



Cyanide removal for ultrafine gold cyanide residues by chemical oxidation methods

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Abstract: Because of the highly toxic cyanide in the gold cyanide residues, cyanide must be removed for environmental protection. The process mineralogy of residues was studied firstly, and then cyanide removal was carried out by three chemical methods. The results showed that the residue mainly contained Si, S and Fe. Pyrite was the main metallic mineral, and the iron-complex cyanides make cyanide removal difficult. The minerals in residues were in ultrafine particle size with high monomer dissociation degrees. In H_2O_2 oxidation process, the self-decomposition and side reactions resulted in high consumption of H_2O_2 . In $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation process, the time for complete process was long because of the reactions between $\text{Na}_2\text{S}_2\text{O}_5$ and O_2 . Na_2SO_3 oxidation method was found to be a new method for cyanide removal without air inflation device. The cyanide content was reduced to the national standard level in 90 min at pH 9.0 with optimum Na_2SO_3 dose of 2.0 g/L.

Key words: gold cyanide residues; process mineralogy; cyanide removal; H_2O_2 oxidation; Na_2SO_3 oxidation

1 Introduction

Cyanidation is used to extract gold in most gold production around the world [1,2]. The residues after gold extraction contain recoverable minerals and other marketable components, such as Cu, Zn, Pb and Fe [3]. The residues also contain plenty of toxic cyanide, causing environmental pollution and safety risks [4]. According to the environmental regulations, gold cyanide residues cannot be stored or discharged until total cyanide content in toxic leaching solution is under 5 mg/L (HJ943, China) [5]. The study on the cyanide removal methods of gold cyanide residues has great significance to the environmental protection and the development of gold industry.

Treatments of the cyanide removal have been widely studied, including acidification,

chemical oxidation, biological treatment and incineration [6–8]. Acidification is commonly used to treat mine wastewater with high cyanide content [6]. Even if the removal efficiency of acidification is high, the content of cyanide could not meet the standard of 0.2 mg/L in wastewater [9,10]. In biological treatment of cyanide, bacteria convert free and metal complex cyanides to bicarbonate and ammonia [7]. The biological treatment is suitable for wastewater with low content of cyanide. In the gold industry, chemical oxidation is the preferred method for deep cyanide removal because of its high efficiency [11]. It has been reported that most of cyanide in tailings or wastewater could be removed by chlorine oxidation [12,13]. Because of by-products such as chloramine, the process has been replaced by other methods in recent years. Cyanide can also be removed by ozone, but the costs of ozone generator

and power consumption are too high [14,15]. At present, the widely used methods are hydrogen peroxide oxidation and Inco method.

Hydrogen peroxide oxidation is effective for the treatment of cyanide-containing wastewater [16]. Free and weak acid dissociable (WAD) cyanide could be removed by hydrogen peroxide oxidation under the alkaline conditions with a metal catalyst (Cu, Fe, and Al). However, this method was limited to treat slurries because of the high consumption of hydrogen peroxide. In 1982, a method for cyanide removal by SO_2 and O_2 was invented in Canada, called Inco method [17]. To avoid the environmental problems resulting from the release of SO_2 , some solid agents were used to improve the Inco method, such as sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium sulfite (Na_2SO_3) [18]. For treatment of cyanide residues, higher consumption of agent is required, because the solids (particularly sulfide minerals) can catalyze some side reactions. Part of cyanide could be strongly adsorbed on the surface of minerals, resulting in the incomplete removal of cyanide [19]. The composition of cyanide residue has influence on the degree of cyanide removal. The study on the process mineralogy of cyanide residue can show the difficulties and some possible problems of cyanide removal, which provides help for the discussion of cyanide removal process.

In this work, the process mineralogy was studied to investigate the phase of gold cyanide residues. The treatments of cyanide by hydrogen peroxide oxidation and $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation were studied to investigate if cyanide existed in residue could be removed. A new method of cyanide removal by Na_2SO_3 oxidation without air addition was carried out and compared with other two oxidation methods. The aims of new method were to overcome the large amount of chemicals consumption and achieve deep cyanide removal of gold cyanide residues.

2 Experimental

2.1 Materials and chemicals

In this study, the gold cyanide residues from a gold production company in Shandong Province (China) were used. After cyanidation leaching of gold ores (slurry concentration of 30–40 wt.%) with 0.5 wt.% sodium cyanide (NaCN) for 48 h, the gold

cyanide residue with moisture content of about 17% was obtained by pressure filtration. The total cyanide (CN_{Total}) content was 1620.39 mg/kg in residue, 135.8 mg/L in cyanide residue slurry (30 wt.%) and 105.4 mg/L in toxic leaching solution. The initial pH of the slurry was 8.0–8.5.

Analytical grade NaOH (Damao, Tianjin, China) was used to adjust pH. Analytical grade 30% hydrogen peroxide, sodium metabisulfite and sodium sulfite (Damao, Tianjin, China) were used as the cyanide removal agents. Analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Damao, Tianjin, China) was used as the catalyst.

2.2 Process mineralogy of gold cyanide residue

The chemical composition of cyanide residue was analyzed with X-ray fluorescence (XRF, M21X, MARCO, Japan). The particle size of minerals in cyanide residue was determined by Laser Particle Sizer (HYDRO 2000M-MU, Malvern, England). The mineral composition and the surface morphologies of residue were observed by Leica polarizing microscope (LEICA-DMLP, Leica, Germany) and scanning electron microscope (SEM, ZEISS, Beijing, China).

2.3 Cyanide removal by chemical oxidation methods

Cyanide residue slurries (30 wt.%) were prepared with deionized water in a 300 mL beaker with mechanical agitation. The pH of slurry was adjusted by NaOH and measured by a pH-meter (pHS-3E, BIOBASE, Shanghai, China). A certain amount of cyanide removal agent and catalyst (200 mg/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were added into the slurry. A pump was used to add air into the slurry in the study of cyanide removal by $\text{Na}_2\text{S}_2\text{O}_5$ –air method. After agitation for a certain time, the cyanide content in slurry was determined. The toxic leaching solution of cyanide residue was obtained by HJ/T299–2007 method [20]. The silver nitrate titration method (HJ484–2009) was applied to determining the cyanide content in the slurry and toxic leaching solution [21].

3 Results and discussion

3.1 Process mineralogy of gold cyanide residue

3.1.1 Chemical composition

The major elements composition of cyanide

residue was analyzed with XRF and presented in Table 1. It was shown that the most abundant non-metallic element was 34.5 wt.% Si, followed by 23.5 wt.% S, indicating that the major minerals were gangue and sulfide minerals in cyanide residue. There was thiocyanate (SCN^-) in cyanide residue, maybe resulting in high consumption of oxidizing agents. The most abundant metal element was 21.1 wt.% Fe, and the contents of Cu, Pb and Zn were all over 0.3 wt.%, showing that the valuable metals in cyanide residue were meaningful to be recovered by flotation. It can be conducted that ferricyanide or ferrocyanide may be the main metal complex cyanide, which decided the results of cyanide removal. In cyanide residues, the precious metals Au and Ag can be enriched and recovered, the contents were 0.54 and 14.4 g/t, respectively.

Table 1 Major elements composition of cyanide residue (wt.%)

Si	S	Fe	Zn	Pb	Cu	Ag*	Au*
34.5	23.5	21.1	0.69	0.62	0.34	14.4	0.54

*: g/t

3.1.2 Particle size distribution

The particle size of minerals in cyanide residue was determined by laser particle sizer, and the results are shown in Table 2. It was shown that the sizes of mineral particles in the sample were not uniform. In cyanide residues, the small mineral particles whose sizes were less than 2.0 μm accounted for 8.30 wt.%, most of them were in size of 2.0–40.0 μm , the big mineral particles whose sizes are over than 40.0 μm only accounted for 8.41 wt.%. The average particle size of cyanide residue was 16.29 μm . According to the results of particle size analysis, the sample belonged to the

Table 2 Particle size distribution of cyanide residue

Particle size/ μm	Content/ wt.%	Accumulative content/wt.%
<2.0	8.30	8.30
2.0–5.0	16.07	24.44
5.0–10.0	20.26	44.70
10.0–20.0	25.77	70.47
20.0–40.0	20.12	91.59
>40.0	8.41	100

ultrafine gold cyanide residue. It may be benefit for cyanide removal due to the high specific surface area resulting from the ultrafine particle size.

3.1.3 Main mineral composition

Based on the Leica Polarizing Microscope and Scanning Electron Microscope, the main mineral composition of cyanide residue was measured. The results showed that the main non-metallic mineral in cyanide residue was quartz, and the main metallic mineral was pyrite. There were other sulfide minerals including chalcopyrite, sphalerite and galena. Figure 1 shows the main metallic minerals observed with polarizing microscope. The occurrence states of minerals directly affected the area of reaction interface and the combination between cyanide and metal elements (such as Fe, Cu and Zn) [22]. The dissociation degrees of main metal sulfide minerals in cyanide residue were investigated and shown in Table 3.

(1) Pyrite

Pyrite is the most widely distributed metallic sulfide mineral in the cyanide residue, and the content was 28.95%. The granularity of most pyrite particles was bigger than that of other three sulfide minerals and generally ranged from 10 to 35 μm . Under the microscope it was observed that pyrite particles were often regular and granular, and some included cracks and holes like Fig. 1(a), showing that corrosion and destruction of cyanide residue occurred during the process of cyanidation and flotation. It was inferred that the iron-complex cyanides inevitably existed in residue and had effects on the flotation of pyrite [23]. As a kind of strong acid dissociable (SAD) cyanides with strong stability, iron-complex cyanide also made cyanide removal difficult. Table 3 shows that pyrite is in the majority of granular monomer, a few of pyrite particles are closely inlaid with gangue minerals or other sulfide minerals.

(2) Chalcopyrite

Chalcopyrite was the main copper-containing mineral in cyanide residue, and the content was 1.13%. Figure 1(b) shows a monomer chalcopyrite particle in cyanide residue, and the surface of which is rough and irregular, indicating that the chalcopyrite particles were corroded by cyanide. According to the stability of complex cyanides, free cyanides are more likely to combine with Cu. It was reported that the interaction between CN^- and the chalcopyrite surface was chemical adsorption [24].

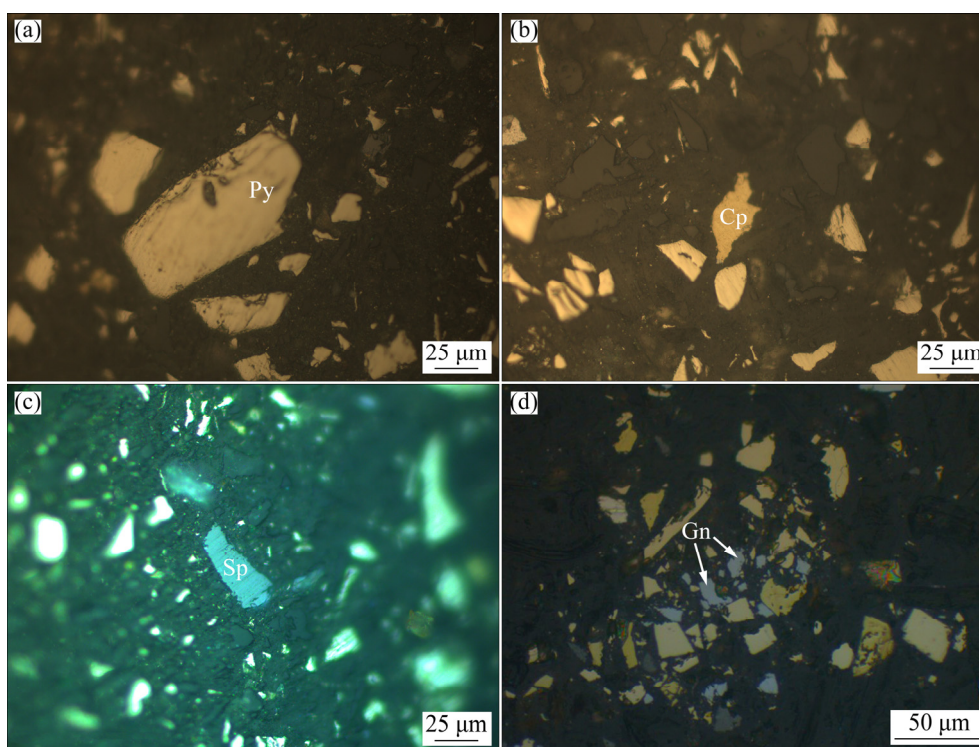


Fig. 1 SEM images of main sulfide minerals under polarizing microscope: (a) Py–Pyrite; (b) Cp–Chalcopyrite; (c) Sp–Sphalerite; (d) Gn–Galena

Table 3 Dissociation degree of main metal sulfide minerals in cyanide residue (%)

Mineral	Monomer	Intergrowth with mineral	Intergrowth with two or more minerals
Pyrite	58.14	17.87	23.99
Chalcopyrite	18.99	25.71	55.30
Sphalerite	38.80	21.54	39.66
Galena	41.54	29.22	29.24

The most seriously corrosion of the chalcopyrite surface among the sulfide minerals was also observed. Moreover, the particle sizes of chalcopyrite were small and often ranged from 5 to 25 μm , making its reaction with cyanide easy. Chalcopyrite particles usually associated with other minerals in cyanide residue, so the content of monomer chalcopyrite particles was only 18.99%.

(3) Sphalerite

In cyanide residue, Zn was the most abundant metal element following Fe, and it was shown that Zn mainly existed in the form of sphalerite. Most of sphalerite particles were regular polygon with small size as shown in Fig. 1(c). The sizes of sphalerite particles were all below 30 μm and similar with

chalcopyrite particles. There were 61.20% sphalerite particles inlaid with other minerals, such as chalcopyrite, and some of sphalerite and chalcopyrite particles formed a solid solution in a local area. That's one of the reasons why Cu and Zn cannot be recovered completely.

(4) Galena

The output forms of galena are divided into two types, one is individual granular particles with large sizes and the other is a group of fine particles. As seen in Fig. 1(d), galena particles in cyanide residue belonged to the second one, and most of them were in size of about 10 μm . Galena particles were smaller than other metal sulfide minerals in cyanide residue. These particles were often disseminated and intimately associated with the chalcopyrite particles, resulting in the difficulty for recovery of Pb by flotation.

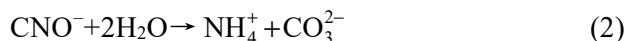
The results of the process mineralogy showed that the composition of total cyanide in cyanide residue was complex, including $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{CN})_3]^{2-}$ and $[\text{Zn}(\text{CN})_2]^{2-}$. It was difficult to remove metal complex cyanides, especially iron-complex cyanides. For the treatment of cyanide residue, the strong oxidant hydrogen peroxide and Inco process which can deal with

iron-complex cyanides may be effective. In the cyanide removal process by strong oxidation agents, cyanide may be oxidized after pyrite, resulting in the high consumption of agents. It was speculated that the consumption of agents by Inco process may be less than that of hydrogen peroxide oxidation. Due to the presence of chalcopyrite, there were copper complex cyanides in residue, which can catalyze the cyanide removal process and decrease the consumption of catalyst agent. The particle size of residue was ultra-fine and the content of monomer minerals was high, which provided more interface for cyanide removal reactions including some side reactions.

3.2 Chemical oxidation of cyanide

3.2.1 Cyanide removal by hydrogen peroxide oxidation

As a powerful oxidizing agent, hydrogen peroxide has been used to treat cyanide. During H_2O_2 oxidation process, cyanide was first oxidized to cyanate, which further oxidized to ammonium and carbonate as follows:



The experiments were conducted with different doses of H_2O_2 under different pH conditions at room temperature. The results are shown in Tables 4–6.

The effect of pH was studied by varying the initial pH of slurry from 8.5 to 11.0. It was seen from Table 4 that the cyanide removal rate increased more significantly at weakly alkaline pH. At pH 8.5, the cyanide content in slurry after cyanide removal was 23.89 mg/L, and at pH 10.0, it decreased to 13.68 mg/L. At pH over 10.0, the

Table 4 Results of cyanide removal by H_2O_2 oxidation under different pH (5.0 mL/L H_2O_2 , reaction time 1 h)

pH	CN_{Total} content*/(mg·L ⁻¹)	Removal rate/%
8.5	23.89	82.41
9.0	16.08	88.16
9.5	14.07	89.64
10.0	13.68	89.92
10.5	13.75	89.87
11.0	13.99	89.70

* The content of total cyanide in the slurry after cyanide removal treatment

Table 5 Results of cyanide removal by H_2O_2 oxidation with different H_2O_2 contents (initial pH 10.0, reaction time 1 h)

H_2O_2 content/(mL·L ⁻¹)	CN_{Total} content/(mL·L ⁻¹)	Removal rate/%
1.0	20.47	84.93
3.0	16.77	87.65
5.0	13.68	89.92
7.0	13.98	89.71
9.0	14.36	89.43

Table 6 Results of cyanide removal by H_2O_2 under different time (initial pH 10.0, 5.0 mL/L H_2O_2)

Reaction time/min	CN_{Total} content/(mg·L ⁻¹)	Removal rate/%
15	34.29	74.75
30	17.93	86.79
60	13.68	89.92
90	13.59	89.99
120	14.29	89.48

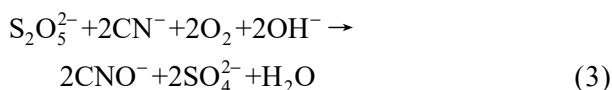
content of cyanide had no obvious changes. The trend was similar to the previous study on the treatment of cyanide-containing wastewater [25]. It was found that stronger oxidant hydroxyl free radical ($\cdot\text{OH}$) was produced by hydrogen peroxide under the condition of pH 9–10, which promoted the removal of cyanide [26].

To achieve higher removal rate, more doses of hydrogen peroxide were added into cyanide residue slurry. It was shown in Table 5 that the H_2O_2 dose larger than 5.0 mL/L didn't have significant impact on cyanide removal. The optimum H_2O_2 dose to the theoretical amount ratio was about 10 (5.0 mL/L H_2O_2). It was found that the filtrate was light yellow and there was 1.43 g/L Fe^{3+} in the slurry, indicating that the pyrite was oxidized by H_2O_2 , leading to the increasing consumption of H_2O_2 [27]. It was also reported that the self-decomposition of H_2O_2 was accelerated due to the consumption of OH^- by Cu^{2+} at pH higher than 10.0 [28]. Previous studies have found that the dose of H_2O_2 was usually 200%–450% of the theoretical amount in industrial treatment of cyanide-containing wastewater [29]. More H_2O_2 was consumed in the treatment of cyanide residue, because the solids in the slurry catalyzed some side reactions. The results were consistent with the conclusions of process mineralogy.

The cyanide contents were determined at reaction time of 15, 30, 60, 90 and 120 min to investigate the kinetics of cyanide removal for cyanide residues. It was shown in Table 6 that the cyanide content decreased quickly in the first 15 min. Under the condition of pH 10.0, H_2O_2 content of 5.0 mL/L, the removal rate reached 89.92% after 60 min, and the process was basically completed. In the study of KITIS et al [30], cyanide removal by H_2O_2 oxidation conducted rapidly in the first 0.5 h, 2–4 h later the reaction reached the limit. In this work, the ultra-fine particle size and high mineral dissociation degree of the cyanide residue provided the surface for oxidation reactions and accelerated the cyanide removal. The slurry after 60 min reaction was separated and the residue was treated by toxic leaching. It was determined that the CN_{Total} content was 7.46 mg/L in toxic leaching solution, which could not meet the national standard. For the cyanide residue, H_2O_2 oxidation method should be optimized in the future.

3.2.2 Cyanide removal by $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation method

For Inco process, sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) was used widely to remove cyanide, and the oxidation process could be described as



The cyanide removal experiment by $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation method was carried out with different doses of $\text{Na}_2\text{S}_2\text{O}_5$ at different pH. The air addition was 250 mL/min, ensuring that the gas–liquid ratio of the reaction system was about 30:1. The results are shown in Fig. 2.

It was demonstrated that the cyanide content in slurry decreased with the initial pH increasing from 8.5 to 9.5 and it had no significant changes at $\text{pH} > 9.5$, as shown in Fig. 2(a). The higher pH condition promoted the hydrolysis of $\text{Na}_2\text{S}_2\text{O}_5$ (Reaction (4)), which made cyanide removal process slow down.



Figure 2(b) showed that the cyanide content in slurry decreased to 4.25 mg/L and reached the lowest one with the $\text{Na}_2\text{S}_2\text{O}_5$ dose of 2.0 g/L. According to Reaction (3), it theoretically required 3.65g $\text{Na}_2\text{S}_2\text{O}_5$ to treat 1 g cyanide. The dose of 2.0 g/L $\text{Na}_2\text{S}_2\text{O}_5$ was about 400% of the theoretical

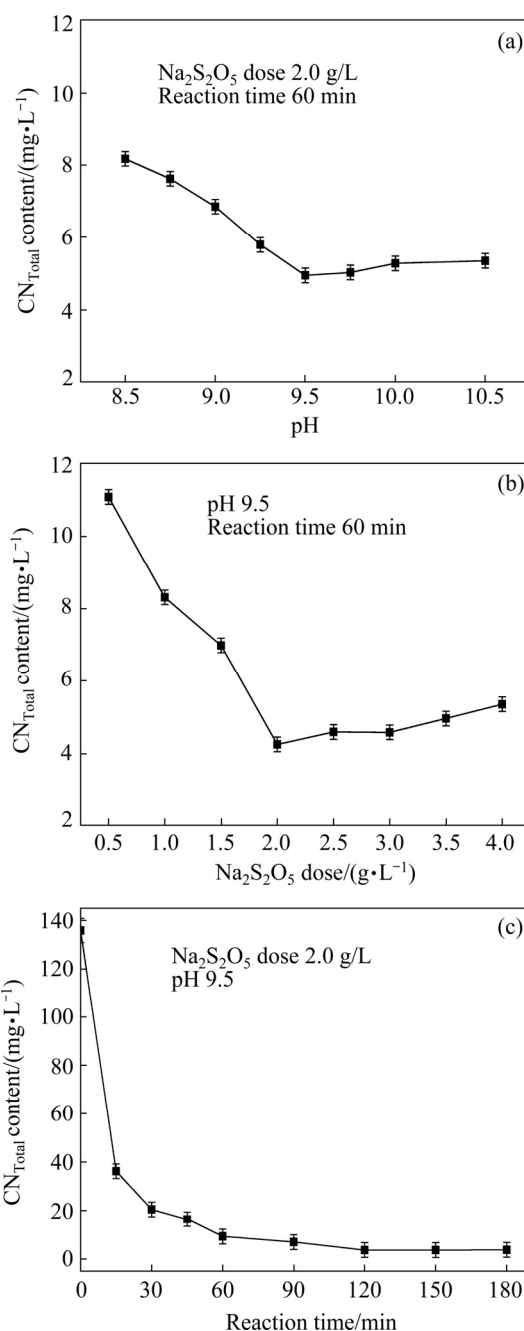
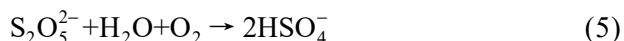


Fig. 2 Effect of initial pH (a), $\text{Na}_2\text{S}_2\text{O}_5$ dose (b) and reaction time (c) on cyanide removal by $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation

amount. The high consumption of $\text{Na}_2\text{S}_2\text{O}_5$ was due to the competitive reactions in cyanide removal process, including hydrolysis and oxidation of $\text{Na}_2\text{S}_2\text{O}_5$, as



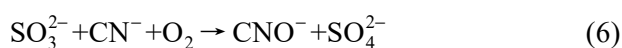
In the study of LI et al [31], the cyanide content in wastewater reduced from 1200 to 2–3 mg/L by adding 10 kg/t $\text{Na}_2\text{S}_2\text{O}_5$, about 230%

of the theoretical amount. Similar with the H_2O_2 oxidation process, the dose of $\text{Na}_2\text{S}_2\text{O}_5$ to remove cyanide in slurry was significantly higher than that of the solution. The solid minerals catalyzed the reactions between $\text{Na}_2\text{S}_2\text{O}_5$ and air, which led to lower removal efficiency of cyanide by $\text{Na}_2\text{S}_2\text{O}_5$.

Figure 2(c) showed the change of cyanide content with time in $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation process. The cyanide content decreased significantly during the first 120 min and stayed almost constant after 120 min. It was suggested that Inco process in slurry may be limited due to the low efficiency of SO_2 and O_2 transportation [32]. The results showed that the time of complete reaction of $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation process was longer than that of H_2O_2 oxidation process. Under the optimal condition (initial pH=9.5, $\text{Na}_2\text{S}_2\text{O}_5$ dose=2.0 g/L, and reaction time=120 min), the cyanide content in the toxic leaching solution of residue after cyanide removal was 1.84 mg/L, which reached the national standard. The disadvantages of $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation process were the complex operation and high cost resulting from the air addition devices.

3.2.3 Cyanide removal by Na_2SO_3 oxidation without air addition

Sodium sulfite (Na_2SO_3) is also applied commonly in Inco process, and the reaction is described as



To avoid the influence of oxygen transport on cyanide removal process, sodium sulfite was conducted without air addition. In the experiments, the slurry was in the open system with the gas–liquid ratio about 3:1. The effects of pH, Na_2SO_3 dose and reaction time on cyanide removal by Na_2SO_3 oxidation are shown in Fig. 3.

It was worth noting that cyanide content in slurry increased significantly when pH was over 9.0. There were new free cyanides produced by the decomposition of metal complex cyanides under high alkalinity. Reaction (4) describes that $\text{Na}_2\text{S}_2\text{O}_5$ hydrolyzes into HSO_3^- , reducing the alkalinity of the solution. Reaction (7) describes that the hydrolysis of Na_2SO_3 will produce OH^- , increasing the pH of the solution.



It was more alkaline in Na_2SO_3 system than $\text{Na}_2\text{S}_2\text{O}_5$ when the two agents were in the same dose.

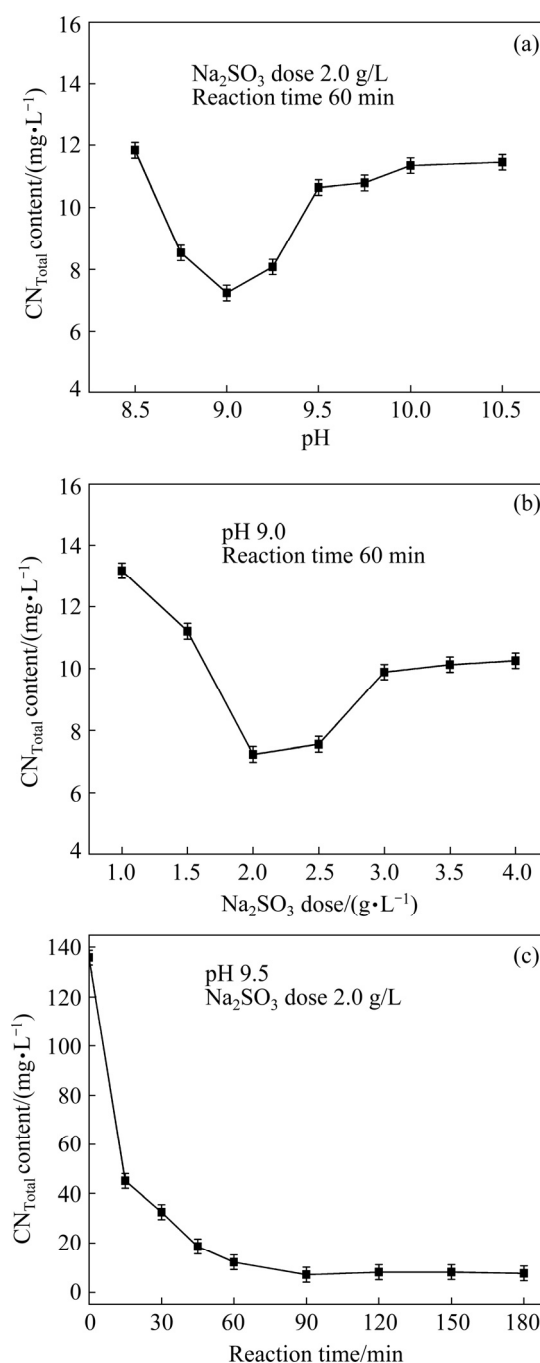


Fig. 3 Effect of initial pH (a), Na_2SO_3 dose (b) and reaction time (c) on cyanide removal by Na_2SO_3 oxidation

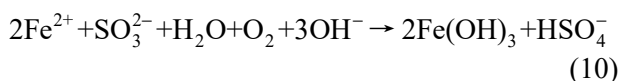
It has been indicated that the amount of lime (or other alkali) requirement to control pH was usually $\text{Na}_2\text{SO}_3 < \text{Na}_2\text{S}_2\text{O}_5 < \text{SO}_2$ [32].

According to Reaction (6), the theoretical consumption ratio of sodium sulfite to CN^- is 4.85:1. As shown in Fig. 3(b), cyanide content was the lowest with the Na_2SO_3 dose of 2.0 g/L (about 300% of the theoretical amount), and the ratio was less than that of $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation process in

Section 3.2.2. It could be indicated that the absence of air addition reduced the consumption of agents in Inco process. It was reported that the direct reactions between SO_3^{2-} and O_2 were the main reasons for low efficiency of Na_2SO_3 –air oxidation process, as [33,34]



The results of process mineralogy showed that there was pyrite in cyanide residue. It was speculated that if there was abundant O_2 addition existed in cyanide removal process, pyrite was oxidized by O_2 first to dissolve Fe^{2+} in aqueous solution, then the double hydrolysis reaction of Fe^{2+} and SO_3^{2-} occurred, and the product $\text{Fe}(\text{OH})_2$ could be oxidized and precipitated into $\text{Fe}(\text{OH})_3$ (Reaction (10)).



In Na_2SO_3 oxidation process, those side reactions like Reactions (8)–(10) were partly avoided due to the absence of air addition, improving the effective utilization of Na_2SO_3 .

Comparing Fig. 2(c) and Fig. 3(c), the time taken for complete cyanide removal was 90 min in Na_2SO_3 oxidation process and it was 120 min in $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation process. The time course of cyanide removal efficiency by Inco process was related to side reactions and the transport of O_2 . The reaction rates of both Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_5$ with O_2 in aqueous solution were similar and increased with rising pH value [35]. The side reactions occurred in $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation process (Reaction (5)) at pH 9.5 were more than those in Na_2SO_3 oxidation process (Reaction (9)) at pH 9.0, resulting in more time for complete cyanide removal by $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation method. The cyanide content was 3.58 mg/L in the toxic leaching solution of cyanide residue after Na_2SO_3 oxidation process under the optimal conditions (initial pH=9.0, Na_2SO_3 dose=2.0 g/L, reaction time=90 min), which reached the national standard.

3.3 Comparison of three cyanide removal methods

Table 7 shows the results of the three cyanide removal methods.

For H_2O_2 oxidation method, the cost of agents

may be the highest due to the requirement of the most lime for pH adjustment and the high consumption of H_2O_2 . This result was consistent with the process mineralogical analysis. The most important one was that the result of H_2O_2 oxidation was the cyanide content of 7.46 mg/L, which did not meet the national standard (<5 mg/L). The results of both Na_2SO_3 oxidation process and $\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation process reached the national standard. The consumptions of the agents for pH adjustment and cyanide oxidation were both lower in Na_2SO_3 oxidation process. The reaction time was short because of less side reactions by the absence of O_2 addition. It was easy to operate in Na_2SO_3 oxidation process without air inflation device. As a new method of cyanide removal, the Na_2SO_3 oxidation process was efficient under laboratory conditions and recommended for application in industry.

Table 7 Comparison of three cyanide removal methods

Method	pH	Actual dosage: theoretical dosage/%	Reaction time/min	CN _{Total} content*/ (mg·L ⁻¹)
H_2O_2 oxidation	10.0	1000	60	7.46
$\text{Na}_2\text{S}_2\text{O}_5$ –air oxidation	9.5	400	120	1.84
Na_2SO_3 oxidation	9.0	300	90	3.58

*: CN_{Total} content in toxic leaching solution of residue

4 Conclusions

(1) In the gold cyanide residue, the main elements were 34.5 wt.% Si, 23.5 wt.% S and 21.1 wt.% Fe. Quartz was the main gangue mineral and pyrite was the main metallic mineral. Plenty of iron-complex cyanides made cyanide removal of cyanide residue difficult. The mineral whose particle size was less than 40 μm accounted for 91.59 wt.%, and the sample belonged to the ultrafine gold cyanide residue. The monomer dissociation degrees of the main sulfide minerals were relatively high, which was beneficial to providing more reaction interface for the cyanide removal.

(2) The cyanide content in the toxic leaching solution of cyanide residue was reduced to 7.46 mg/L within 60 min at pH 10.0 using 5.0 mL/L

H₂O₂. The self-decomposition and side reactions of H₂O₂ resulted in high consumption of agents. The result of cyanide removal was not up to standard.

(3) The results of two kinds of Inco method both reached the standard. Na₂S₂O₅–air oxidation using 2.0 g/L Na₂S₂O₅ occurred in 120 min at pH 9.5. In Na₂SO₃ oxidation process, cyanide was removed with 2.0 g/L Na₂SO₃ at pH 9.0, lower than Na₂S₂O₅–air oxidation process, and the time required was 90 min, shorter than that of Na₂S₂O₅–air oxidation process. The reaction between Na₂S₂O₅ and O₂ was the reason of the long time for complete process in Na₂S₂O₅–air oxidation process.

(4) The advantages of Na₂SO₃ oxidation method are the convenience operation and low cost because of no need for air inflation device. The Na₂SO₃ oxidation process could be tried to apply for cyanide residues in industry.

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化学氧化法脱氰处理超细黄金氰渣

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摘要: 黄金氰渣中含有大量高毒性氰化物, 为保护环境必须对其进行脱氰处理。首先对氰渣的工艺矿物学进行研究, 然后使用三种化学氧化法进行脱氰处理。研究发现, 该氰渣中主要含有元素 Si, S 和 Fe。黄铁矿是渣中主要的金属矿物, 其产生的铁络合氰化物给脱氰过程造成困难。氰渣中矿物粒度超细, 单体解离度高。在 H_2O_2 氧化过程中, 自分解和副反应导致 H_2O_2 大量消耗。在 $Na_2S_2O_5$ -空气氧化过程中, 由于 $Na_2S_2O_5$ 与 O_2 发生反应, 因此整个脱氰过程耗时较长。 Na_2SO_3 氧化法是一种无充气装置的脱氰新方法。当 pH 为 9.0, Na_2SO_3 添加量为 2.0 g/L, 反应 90 min 后尾渣中氰化物含量降至国家标准水平。

关键词: 黄金氰渣; 工艺矿物学; 脱氰; 过氧化氢氧化; 亚硫酸钠氧化

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