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Study on Process Optimization of Sodium Percarbonate Oxidation for Treating Cyanide-Containing Tailings from Gold Mines

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Abstract. To address the issues of secondary pollution and unstable treatment efficiency in the harmless disposal of cyanide-containing wastewater from gold mines, this study took cyanide-containing tailings slurry as the research object. The single-factor variable method and conditional experiments were adopted to investigate the process characteristics and optimized parameters of the sodium percarbonate oxidation method, as well as to analyze the effects of pH value, reagent dosage, and reaction time on cyanide removal efficiency. The results showed that under the optimal process parameters, the content of readily releasable cyanide in the filtrate was 3.44 mg/L, the total cyanide content was 4.54 mg/L, with a total cyanide removal rate of 98.77%. The content of readily releasable cyanide in the toxic leachate of cyanide residue was 0.03 mg/L, and the total cyanide content was 0.46 mg/L. This process features no secondary pollution, outstanding environmental friendliness, and simple operation. It provides a new technical approach for the green treatment of cyanide-containing wastewater from gold mines and has important practical significance for promoting the environmental protection upgrading of the industry.

1 Introduction

Cyanide has become a key reagent in the mineral processing and extraction processes of gold mines due to its high selective complexation ability with precious metals such as gold and silver[1,2]. However, the cyanide-containing wastewater produced at the end of the process contains free cyanide and various cyanide complexes, which are highly toxic and bioaccumulative. Direct discharge without effective treatment will pollute groundwater, destroy the aquatic ecosystem, and can cause serious health problems such as damage to the human nervous system and respiratory failure through food chain enrichment. With the tightening of environmental protection regulations, China has reduced the emission limit of total cyanide in some scenarios to below 0.5 mg/L. The harmless treatment of cyanide residue and cyanide-containing wastewater has become a core bottleneck for the green and sustainable development of the industry[3,4].

Compared with the sodium percarbonate oxidation method, other existing cyanide removal methods applied in gold mines have distinct shortcomings: alkaline chlorination is prone to generating highly toxic by-products and has a poor treatment effect on complex cyanides[5]; ozone oxidation features high equipment and operation costs with low ozone utilization efficiency[6]; ferrous sulfate precipitation achieves incomplete cyanide removal, meanwhile producing hazardous waste sludge that is liable to re-dissolve and release cyanide[7]; ion exchange is susceptible to impurity interference and has high resin regeneration costs, being only suitable for low-turbidity wastewater[8]; biodegradation has a long treatment cycle and weak shock resistance, incapable of handling high-concentration cyanide wastewater; electrolysis involves high equipment and operation costs, suffers from severe electrode wear and tear, and has limited treatment capacity[9]. All these methods are plagued by problems such as secondary pollution, unsatisfactory treatment efficiency, poor economic efficiency or low adaptability to mine scenarios, making it difficult for them to meet the current stringent environmental discharge standards and industrial production requirements.

Targeting the demand for cyanide residue treatment in gold mines, this study systematically conducts research on the process optimization of the sodium percarbonate oxidation method, clarifies the key influencing factors and optimal parameter combination, and provides a scientific basis and technical support for the industrial application of this technology.

2 Experimental Section

2.1 Experimental Raw Materials

The toxicity leaching analysis of cyanide-containing tailings slurry was carried out in accordance with HJ/T299—2007 Solid Waste—Extraction Procedure for Leaching Toxicity—Sulfuric Acid and Nitric Acid Method, and the results are shown in Table 1. It can be seen from the table that the content of readily releasable cyanide in the filtrate of cyanide-containing tailings slurry is 107.52 mg/L, and the total

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cyanide content is 373.07 mg/L. The contents of other heavy metals do not exceed the limits specified in HJ943—2018 Technical Specifications for Cyanide Residue Pollution Control in Gold Industry. Therefore, the core target of the experiment is to remove cyanide.

Table 1. Pollutant Composition Analysis of Filtrate from Cyanide-Containing Tailings Slurry and Toxicity Leaching Results of Cyanide Residue (mg/L).

Component	Filtrate of cyanide-containing tailings slurry	Toxic leaching of cyanide residue	Standard limit
RRC	107.52	3.56	0.05
TC	373.07	8.78	0.50
Cu	2.18	0.38	0.50
Pb	0.90	0.20	1.00
Zn	1.030	0.132	2.00
As	0.0043	-	0.50
Hg	0.0049	-	0.05
Cd	0.027	-	0.10
Cr	0.08	-	1.50
Cr^{6+}	<0.05	-	0.50

2.2 Experimental Instruments

The main experimental instruments include a multi-functional leaching mixer, leaching tank, pH meter, and electronic balance.

2.3 Experimental Method

Take 1 L of cyanide-containing tailings slurry with a concentration of 40% and place it in a leaching tank. Adjust the stirring speed to 15.0 Hz, and adjust the pH of the reaction system with quicklime and dilute sulfuric acid. Dissolve sodium percarbonate and copper sulfate in water to prepare 50 mL aqueous solutions respectively, and carry out the reaction at room temperature. The single-factor variable method was used to investigate the effects of pH, sodium percarbonate dosage, copper sulfate dosage, and reaction time on cyanide removal efficiency.

2.4 Principle of Cyanide Removal

Sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) will slowly decompose to release hydrogen peroxide (H_2O_2) under weakly alkaline conditions. H_2O_2, as the core oxidant, undergoes an oxidation reaction with cyanide (CN^-). At the same time, copper sulfate ($CuSO_4$) added to the system provides Cu^{2+} as a catalyst to enhance the reaction process. The final products are CO_2 and N_2 without any toxic by-products. Combined with the chemical reaction principle, the core reaction equations of cyanide removal by sodium percarbonate oxidation in a weakly alkaline system are as follows:

$$2Na_2CO_3 \cdot 3H_2O_2 \rightarrow 2Na^+ + 2CO_3^{2-} + 3H_2O_2$$

$$Cu^{2+} + CN^- \rightarrow [Cu(CN)_4]^{3-}$$

$$[Cu(CN)_4]^{3-} + H_2O_2 \rightarrow Cu^{2+} + CNO^- + 2H_2O$$

$$2CNO^- + H_2O + 3H_2O_2 \rightarrow CO_2\uparrow + N_2\uparrow + 4OH^-$$

$$CN^- + H_2O_2 \rightarrow CNO^- + H_2O$$

$$2CN^- + 5H_2O_2 \rightarrow 2CO_2\uparrow + N_2\uparrow + 4OH^- + 2H_2O$$

3 Results and Discussion

3.1 Effect of pH on Cyanide Removal Efficiency

PH has a significant effect on the cyanide removal efficiency of the sodium percarbonate oxidation method (Table 2, Fig1 and Fig2). When pH=8.5, the content of readily releasable cyanide in the filtrate after cyanide removal is 0.29 mg/L, the total cyanide content is 1.63 mg/L, and the toxicity leaching index of cyanide residue is optimal; with the increase of pH, the cyanide content gradually increases. When pH=12.5, the content of readily releasable cyanide in the filtrate rises to 24.12 mg/L, and the total cyanide content reaches 36.03 mg/L, indicating that the treatment effect deteriorates significantly.

Table 2. Analysis Results of pH Value Tests.

pH	Cyanide-removed filtrate		Toxic leaching of cyanide-removed filter residue	
	RRC (mg/L)	TC (mg/L)	RRC (mg/L)	TC (mg/L)
8.5	0.29	1.63	0.01	0.22
9.5	0.42	3.83	0.02	0.26
10.5	4.68	7.30	0.19	3.33
11.5	13.81	24.70	0.71	10.02
12.5	24.12	36.03	1.37	26.72

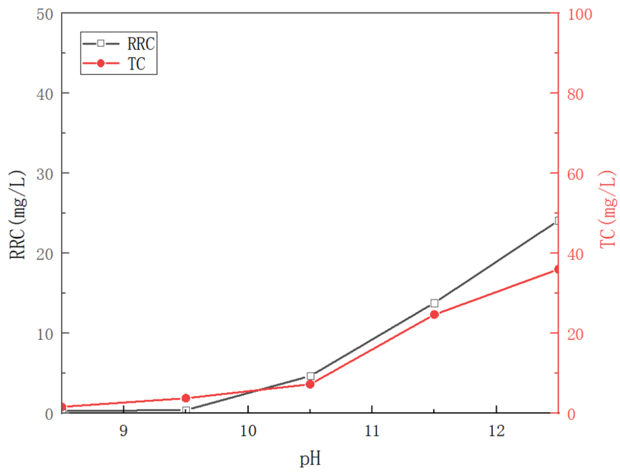

Fig. 1. Effect of pH Value on Cyanide in Cyanide-containing Tailings Slurry Filtrate.

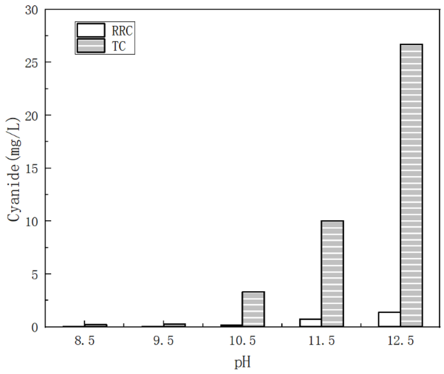

Fig. 2. Effect of pH Value on Toxicity Leaching Results of Cyanide Residue after Cyanide Removal**.**

The main reasons are as follows: the high pH environment will inhibit the decomposition of sodium percarbonate to produce hydrogen peroxide, reducing the oxidation activity; at the same time, Cu^{2+} is easy to combine with OH^- to form copper sulfate precipitation, leading to the deactivation of the catalyst; in addition, the cyanide form is more stable under the high pH environment, which is difficult to be oxidized and removed. Comprehensive analysis shows that the suitable pH range for the sodium percarbonate oxidation method is 8.5~9.5.

3.2 Effect of Sodium Percarbonate Dosage on Cyanide Removal Efficiency

As the sodium percarbonate dosage increases from 5 kg/t to 30 kg/t, the readily releasable cyanide decreases from 13.53 mg/L to 0.13 mg/L, and the total cyanide decreases from 17.33 mg/L to 0.74 mg/L(Table 3,Fig3 and Fig4).

Table 3. Analysis Results of Sodium Percarbonate Dosage Tests.

$Na_2CO_3{\cdot}H_2O_2$ (kg/t)	Cyanide-removed filtrate		Toxic leaching of cyanide-removed filter residue	
	RRC (mg/L)	TC (mg/L)	RRC (mg/L)	TC (mg/L)
0	107.52	373.07	3.56	8.78
5	13.53	17.33	0.39	1.22
10	9.15	14.82	0.33	0.98
15	0.72	6.69	0.07	0.67
20	0.35	4.18	0.04	0.45
25	0.29	2.26	0.02	0.3
30	0.13	0.74	-	0.11

For readily releasable cyanide, hydrogen peroxide produced by the decomposition of sodium percarbonate can oxidize part of the free CN^- to generate CNO^-. After the addition amount reaches the critical value, the oxidation reaction is complete, and the removal rate is close to 100%; when excessively added, the remaining hydrogen peroxide reacts with other reducing substances in the system, which has no negative impact on the content of readily releasable cyanide but increases the treatment cost. For total cyanide, sodium percarbonate can further oxidize CNO^- and some moderately stable cyanide complexes (such as $Cu(CN)_4^{3-}$). The total cyanide removal rate continues to increase with the increase of the addition amount until the strongly stable cyanide complexes reach the oxidation limit. Considering the cost and treatment effect, the optimal dosage of sodium percarbonate is determined to be 21 kg/t. At this time, the toxicity leaching index of cyanide residue after cyanide removal meets the standard of Class I general industrial solid waste.

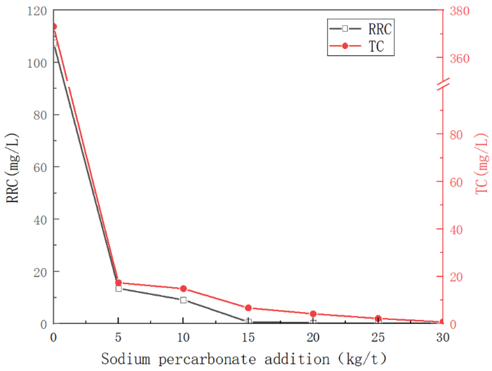

Fig. 3. Effect of Sodium Percarbonate Dosage on Cyanide in Cyanide-containing Tailings Slurry Filtrate.

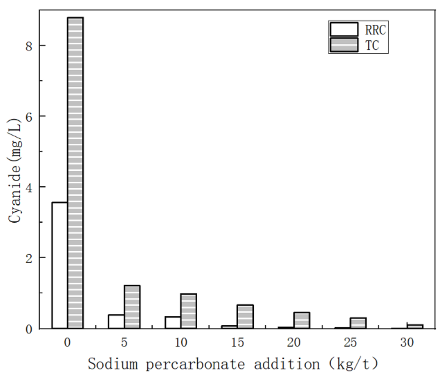

Fig. 4. Effect of Sodium Percarbonate Dosage on Toxicity Leaching of Cyanide Residue after Cyanide Removal.

3.3 Effect of Copper Sulfate Dosage on Cyanide Removal Efficiency

As a catalyst, copper sulfate has a significant enhancing effect on cyanide removal efficiency (Table 4,Fig 5 and Fig6).As the copper sulfate dosage increases from 0.05 kg/t to 0.5 kg/t, the readily releasable cyanide decreases from 27.5 mg/L to 0.72 mg/L, and the total cyanide decreases from 43.53 mg/L to 6.69 mg/L.

Table 4. Analysis Results of Copper Sulfate Dosage Tests.

$CuSO_4$ (kg/t)	Cyanide-removed filtrate		Toxic leaching of cyanide-removed filter residue	
	RRC (mg/L)	TC (mg/L)	RRC (mg/L)	TC (mg/L)
0	107.52	373.07	3.56	8.78
0.05	27.5	43.53	0.75	5.32
0.1	7.05	21.32	0.15	1.09

0.15	3.23	11.28	0.06	0.94
0.3	1.23	7.87	0.02	0.42
0.45	0.88	7.13	0.02	0.37
0.5	0.72	6.69	0.01	0.33

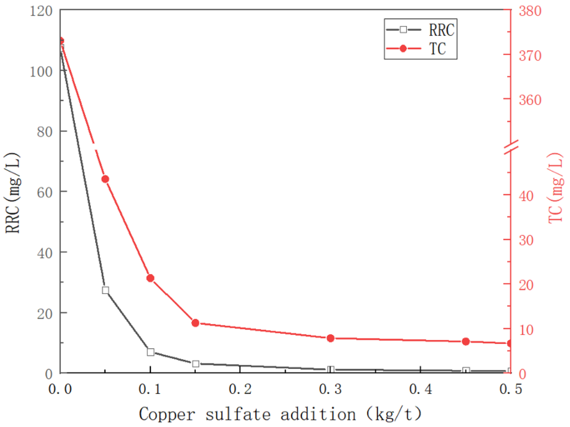

Fig. 5. Copper sulfate addition Tests.

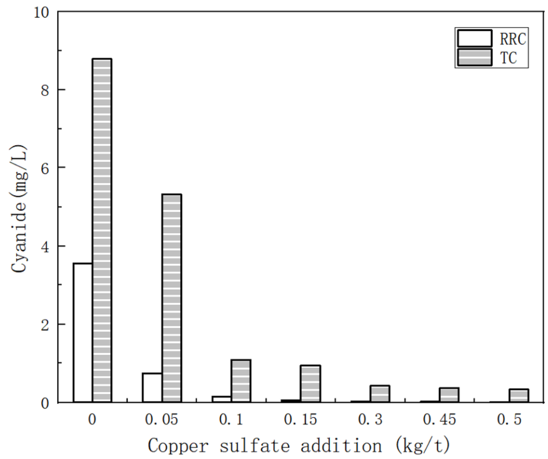

Fig. 6. Effect of Copper Sulfate Dosage on Toxicity Leaching of Cyanide Residue after Cyanide Removal.

At low addition amounts, Cu^{2+} rapidly reacts with CN^- to form stable $Cu(CN)_4^{3-}$ complexes, and the content of readily releasable cyanide drops sharply. Excessive Cu^{2+} will promote the polymerization and precipitation of complexes, and the removal rate tends to reach a peak (up to more than 90%).

3.4 Effect of Reaction Time on Cyanide Removal Eff iciency

The effect of reaction time on cyanide removal efficiency is shown in Table 5, Fig7 and Fig8. When the reaction time is 0 h, the readily releasable cyanide is 3.56 mg/L and the total cyanide is 8.78 mg/L; after 1 h of reaction, the readily releasable cyanide drops to 0.82 mg/L and the total cyanide drops to 1.94 mg/L; when the reaction time is 3 h, the readily releasable cyanide is 0.03 mg/L and the total cyanide is 0.46 mg/L, which meets the standard of Class I general industrial solid waste; continuing to extend the reaction time, the cyanide removal effect is not significantly improved, but it will increase energy consumption and treatment cost. Therefore, the optimal reaction time is determined to be 3 h.

Table 5. Cyanide removal results at different reaction times.

Time (h)	Cyanide-removed filtrate		Toxic leaching of cyanide-removed filter residue	
	RRC (mg/L)	TC (mg/L)	RRC (mg/L)	TC (mg/L)
0	107.52	373.07	3.56	8.78
1	20.94	31.54	0.82	1.94
2	4.14	12.06	0.09	1.03
3	3.57	10.54	0.03	0.46
4	0.92	6.36	<0.01	0.38
5	0.42	3.83	<0.01	0.35

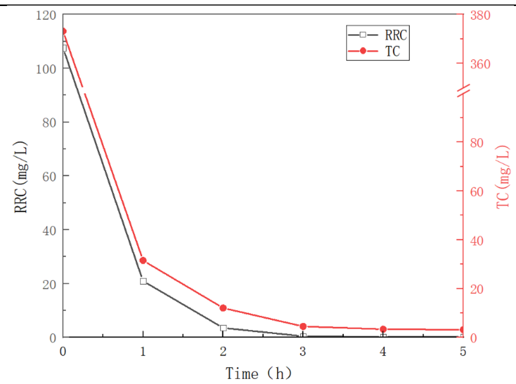

Fig. 7. Effect of reaction time on cyanide removal efficiency.

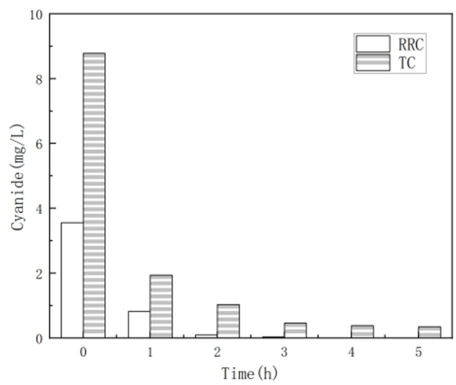

Fig. 8. Effect of reaction time on toxic leaching of cyanide residue after cyanide removal.

4 Conclusions

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) The optimal process parameters for treating cyanide-containing wastewater from gold mines by the sodium percarbonate oxidation method are: sodium percarbonate dosage 21 kg/t, copper sulfate dosage 0.30 kg/t, reaction time 3 h, stirring speed 15.0 Hz, and the suitable pH range is 8.5~9.5.

(2) After optimization, the treatment effect is as follows: the content of readily releasable cyanide in the filtrate is 3.44 mg/L, the total cyanide content is 4.54 mg/L; the content of readily releasable cyanide in the toxic leachate of cyanide residue is 0.03 mg/L, the total cyanide content is 0.46 mg/L, and the contents of main heavy metals all meet the relevant standards of Class I general industrial solid waste.

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