Experimental Study on Desulfurization and Ceramic Tile Preparation of Gold Cyanide Tailing

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Abstract. Desulfurization and ceramic tile preparation of gold cyanide tailing have been carried out. A novel oxidant DDTQ has been successfully applied to collaborative decyanation and desulfurization. The removal efficiency of cyanide ions can exceed 99%, and the reduction rate of pyrite and chalcopyrite can be achieved above 90% at the same time with wet oxidation process. Ceramic tiles have been successfully prepared by adding sulfur fixing agent composites during the firing process. The fixing mechanism of residual sulfur after oxidative desulfurization has also been proposed.

Keywords:cyanide tailing; desulfurization; ceramic tile; gold; residue.

1. Introduction

Currently, the main smelting technology in the gold industry in China is the cyanide leaching process. About 95% of gold mines in the world use cyanide leaching to extract gold [1]. 25,000 to 30,000 tons of cyanide residue will be produced for obtaining each ton of gold produced. The total annual discharge of gold cyanide residue in China is about 10 million tons. The accumulated stockpile exceeds 70 million tons, making it a major industrial hazardous waste in China's gold industry. Due to its sulfur affinity, gold is often closely associated with sulfides, such as pyrite and chalcopyrite [2]. For the most gold smelting enterprises, cyanide residue is usually dealt with decyanation and flotation processes to recover its valuable components [3-5]. However, a large number of unrecyclable flotation tailings will remain and need to be treated for further processing. In order to maximize the utilization of limited mineral resources and reduce the environmental pollution, further researches need to be carried out.

In the present paper, novel oxidant DDTQ was applied for deep decyanation and desulfurization of flotation tailings of cyanide residue, and then sulfur fixing agents were used to fix the residual sulfur during the tile preparing process. The effects of decyanation and desulfurization reactions, sintering systems, and sulfur fixing effects with different agents were studied in detail.

2. Experimental

2.1 Reagents and apparatus

The raw cyanide residue is obtained from the flotation tailings discharged through pressure filtration after flotation separation of pyrite by a cyanidation gold extraction process in a Shandong enterprise.

The novel reagent DDTQ for decyanation and desulfurization were home-made. Fe(NO3)3, V2O5, Na2CO3 and KMnO4 were purchased from Sinopharm Chemical Reagent Co., Ltd. of China. The reagents were all of analytical grade. The subsidiary materials for ceramic tile preparation, such as feldspar, calcite, Laiyang soil, limestone and diopside, were obtained from

building materials enterprises in Shandong. Deionized water was applied during the material preparation and tests.

The cyanide residue was mixed with resin to make polished sections, and a polarizing microscope (LEICA DM6000 M) analysis was performed to determine the occurrence state of metallic sulfide minerals.

2.2 Decyanation and desulfurization

Firstly, cyanide residue was weighed and placed into a 250 mL beaker to prepare 25 wt. % slurries with water by ultrasound. The pH value was measured and adjusted to 1. Then a certain amount of novel oxidant was added into the slurry under stirring. After reaction for a certain time, the suspension was filtered. The cyanide content before and after oxidation were determined by the silver nitrate titration method in HJ/T299−2007. The content of iron and copper in the leaching solution were test by ICP-MS (Inductively Coupled Plasma Mass Spectrometry), which were applied to calculate the dissolution efficiencies of sulphides. The removal efficiency of cyanide was thus obtained using the following equation:

$R = (C_0-C_t) / C_0 \times 100\%$

where C_0 is the initial cyanide concentration in the slurry and C_t is the cyanide concentration at reaction time t.

2.3 Ceramic tile preparation and sulfur fixing

The cyanide residue, sulfur fixing agents and auxiliary raw materials were mixed with water by a high-speed ball mill at a rate of 300 r min-1 for 30 minutes. The mixture were then dried at 105 °C for 6 hours. After aging for 24 hours, 50 g of powder was pressed under the condition of 21 MPa and holding time of 20 s to form φ 20 mm × 10 mm embryo material. Then the sample was placed into an atmosphere furnace to sintering ceramic tiles under a certain range of temperatures.

XRD patterns of cyanide floating tailing and ceramic tiles were measured using an X-ray diffractometer (D8 Advanced Bruker, Germany) with a Cu Kα radiation source. The detection ranges from 5° to 70° and from 5° to 40° respectively with a scanning speed of 0.1°s-1.

3. Results and discussion

3.1 Characterization of cyanide floating tailings

Table 1 shows the main chemical composition of cyanide residue and conventional raw materials for sintering ceramic tiles. The total amount of oxides such as SiO_2, Al_2O_3, and Fe_2O_3 in cyanide floating tailings is over 71%. The main minerals are quartz, pyrite (FeS_2), albite, and a small amount of calcium sulfate, muscovite, etc. The main difference between cyanide residue and conventional raw tile material is the high content of sulphur and iron in cyanide residue.

From the process mineralogy characteristics of cyanide residue in Fig. 1, pyrite is the most important and the most abundant metal sulphide in the sample of cyanide floating tailings. It is mainly distributed in granular and irregular forms, followed by a small amount of pyrite embedded in the form of semi-idiomorphic crystals. In addition, some pyrite is embedded in star point form, mainly distributed in 43 ~ 147 μ m. Chalcopyrite is also found in the sample of cyanide floating tailings, mainly distributed in heteromorphic granular form, with a particle size distribution range of 43 ~ 74 μ m. According to the XRD patterns shown in Fig. 1, the main gangue minerals for cyanide residue are quartz, anhydrite, albite, and muscovite, which are the basic materials for firing ceramic tiles. This result confirms that the main desulfurization treatment is to remove pyrite and chalcopyrite in cyanide tailings.

Table 1 Main components of cyanide tailings (wt. %)
(1#, 2# cyanide flotation tailings obtained during different flotation processes; 3# conventional raw materials for sintering ceramic tiles)

Components	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	K$_2$O	Na$_2$O	SO$_3$	Loss
1#	53.15	10.65	7.24	2.45	1.17	2.62	1.84	12.22	11.53
2#	54.74	11.35	7.70	2.44	1.05	2.95	1.61	12.42	7.73
3#	67.77	17.21	1.81	2.86	1.11	1.67	0.66	-	6.32
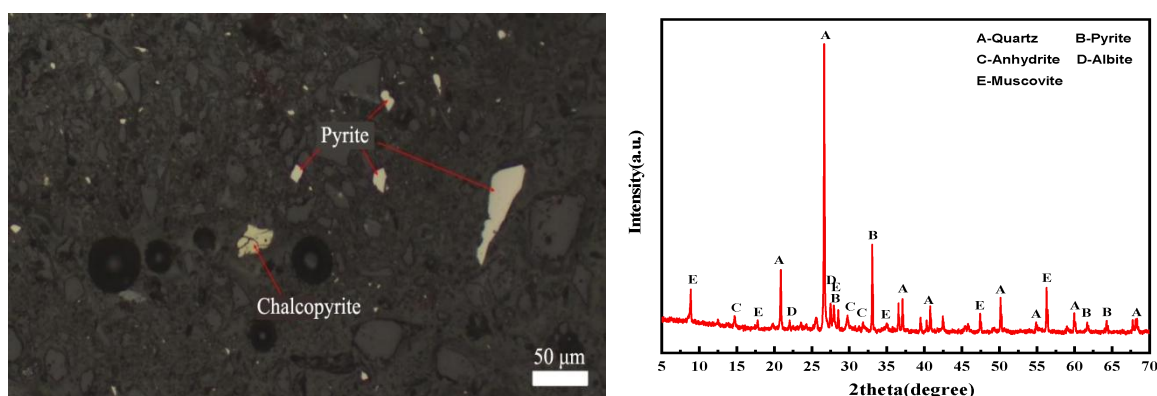
Figure 1. Occurrence state of sulphides in the cyanide residue.

3.2 Decyanation and desulfurization

The main influencing parameters that change the removal efficiencies for decyanation and desulfurization, reaction time and the initial oxidant concentration, were investigated and the results were shown in Fig. 2. It is clearly presented that the removal efficiency of both cyanide ions and sulphides raises quite fast from Fig. 2a. Within the first 10 mins applying the novel oxidant DDTQ, the removal efficiency of cyanide ions can obtain 98.36% already. While the reduction rate of pyrite and chalcopyrite in cyanide tailings can reach 72.64% and 85.65%, respectively at the same time. It is inferred that the order of removal difficulty is: FeS2 > CuFeS2 > CN-. The max removal efficiencies for pyrite and chalcopyrite were 89.87% and 91.49% respectively at 120 mins. It is easy to note that the initial oxidant concentration affects the removal efficiency of sulphides more obviously than that of cyanide ions. By comparison, the removal efficiency of cyanide ions is observed to change little during the whole range of the initial oxidant concentrations from 0.005 to 0.06 mol L-1. While the reduction rate of pyrite and chalcopyrite raise 71.42% and 71.64% respectively with the increase of the initial oxidant concentration. The result confirms that the home-made oxidant DDTQ is an excellent reagent for decyanation and desulfurization of cyanide residue.
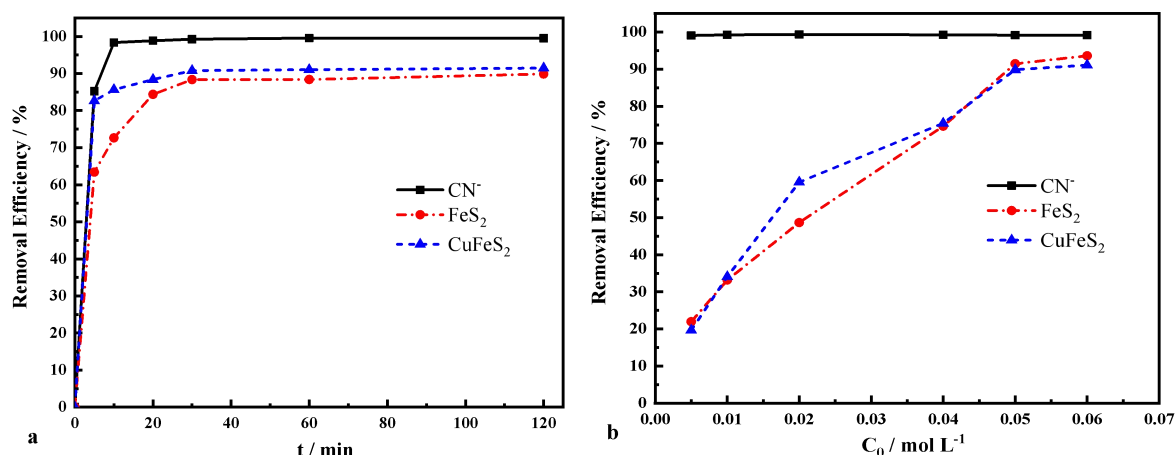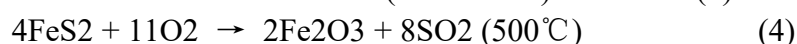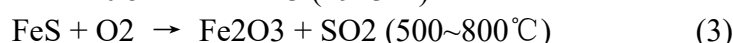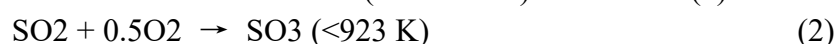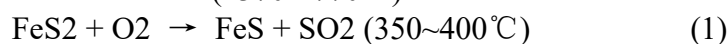
Figure 2. Influencing factors for removal efficiencies of decyanation and desulfurization.

3.3 Ceramic tile preparation and sulfur fixing

Figure 3 shows the appearance images and XRD patterns of cyanide tailings calcined at different sintering temperatures. It is interesting to find that with the continuous increase of firing temperature, the color and appearance of ceramic tile products have undergone significant changes. The sample exhibits melting, foaming, and other overburning phenomena when the firing temperature was at 1150 ℃. If the sintering temperature increases further, the phenomenon of over burning will become more serious.

The heating process of cyanide residue from room temperature to 1300 ℃ can be divided into four main stages. The first stage is from room temperature to 200 ℃, due to the discharge of residual free water and adsorbed water in cyanide tailings. The second stage is 200~470 ℃, which is caused by the oxidation and decomposition process of pyrite in the tailings. FeS_2 can be decomposed into FeS and SO_2 within the range from 350 to 400 ℃ (Reaction (1)). The decomposition products may undergo further reactions. A small portion of SO_2 continues to oxidize to SO_3 during the escape process (Reaction (2)). As shown in Fig. 3, the tailings calcined at 400 ℃ contain a small amount of hematite, which is an oxidation product of FeS_2 (Reaction (2)). The third stage is 470~1000 ℃, which should be the continuation process of the sulfur containing products from the decomposition of pyrite in the second stage. It may involve the oxidative decomposition of a large amount of FeS and the result of dehydroxylation of muscovite in cyanide tailings. As seen in Fig. 3, the diffraction peak of muscovite minerals in the tailings decreases after calcination at 600 ℃.The fourth stage is the decomposition of $CaSO_4$ at 1000~1300 ℃. Anhydrite is not detected in the tailings calcined at 1200 ℃. Although the direct pyrolysis temperature of pure calcium sulfate is 1913.83 K, the complex composition of cyanide tailings, especially the presence of fluxing oxides such as Fe_2O_3, Na_2O, and K_2O, reduces the decomposition temperature of calcium sulfate to about 1127.8 ℃ (1400.95 K), which is within the actual decomposition temperature range of calcium sulfate (1370-1770 K).
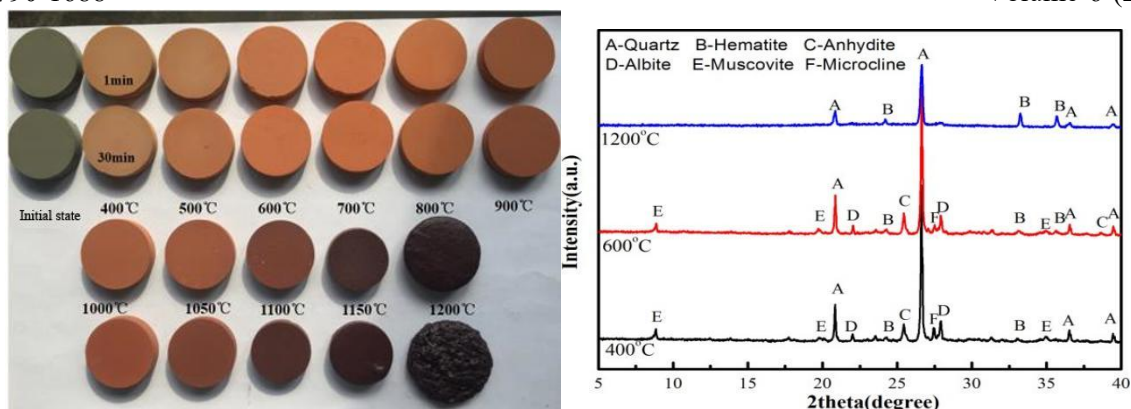
$$FeS2 + O2 \rightarrow FeS + SO2 \ (350\sim400℃) \qquad (1)$$

$$SO2 + 0.5O2 \rightarrow SO3 \ (<923\ K) \qquad (2)$$

$$FeS + O2 \rightarrow Fe2O3 + SO2 \ (500\sim800℃) \qquad (3)$$

$$4FeS2 + 11O2 \rightarrow 2Fe2O3 + 8SO2 \ (500℃) \qquad (4)$$

Figure 3. Appearance images and XRD patterns of cyanide tailings calcined at different sintering temperatures

Sulfur fixing technology is a simple, convenient, low-cost process that can comprehensively utilize raw material resources to prevent defects such as black cores and bulges in the process of firing ceramic tiles with cyanide tailings. At present, calcium-based sulfur fixing agents are widely used in industry, and their sulfur fixing process involves the absorption of SO_2 gas by forming calcium sulfate. Adding transition metal compounds, such as Fe_2O_3, $Fe(NO_3)_3$, V_2O_5, and other alkali metals, to calcium-based sulfur fixing agents can promote the conversion of SO_2 to SO_3. As presented in Fig. 4, the comparison results show that $KMnO_4$ can enhance the sulfur fixing effect best. After $KMnO_4$ is heated, it will form a molten liquid phase and a low melting point liquid phase eutectic with CaO and $CaSO_4$, making the pores of the sulfur fixing agent more numerous and larger, increasing the porosity of the sulfur fixing agent and forming an appropriate pore size distribution. The larger the pore size, the smaller the diffusion resistance of gases such as SO_2 in the sulfur fixing agent, which is beneficial to lift up the sulfur fixing rate. At the same time, the $CaSO_4$ formed by sulfur fixing is not easy to block pores, which is conducive to the gas penetration into the interior of CaO, and thereby enhancing the sulfur fixing effect.
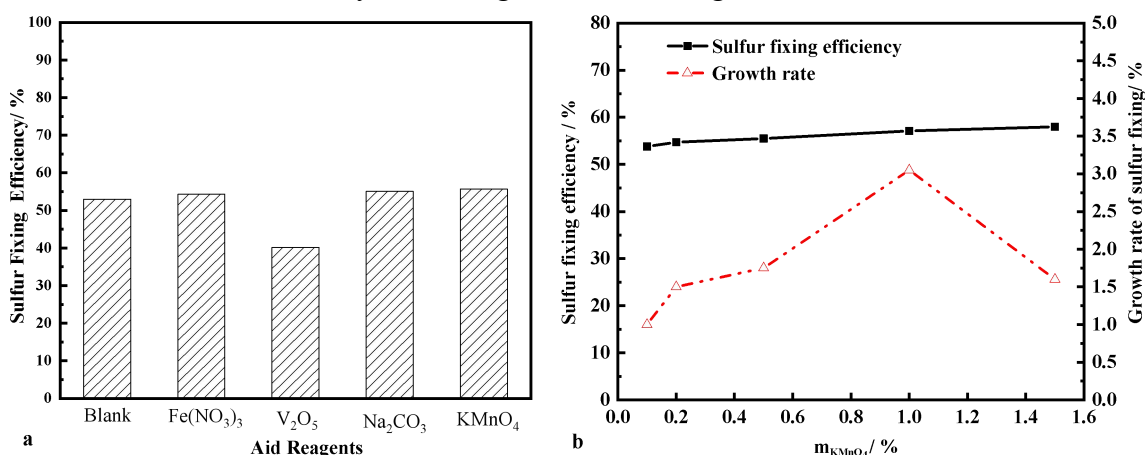

Figure 4. (a) Sulfur fixing efficiency of different aid reagents; (b) Effect of $KMnO_4$ on sulfur fixing efficiency

Figure 5 shows the comparison of micromorphology of ceramic samples containing cyanide tailings without and with sulfur fixing agents. It is leant that samples containing sulfur fixing agents are easier to achieve sintering, with lower sintering temperature and better sulfur fixing effect, from the microscopic morphology observation.
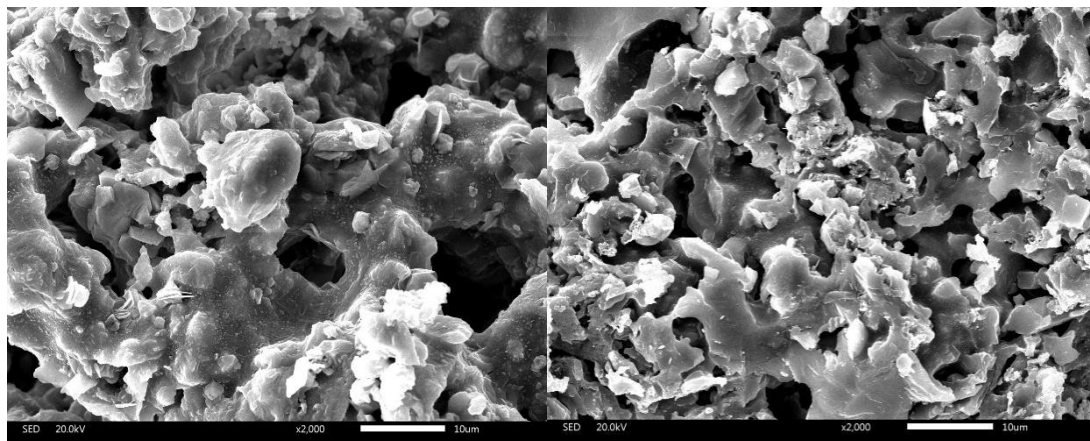
Figure 5. Comparison of micromorphology of ceramic samples containing cyanide tailings without (a) and with (b) sulfur fixing agents

4. Conclusion

The deep collaborative decyanation and desulfurization can be successfully realized with the novel oxidant DDTQ. When the removal efficiency of cyanide ions exceeds 99%, the removal rate of pyrite and chalcopyrite can be achieved above 90% at the same time. Proper firing temperature is the key to firing ceramic tile products from cyanide tailings. When the firing temperature increases, the residual sulfide is oxidized and decomposed, resulting in the formation of black centers. Aiming at the adverse effects of sulfur containing compounds on sintering, a new type of composite sulfur fixing agent system was developed, mainly consisting of calcium-based sulfur fixing agents, supplemented by various compounds. The experimental results show that the samples containing sulfur fixing agents are not only easier to achieve low-temperature sintering, but also avoid the occurrence of defects such as black centers and bulges in ceramic samples from the rapid firing process.

Acknowledgment

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