Removal of cyanide adsorbed on pyrite by H₂O₂ oxidation under alkaline conditions

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Abstract

Large amounts of cyanide tailings are produced during the cyanidation process in gold extraction, which are hazardous solid wastes due to the toxic cyanide. Pyrite is one of the main minerals in cyanide tailings. The removal of cyanide adsorbed on pyrite by H₂O₂ oxidation under alkaline conditions was investigated in this study. It was found that the removal efficiency was positively correlated with pH from 5 to 12, but remained almost constant when pH was higher than 12. The highest cyanide removal efficiency of 91.10% was achieved by adding no less than 0.6 wt.% of H₂O₂. Cyanide removal was positively correlated with the CN⁻ adsorption amount between 1.06 and 8.5 mg/g, and temperature between 25 and 85°C. The removal of cyanide adsorbed on pyrite by H₂O₂ oxidation under alkaline conditions was due to the oxidation of pyrite. Hexacyanoferrate, thiocyanate and sulfate were generated with mole ratios of about 2.03:1.12:3.17 during the cyanide removal.

Keywords: Cyanide removal, Pyrite, H₂O₂ oxidation, Alkaline conditions

Introduction

Cyanidation is an important process in gold extraction. At present, about 90% of gold ores in the world is treated with this process. As a result, large amounts of cyanide tailings are produced, which are hazardous solid wastes due to the toxic cyanide (Habashi, 1987; Yang and Wang, 2007). Cyanide tailings lead to land occupation and severe environmental pollution, and further pose a serious threat to life and property safety. In 2016, cyanide tailings were included in the National Hazardous Waste List (China) and strict criteria have to be met for their storage, transportation, disposition and utilization. Therefore, cyanide tailings have hindered the development of the gold industry and need to be properly dealt with.

In recent years, studies on the treatment of cyanide tailings have intensified and many cyanide disposal technologies have been developed, including incineration (Guo, 2004; Koger and Bockhorn, 2005), chemical oxidation (Dutra et al., 2008; Felix-Navarro et al., 2003; Yngard et al., 2008), biological treatment (Akcil, 2003; White et al., 2000) and strengthening natural degradation (Li et al., 2001). The removal efficiency of cyanide by incineration is high. It was reported that about 94.6% of cyanide was removed (Guo, 2004). However, the energy consumption involved is huge in keeping an incinerator at high temperatures for a long period of time. For chemical oxidation, biological treatment and strengthening natural degradation methods, cyanide tailings are leached to remove the residual cyanides from the cyanide tailings, and then the leaching solution is treated to destroy or recycle...
cyanides. Most of the residual cyanide in tailings are strongly adsorbed on the surface of minerals in the cyanide tailings and only a small amount of free cyanides and hydrolytic complex cyanides are able to enter into the leaching solution (Lv, 2017). Therefore, these methods could not completely destroy the residual cyanides in cyanide tailings.

A typical composition of cyanide tailings is 23.50 wt.% S, 24.80 wt.% Fe, 34.13 wt.% Si, 3.21 wt.% Al, 1.22 wt.% Ca, 0.47 wt.% Mg, 0.35 wt.% Zn, 0.24 wt.% Cu and 0.22 wt.% Pb (Lv et al., 2016). Pyrite (FeS2) is one of the main minerals in cyanide tailings (Lv et al., 2016), which is a porous medium and natural absorbent due to the large total pore volume and specific surface area (Zhao et al., 2008). Cyanides exist in various forms in cyanide tailings and most of the cyanides adsorbed on pyrite are driven by chemisorption of cyanide carbon onto Fe in pyrite (Zhao et al., 2016). Therefore, the detoxification degree of cyanide tailings mainly depends on the removal of cyanide from the surface of pyrite.

The aim of this study was to investigate if cyanide adsorbed on the pyrite surface could be removed by hydroxyl free radical generated from reaction between H₂O₂ and FeS₂ under alkaline conditions. Factors affecting cyanide removal efficiency were also investigated, which included temperature, pH, adsorption amount of CN⁻ on pyrite, and amount of H₂O₂ added. The mechanism of cyanide removal from pyrite was also discussed.

1. Materials and methods

1.1. Materials and chemicals

Analytical grade NaOH (Aladdin, Shanghai, China) was used to adjust pH. Analytical grade hydrogen peroxide (Aladdin, Shanghai, China), which contained 30 wt.% H₂O₂, was used as the oxidizing agent. The composition of the industrial pyrite (Dexing, Jiangxi, China) used in this study was >48 wt.% S, >44 wt.% Fe, <0.08 wt.% As, <2 wt.% SiO₂. The particle size of pyrite powders was less than 74 μm.

1.2. Preparation of cyanide-loaded pyrite

About 10 g of pyrite powder was added into 40 mL sodium cyanide solutions with initial concentrations of 500, 1000, 2000 and 5000 mg/L, respectively. After reaching adsorption equilibrium, the mixture was filtered and the residue was dried in an electrothermal blast drying oven. The white crystal was then ground and sifted to obtain the pyrite powders. The HJ745 method was again applied to determine the residual adsorption amounts of CN⁻ on the pyrite powders after cyanide removal.

1.3. Cyanide removal with H₂O₂ oxidation under alkaline conditions

Cyanide-loaded pyrite pulps (20 wt.%) were prepared with deionized water in a 250-mL beaker with mechanical agitation. The solution temperature was controlled by an electric-heated thermostatic water bath (RHDY-6S, Renhe, Changzhou, China). The solution pH was adjusted by NaOH and measured with a pH-meter (FE20, Mettler Toledo, Shanghai, China). At about the same time, a certain amount of hydrogen peroxide was added into the solution. After holding for a certain time, the mix was filtered, and the filter residue was dried in an electrothermal blast drying oven. The HJ745 method was again applied to determine the residual adsorption amounts of CN⁻ on the pyrite powders after cyanide removal.

1.4. Characterization

The surface morphologies of pyrite before and after oxidation were observed by scanning electron microscope (SEM) (JSM-5600F, JEOL, Japan). The filtrate was used to further investigate the cyanide removal mechanism under the conditions that adsorption amount of CN⁻, amount of H₂O₂ added, pH and temperature were 4.77 mg/g, 0.6 wt.%, higher than 12 and 25°C, respectively. The filtrate was divided into two parts. There was a white crystal precipitate in the first part that was subjected to low-temperature drying at 100°C. The white crystal was analyzed by X-Ray Diffraction (XRD) (X’Pert Pro, Philips, Netherlands). Another part of the solution became a blue suspension when a certain amount of ferric ions was added. The resulting blue precipitate was also analyzed by XRD after filtration.

1.5. Calculation of cyanide removal efficiency

Cyanide removal efficiency (η) was calculated according to the following equation.

\[ \eta = \frac{(q_1 - q_2)}{q_1} \times 100\% \]  

where, \( q_1 \) (mg/g) and \( q_2 \) (mg/g) are CN⁻ adsorbed on pyrite before and after H₂O₂ oxidation, respectively.

2. Results and discussion

2.1. Time course of cyanide removal efficiency

To investigate the change of cyanide removal efficiency with time, experiments were carried out under the conditions that the adsorption amount of CN⁻, amount of H₂O₂ added, pH and temperature were 4.77 mg/g, 0.6 wt.%, higher than 12 and 25°C, respectively. The time course of cyanide removal efficiency is shown in Fig. 1. It was demonstrated that cyanide removal efficiency increased significantly during the first 40 min with an average removal rate of 2.275% min⁻¹ and stayed almost constant after 40 min. Therefore, 1 hr was sufficient for H₂O₂ oxidation and chosen for all the subsequent experiments.

2.2. Effect of amount of H₂O₂ added at different pH

To investigate the effect of amount of H₂O₂ added on cyanide removal, different amounts of H₂O₂ were added to the mixture under the conditions that the adsorption amount of CN⁻ and temperature were 4.77 mg/g and 25°C,
respectively. A trial without \( \text{H}_2\text{O}_2 \) was used as a control. It was demonstrated that the removal efficiency was positively correlated with the amount of \( \text{H}_2\text{O}_2 \) added. When no \( \text{H}_2\text{O}_2 \) was added to the reaction mix, the removal efficiency was about 50.19% at pH 12. When 0.2, 0.4, 0.6, 0.8 and 1 wt. % of \( \text{H}_2\text{O}_2 \) were added to the mixture, the removal efficiency increased to 65.67%, 79.01%, 90.28%, 90.28% and 90.28%, respectively (Fig. 2), indicating that high amount of \( \text{H}_2\text{O}_2 \) added had a positive effect on cyanide oxidation between 0.2 and 0.6 wt. %. The efficiency did not further increase when the amount of \( \text{H}_2\text{O}_2 \) added was over 0.6 wt. %, suggesting this amount was optimal for improving the removal efficiency. For a specific \( \text{H}_2\text{O}_2 \) concentration, the removal efficiency was positively correlated to pH from 5 to 12. When pH was over 12, the cyanide removal efficiency remained almost constant. The explanation for this result is given in Section 2.5.2.

### 2.3. Effect of amount of \( \text{CN}^- \) adsorbed on pyrite

Mixtures prepared from pyrite with different cyanide loadings were used to investigate the effect of the adsorbed amount of \( \text{CN}^- \) on cyanide removal, under the conditions that the amount of \( \text{H}_2\text{O}_2 \) added, pH and temperature were 0.6 wt.%, higher than 12 and 25°C, respectively. It was demonstrated that cyanide removal efficiency was positively correlated to the amount of \( \text{CN}^- \) adsorbed on pyrite (Fig. 3). The increase was initially significant, from 76.60% to 91.10%, when the amount of \( \text{CN}^- \) adsorbed on pyrite increased from 1 to 4.8 mg/g. When the adsorption amount was further increased from 4.77 to 8.50 mg/g, the increase became less significant, from 91.10% to 93.20%. Cyanide adsorption on pyrite existed mainly in the form of strong chemical adsorption with small adsorption amounts (Zhao et al., 2016), and it was difficult to remove cyanide from the surface of pyrite. The main adsorption form gradually changed from strong chemical adsorption to weak physical adsorption with increasing adsorption amount, which led to easier cyanide removal from the surface of pyrite.

### 2.4. Effect of temperature

To investigate the effect of temperature on cyanide removal efficiency with time, experiments were carried out under the conditions that the adsorption amount of \( \text{CN}^- \), amount of \( \text{H}_2\text{O}_2 \) added and pH were 4.77 mg/g, 0.6 wt.% and higher than 12, respectively. It was demonstrated that the cyanide removal efficiency was positively correlated to temperature, but the effect was not significant (Fig. 4). At 25°C, the removal efficiency was 91.10%. When the temperature was increased to 85°C, the removal efficiency was 95.60%. The generation of hydroxyl free radical was promoted with the increase of temperature, which helped to increase cyanide removal efficiency (Yu et al., 2008). However, the decomposition of hydrogen peroxide was also promoted with the increase of temperature (Yu et al., 2008). Because cyanide removal efficiency only increased by 4.50% when temperature
increased from 25 to 85°C, cyanide removal could be carried out at room temperature with little loss in efficiency.

2.5. Mechanism of cyanide removal by H2O2 oxidation under alkaline conditions

2.5.1. Cyanide adsorption on FeS2

Pyrite is a porous medium and has strong cyanide adsorbability, but the adsorption mechanism of CN− on FeS2 is debatable. One study concluded that ferricyanide was formed on the surface of FeS2 (Elgillani and Fuerstenau, 1968). However, a large quantity of iron hydroxide was found on the surface of pyrite, and only small amounts of ferricyanide existed under neutral conditions (Brion et al., 1980). It was also considered that CN− adsorbed electrochemically on the surface of pyrite and formed a hexacyano complex (Prestidge et al., 1993; Wang and Forssberg, 1996). The forms of CN− on FeS2 crystal include C bonded on Fe, C bonded on S, N bonded on Fe and N bonded on S (Li, 2011). The adsorption energies were calculated as −327.94, −196.56, −274.79 and −118.83 kJ/mol, respectively (Li, 2011). Therefore, the main form of CN− adsorbed on FeS2 crystal might be C bonded on Fe.

2.5.2. Cyanide removal by FeS2 oxidation under alkaline conditions

The oxidation process of FeS2 in aqueous solution at room temperature could be described as (Garrels and Thompson, 1980; Mckibben and Barnes, 1986; Moses et al., 1987):

\[
\begin{align*}
\text{FeS}_2 + \text{H}_2\text{O} + 3.5\text{O}_2 & \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \\
4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2 & \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \\
\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} & \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+
\end{align*}
\]

Thus, ferrous ions, ferric ions, hydrogen ions and sulfate ions were generated due to FeS2 oxidation. When base was introduced into the solution, neutralization occurred. There were extra hydroxide ions when the solution changed from acidity to alkalinity. The adsorption energy was −264.99 kJ/mol for O of OH− bonded on Fe of FeS2 (Li, 2011).
The smaller adsorption energy led to OH\(^-\) being rapidly adsorbed on the surface of pyrite. CN\(^-\) in the form of N and C bonded on S of FeS\(_2\) was replaced by OH\(^-\), and CN\(^-\) in the form of N bonded on Fe of FeS\(_2\) was partly replaced. Soluble iron–cyanide complexes were formed by coordinate bonds between iron ions and CN\(^-\) replaced by OH\(^-\). Therefore, cyanide removal efficiency increased with the increase of pH value. Ferric hydroxide and ferrous hydroxide gradually precipitated on the surface of FeS\(_2\) as the pH value increased. When the FeS\(_2\) crystal was completely enveloped by precipitates, CN\(^-\) was difficult to replace. This led to cyanide removal efficiency remaining almost constant at pH higher than 12. However, the adsorption energy of O of OH\(^-\) bonded on Fe of FeS\(_2\) was less than that of C of CN\(^-\) bonded on Fe of FeS\(_2\), which led to the incomplete removal of cyanide.

2.5.3. Cyanide removal with H\(_2\)O\(_2\) oxidation under alkaline conditions

H\(_2\)O\(_2\) is a strong oxidant. The oxidation of pyrite by H\(_2\)O\(_2\) was investigated using the isotope labelling method (Lefticariu et al., 2007). Ferrous ions, ferric ions, hydrogen ions and sulfate ions were generated through Reactions (5) and (6) in the FeS\(_2\)–H\(_2\)O\(_2\)–H\(_2\)O system. H\(_2\)O\(_2\) reacted rapidly with FeS\(_2\), ferrous ions and ferric ions in the solution, including Reactions (7)–(9) in the solution and Reactions (10)–(14) on the surface of pyrite. The former could be considered as a Fenton reaction, and the latter could be attributed to the Fenton-like reaction (Haber and Weiss, 1934).

\[
\begin{align*}
2\text{FeS}_2 + 15\text{H}_2\text{O}_2 &\rightarrow 2\text{Fe}^{3+} + 4\text{SO}_4^{2-} + 14\text{H}_2\text{O} + 2\text{H}^+ \tag{5} \\
\text{FeS}_2 + 10\text{Fe}^{3+} + 4\text{H}_2\text{O} + 2\text{H}_2\text{O}_2 &\rightarrow 11\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 12\text{H}^+ \tag{6} \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \tag{7} \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{O}_2 + 2\text{H}^+ \tag{8} \\
\text{Fe}^{3+} + \text{O}_2 &\rightarrow \text{Fe}^{2+} + \text{O}_2^- \tag{9} \\
\text{M}^+ + \text{H}_2\text{O}_2 &\rightarrow \text{M}^{2+} + \text{OH}^- + \text{OH}^- \tag{10} \\
\text{OH}^- + \text{H}_2\text{O}_2 &\rightarrow \text{H}_2\text{O} + \text{O}_2^- + \text{H}^+ \tag{11} \\
\text{H}_2\text{O}_2 + \text{O}_2^- + \text{H}^+ &\rightarrow \text{OH}^- + \text{H}_2\text{O} + \text{O}_2 \tag{12} \\
\text{M}^+ + \text{O}_2^- &\rightarrow \text{M} + \text{O}_2 \tag{13} \\
\text{M}^+ + \text{HO}_2^- &\rightarrow \text{M} + \text{HO}_2^- \tag{14} \\
\end{align*}
\]

Hydroxyl ions could neutralize hydrogen ions generated through Reactions (5)–(6) under alkaline conditions, which promoted the formation of ferrous ions, ferric ions and sulfate ions. Iron and sulfur atoms were stripped from the surface of pyrite. As a result, the surface of pyrite became smooth and clean, which could weaken the adsorbability of pyrite. The natural pyrite had an alveolate surface (Fig. 5a). The alveolate structure disappeared after H\(_2\)O\(_2\) oxidation under alkaline conditions (Fig. 5b). Oxidation of pyrite led to the formation of iron and sulfur vacancies on the pyrite surface. Iron vacancies led to the increase of the adsorption energy of C bonded on Fe from −327.94 to −264.04 kJ/mol (Li, 2011). Sulfur vacancies could also lead to the increase of adsorption energy of C bonded on S. Iron and sulfur vacancies weakened the adsorbability of pyrite. Metal ions were continuously generated and subsequently reacted with H\(_2\)O\(_2\), which promoted the generation of hydroxyl free radical, peroxy free radical and peroxide hydroxyl free radical. Hydroxyl free radical was rapidly adsorbed on the surface of pyrite. Bonding occurred between the oxygen atom of hydroxyl free radical and iron atom of FeS\(_2\) crystal. The adsorption energy of hydroxyl free radical bonded on FeS\(_2\) was −276.62 kJ/mol (Li, 2011). Therefore, hydroxyl free radical could be steadily chemically bonded on iron site of pyrite, and could replace the CN\(^-\) in the form of C bonded on Fe. The replaced CN\(^-\) entered into the solution.

![Fig. 7 – XRD pattern of Prussian Blue.](image_url)

![Fig. 8 – Suspension liquid composition.](image_url)
In Section 1.4, the white crystal formed was Na₂SO₄ (Fig. 6), indicating that sulfate ions were generated during cyanide removal. The blue precipitate was Prussian Blue, demonstrating that hexacyanoferrous ions were generated during cyanide removal (Fig. 7). The corresponding filter liquor of the blue precipitate was blood red in color (Fig. 8), which was due to ferric thiocyanate in solution. According to the quantitative analysis results, the mole ratios of [Fe(CN)₆]₄⁻, SCN⁻ and SO₄²⁻ were about 2.03:1:12.3.17.

3. Conclusions

The following conclusions can be drawn from this study.

(1) Cyanide removal efficiency was close to zero when pH was lower than 6. Cyanide removal efficiency was positively related to pH between 7 and 12 and remained constant when pH was higher than 12.

(2) When pH was higher than 7, the cyanide removal efficiency was positively correlated to amount of H₂O₂ added, up to 0.6 wt.%.

(3) Cyanide removal efficiency was positively correlated to the amount of CN⁻ adsorbed on pyrite.

(4) Temperature had a limited effect on cyanide removal efficiency.

(5) The removal of cyanide adsorbed on pyrite by H₂O₂ oxidation under alkaline conditions was due to the oxidation of pyrite. [Fe(CN)₆]₄⁻, SCN⁻ and SO₄²⁻ were generated during the cyanide removal, with mole ratio about 2.03:1.12:3.17.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (No. 2017YFC0703200). The authors also thank Prof. Yu from Lakehead University and Jilin Jianzhu University for discussion and advice in writing.

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