

Research Article

Decomposition of Cyanide from Gold Leaching Tailings by Using Sodium Metabisulphite and Hydrogen Peroxide

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Cyanidation is widely used by most gold mine worldwide and will remain prevail in years (or decades) to come, while cyanide is hazardous, toxic pollutants whose presence in wastewater and tailings can seriously affect human and its environment; hence, it is necessary to control these contaminants. The purpose of this study was to examine the effects through the investigation of changes in pH, concentration, and contact time, and the optimal conditions were obtained. It has been proven that the decomposition of cyanide in solution and tailings increased as the alkalinity in the presence of $0.5 \text{ g/L Na}_2\text{S}_2\text{O}_5$. An increase in H₂O₂ (30%) concentration (from 1 to 4 mL/L) increased the decomposition in solution, while the effect on removing cyanide was better when pH was 9 than 8 and 10 in tailings. The cyanide in tailings decreased in the first 4 h and increased after 4 h. The effective and economic conditions for maximum decomposition of cyanide from leach tailings are first treated in $0.5 \text{ g/L Na}_2\text{S}_2\text{O}_5$ at pH 10 for 3 hours and then 2 mL/L H₂O₂ (30%) is added to the tailings at pH 9 for 4 hours through comparative study. The findings provide the basis to optimize the decomposition of cyanide from gold leaching tailings in mining or backfilling by using the synergetic effect of Na₂S₂O₅ and H₂O₂.

1. Introduction

Cyanide leaching (cyanidation), which converts the gold into a cyanide complex $(Au(CN)_2^-)$ that is soluble in water, is currently the most prevailing and effective process to extract gold from ores [1, 2]. This process requires excess cyanide to improve gold recovery and produces exceptionally large quantities of cyanide-bearing wastes in the form of tailings and waters. Free cyanide, which is the main byproduct that results from metallurgical processes [3], is considered the most toxic cyanide form as it causes harmful effects at relatively low concentration. Other cyanide species are easily dissolved to free cyanide in the tailings to be reduced to biologically harmless through natural attenuation [5–7], so tailings containing cyanide should be treated before

they are released into the environment to avoid detrimental effects on the receiving environment [8]. The decomposition of cyanide from gold leaching tailings is one of the biggest challenges for the gold mine in the last decades, so the appropriate treatment of the cyanide in the tailings is required to avoid or minimize environmental and health issues.

Several biological, physical, and chemical techniques, electrolytic oxidation, and other methods to decompose or recycle cyanide have been developed for the treatment of cyanide solutions. Currently, as the widely used technologies for industrial production of the decomposition of cyanide are INCO process, alkali-chlorine process, activated carbon process, ozone oxidation process, hydrogen peroxide oxidation process [9], and recovery hydrogen cyanide [10–12]. INCO and alkali-chlorine processes are used to remove high concentration cyanide, while they cannot completely accomplish the degradation of cyanide species [13, 14]. Activated carbon can absorb cyanide and make it gather, but cannot decompose it [15]. Ozonation and hydrogen peroxide oxidation processes, which are not easy to produce secondary pollution in the treatment of cyanide, are used to treat low concentration cyanide [16, 17], but the cost is higher. Recovery hydrogen cyanide can reduce cyanide content and cost, but it cannot meet the requirements of tailings' backfilling [10–12].

Backfilling technology is the best choice for the mine to break through the bottleneck of resources, environment, and safety [18], but harmful substances such as metal materials and solvent left in the gold leaching tailings should be treated before backfilling in order to prevent them from polluting groundwater. Many organizations and countries around the world have already issued effective cyanide management policies; some countries, include Costa Rica, Argentina, Germany, the Czech Republic, and Turkey, have an outright ban on the use of cyanide in gold extraction throughout the country [19, 20]. In 2018, China issued the technical specification for pollution control of cyanide leaching residue in gold industry (TSPC), in which ozonation and hydrogen peroxide oxidation are selected as a method of deep decyanation. The study on cyanide removal is mainly focused on industrial wastewater [21]; the study on cyanide removal in gold leaching tailings, which contains wastewater and tailings, is still limited. While the mineral composition of gold ore is complex, cyanide, powder of activated carbon, hydrogen peroxide (H₂O₂) and other chemical were also added in the mineral processing flowsheet, which made the composition of tailings more complex. Most of the residual cyanide in tailings are strongly adsorbed on the surface of minerals, only a small amount of free cyanides and hydrolytic complex cyanides are able to enter into the leaching solution [22]. Therefore, it is necessary to explore more efficient methods to remove cyanide. The appropriate decomposition of CN⁻ is a complex process that requires several approaches are combined to improve the efficiency of the treatment and consider treatment economy, and combination methods were used to try to remove cyanide [23].

Based on the method of cyanide removal in solution, the effects of pH, concentration, and contact time of H_2O_2 for the decomposition of cyanide from leach tailings were analysed after $Na_2S_2O_5$ reaction. The mechanism of cyanide removal was also discussed. The outcome of this study was to find the best conditions for decomposition of cyanide from leach tailings, lead to bulk utilization of tailings in gold metal mine, and alleviate the ground collapse and soil pollution caused by traditional mining.

2. Materials and Methods

2.1. Tailings. The gold leaching tailings used in the experiment comes from Xiajiadian gold mine, Shaanxi province, China, which belongs to orogenic gold deposit, accounting for 52% in China [24]. The concentration of gold leaching tailings, where the diameter of tailings is $100-600 \,\mu$ m, is 35%, pH is 10.78, the initial cyanide concentration in the

solution is 30.66 mg/L, and the cyanide leached from the leach tailings is 11.78 mg/L. The total carbon content of tailings is 2.47–6.67%, in which the organic carbon content is 1.47–4.29%. The solution temperature was controlled at $23 \pm 2^{\circ}$ C.

2.2. Reagents. H_2O_2 (30%) and sodium metabisulphite ($Na_2S_2O_5$) were employed as received. Copper employed as the decomposition catalysts [25, 26] was added as the copper sulfate for experiments. Concentrated (98%) H_2SO_4 and NaOH were employed for pH adjustment. All chemicals were of analytical reagent grade. Agitated air was used in this experiment in order to accelerate the decomposition of cyanide, and the inflation rate was 50 mL/min.

2.3. Methods

2.3.1. Experiment of Decomposition of Cyanide from Leach Tailings. 0.5 g/L of Na₂S₂O₅ and 0.2 g/L of CuSO₄ (as catalyst) were added to 1000 mL gold leaching tailings, and the solutions were air stirred at a constant rate of 50 mL/min to accelerate cyanide oxidation. Individual experiments were carried out at pH values ranging from 8 to 11. After 3 h at each pH, 10 mL sample solutions, which were filtered with a $0.45\,\mu m$ filter paper and a 100 g solid which was leaching residue, were analysed for residual cyanide. Then, 1, 2, or 4 mL/L of H₂O₂ (30%) was added to 1000 mL gold leaching tailings, which had been treated with Na₂S₂O₅ at pH 10 for 3 h. Individual experiments were carried out at pH values ranging from 8 to 10, the solutions were air stirred at a constant rate of 50 mL/min to accelerate cyanide oxidation. After 1 h, 2 h, 4 h, and 8 h at each pH, a 100 g solid which was leaching residue and some 10 mL sample cyanide wastewater were analysed for residual cyanide. NaOH or H₂SO₄ was added to maintain a pH of 8-11 throughout each test.

2.3.2. Experiment of Cyanide Leaching from Leach Tailings. The steps of cyanide leaching of leach tailings follow the technical specification for pollution control of cyanide leaching residue in gold industry issued by China. Contaminated cyanide solution was prepared by mixing the pregnant solution and water (extractant) according to the ratio of 10 L water to 1 kg tailings and oscillated at 30 ± 2 revolutions per min by flip oscillator with $23 \pm 2^{\circ}$ C for 18 ± 2 hours referring to the technical specification for pollution control of cyanide leaching residue in gold industry.

2.3.3. Analytical Method. Total cyanide (CNT) content was determined by isonicotinic acid-pyrazolone spectrophotometry referring to the water quality-determination of cyanide volumetric and spectrophotometry method. The cyanide reacts with chloramine T to give cyanogen chloride, which reacts with isonicotinic acid to give pentenedialdehyde, and finally condenses with pyrazolone to give blue dye; then, it is measured at 638 nm by UV9100 A ultravioletvisible spectrophotometer (YQ00302), with a detection limit of 0.004 mg/L.



FIGURE 1: Cyanide as a function of pH in the presence of 0.5 g/l Na₂S₂O₅ in 3 hours.

3. Results and Discussion

3.1. Effect of pH on the Decomposition of Cyanide by $Na_2S_2O_5$. Individual experiments were carried out at pH values ranging from 8 to 11. Figure 1 shows the effect of equilibrium pH on the cyanide of solution and lixiviant in the presence of 0.5 g/L $Na_2S_2O_5$ in 3 hours. It is evident that an increase in pH increased the extent of decomposition of cyanide in solution and lixiviant of tailings. This result showed that the decomposition of cyanide increased as the alkalinity of the solution increased, the cyanide in lixiviant of tailings was the least when the pH was 10 under the same conditions, and the effect of cyanide decomposition in tailings was equivalent to that of pH 9, 10, and 11. Considering the investment cost, the effect of decomposition of cyanide from solution and tailing by $Na_2S_2O_5$ is the best when pH is 10.

3.2. Effect of pH on the Decomposition of Cyanide by H_2O_2 . The pH value had a significant effect on cyanide removal [21, 27]. The tailings were treated with $0.5 \text{ g/L} \text{ Na}_2 \text{S}_2 \text{O}_5$ for 3 hours at pH 10, and then individual experiments were carried out at pH values ranging from 8 to 11. Figures 2(a)-2(c) show the effect of equilibrium pH on the cyanide of lixiviant of tailings after Na₂S₂O₅ treatment in the presence of H_2O_2 , and it is evident that the effect on removing cyanide was better when pH was 9 than 8 and 10 in lixiviant. Figure 2(d) shows effect of equilibrium pH on the cyanide of solution added with 2 mL/L H₂O₂ for 2 hour, and it is evident that an increase in pH increased the extent of decomposition in solution, which is in agreement with those of Tu et al. [28] who observed that the decomposition of cyanide in mine wastewater added with H₂O₂ increased as the alkalinity of the solution increased.

Figure 2 shows that the effect of removing cyanide by H_2O_2 in solution is different from tailing under the same conditions. The reason for this phenomenon may be that the cyanide in the solution, which is free cyanide, is easy to be treated, while the diffusion rate of cyanide in the tailings to

the solution is lower than the removal rate by H_2O_2 of the solution.

3.3. Effect of H_2O_2 Concentration on the Decomposition of Cyanide. The ability of the decomposition of cyanide will be affected by the concentration of H_2O_2 . Figure 3 shows the effect of H_2O_2 concentrations ranging from 1 to 4 mL/L on the decomposition of cyanide. It is evident that an increase in H_2O_2 concentration increased the extent of decomposition in tailings; the most cyanide is leached from the tailings when 2 mL/L H_2O_2 is added to the solution.

In order to remove cyanide in tailings as much as possible, excessive $Na_2S_2O_5$ was added to the pretreatment, and the reaction occurs when H_2O_2 reached a certain concentration, resulting in the low efficiency of cyanide treatment at 2 mL/L:

$$Na_2S_2O_2 + 5H_2O_2 \longrightarrow Na_2SO_4 + H_2SO_4$$
(1)

$$H_2SO_4 + Na_2SO_3 \longrightarrow Na_2SO_4 + S + SO_2 + H_2O$$
(2)

$$SO_2 + H_2O_2 \longrightarrow H_2SO_4$$
 (3)

3.4. Effect of Contact Time on the Decomposition of Cyanide. Contact time is also the influence factor of H_2O_2 for the decomposition of cyanide [28]. Figure 4 shows the effect of contact time ranging from 1 to 8 h on the rate of decomposition of cyanide of lixiviant in tailings. The figure showed that cyanide decreased in the first 4 h and the content of cyanide increased after 4 h. In the first four hours, H_2O_2 reacted with cyanide in the tailings, which caused the cyanide content in the solution to decrease, while most of the cyanides adsorbed on pyrite [28, 29] and chalcopyrite [30], which is widely distributed in gold ore, are driven by chemisorption of carbon. The remaining H_2O_2 could not continuously reduce the cyanide content in the tailings, and it might be that the



FIGURE 2: CNT as a function of pH in the presence of H_2O_2 .



FIGURE 3: Continued.



FIGURE 3: Cyanide as a function of H_2O_2 concentration.





FIGURE 4: Cyanide as a function of contact time.

unreacted cyanide in the tailings adsorbed by activated carbon reentered the tailings with the concentration of H_2O_2 decreased. It is possible that the cyanide adsorbed

by pyrite and activated carbon is gradually converted into free cyanide, and the unreacted cyanide in pulp re-enters the tailings with the decrease of $\rm H_2O_2$ concentration.

As explained above, the best conditions for decomposition of cyanide from leach tailings are first treated in 0.5 g/L $Na_2S_2O_5$ at pH 10 for 3 hours and then 2 mL/L H_2O_2 is added to the tailings at pH 9 for 4 hours.

4. Conclusions

The decomposition of cyanide increased as the alkalinity of the solution and tailings increased in the presence of 0.5 g/L $Na_2S_2O_5$. An increase in pH increased the extent of decomposition in solution in the presence of H_2O_2 , while the effect on removing cyanide was best when pH was 9 in lixiviant of tailings. An increase in H_2O_2 concentration increased the extent of decomposition in solution. The cyanide decreased in the first 4 h, and the content of cyanide increased after 4 h by the adsorption effect of active carbon and pyrite.

All the leaching metal of gold leaching tailings treated by $Na_2S_2O_5$ and H_2O_2 can meet the backfilling requirements (0.05 mg/L) of TSPC. Considering fully with effectiveness and practicability, the best conditions for decomposition of cyanide from leach tailings are first treated in 0.5 g/L $Na_2S_2O_5$ at pH 10 for 3 hours and then 2 mL/L H_2O_2 is added to the tailings at pH 9 for 4 hours.

Data Availability

The data used to support the findings of the study are available from the corresponding author upon request.

Additional Points

Highlights. (i) Sodium and hydrogen peroxide for cyanide decomposition are applied. (ii) The factors affecting cyanide removal were explored. (iii) The optimal conditions for cyanide removal were examined. (iv) The lessons are useful for backfilling by gold tailings to develop efficient circularity.

Conflicts of Interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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