text{Zn}^{2+} + \text{S} + \text{H}_2\text{O} \quad (16)
\end{align*}
\]

Oxidation of protonized zinc sulfide (Reaction 14) is key reaction in the mechanism. Slow oxidation of aqueous ferrous iron and extremely low solubility of zinc sulfide leads to little possibility to occurrence of Reaction 19.

In green predominance color area, the possible main mechanism is as follows.

\[
\begin{align*}
\text{ZnS} & \rightleftharpoons \text{Zn}^{2+} + \text{S}^2_\downarrow \quad (17) \\
2\text{Fe}^{2+} + 0.5\text{O}_2 + 2\text{H}^+ & \rightleftharpoons 2\text{Fe}^{3+} + \text{H}_2\text{O} \quad (18) \\
2\text{Fe}^{3+} + \text{S}^2_\downarrow & \rightleftharpoons 2\text{Fe}^{2+} + \text{S}_\downarrow \quad (19)
\end{align*}
\]

In such mechanism, exclusively aqueous ferric iron is the oxidizing agents for the dissolution. While O₂ and Fe³⁺ are two competing oxidants, isotope studies. Show that oxygen in sulfate comes mainly from water. This shows that Fe³⁺ as the direct oxidant and O₂ probably regenerate Fe³⁺ through reoxidation of aqueous ferrous iron (Reaction 18). Solubility of zinc sulfide increases with elevated temperature. And solubility of hydrogen sulfide decreases with the same trend. Oxidation rate of aqueous ferrous iron increases with it, and it can’t be ignored. If the redox potential is very high, sulfur ion will be oxidized to high value, even sulfur dioxide and sulfuric acid

4. Conclusions

In oxidative pressure leaching of sphalerite, kinetics of aqueous ferrous iron depends on the leaching
temperature and oxygen pressure (or dissolved oxygen). Generally speaking, slow kinetics will result in easy occurrence of polysulfide. In such cases, the leaching liquor looks red. Otherwise, fast kinetics will lead to no presence of polysulfide. In such cases, the leaching liquor looks green.

There are many paths for polysulfide anion to form in the oxidative pressure leaching of sphalerite with leaching condition within the red predominance area. In spite of the formation mechanism, with big value of $x$ is rather stable, and can’t be easily oxidized by dissolved oxygen.

Plenty of experiments prove that such oxidative pressure leaching of sphalerite with leaching condition within the red predominance area has much slower kinetics than that with condition within the green does, which is attributed to the different leaching mechanism. Therefore, that provides a convenient method to estimate and control the leaching conditions such as temperature and oxygen partial pressure in industrial practice.

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