Experimental Study on key technologies for risk prevention and control of thallium pollution in A lead-zinc mine wastewater

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Abstract. In order to reduce the environmental risk of thallium pollution by enterprises and determine key technologies for thallium pollution prevention and control, the researcher conducted a deep exploration experiment on thallium removal in the inflow water of a certain lead-zinc mine. The experimental results showed that both sulfide precipitation method and catalytic oxidation & resin adsorption can achieve good thallium removal effect. Based on the actual characteristics of the lead-zinc industry, The author recommends a thallium pollution risk control technology scheme that combines terminal sulfide precipitation and source resin adsorption for thallium removal.

Keywords: Lead-zinc mine wastewater, thallium, pollution control.

1. Background

In recent years, there have been several environmental risk incidents of thallium pollution in China. For example, on May 5, 2017, the Environmental Protection Bureau of Guangyuan City, Sichuan Province discovered that the water quality of the Jialing River from Shaanxi to Sichuan was abnormal, and the thallium concentration in the drinking water source area of Xiwan Water Plant exceeded 4.6 times; On January 20, 2021, the Department of Ecology and Environment of Gansu Province reported abnormal thallium concentration in the Jialing River; On November 24, 2022, the ecological environment monitoring department of Yichun City, Jiangxi Province discovered abnormal thallium concentration during the monitoring and analysis of all indicators of drinking water sources in the main stream of the Jinjiang River. The frequent occurrence of thallium pollution incidents has attracted widespread attention to the heavy metal thallium. The discharge of industrial wastewater from non-ferrous metals, metallurgy, and mining is an important way for thallium pollutants to enter environmental water bodies. The discharge of thallium pollutants can cause a series of environmental pollution problems such as soil thallium pollution, water thallium pollution, and chronic thallium poisoning in humans and animals. As a result, a series of stricter requirements for thallium pollution control have been introduced by the national and local governments. Some regions require the lead and zinc industry to comply with the " Emission standard of pollutants for lead and zinc industry" (GB 25466-2010) modification list and the standard of $Tl<5\mu g/L$, therefore, the lead and zinc industry urgently needs to seek technically feasible and economically reasonable risk prevention and control technologies for thallium deep treatment.

2. Comparison of Common Thallium Removal Technologies

Thallium compounds are one of the main hazardous waste listed in the WHO's Key Restricted List, and have also been included in the list of priority controlled pollutants in China. They are included in Appendix A of the " Identification standards for hazardous wastes-Identification for toxic substance content" (GB 5085.6-2007). Thallium in environmental media usually exists in two valence states: $Tl^{+}$and Tl^{3+}. At present, common treatment technologies for thallium containing wastewater mainly include oxidation coagulation sedimentation, sulfide sedimentation, adsorption, biochemical treatment, electrochemical treatment, etc. Among them, chemical sedimentation, biological, and adsorption method are research hotspots. Through research on existing technologies, the comparison results of thallium removal technologies are as follows:

Table 2-1. Comparison Results of Thallium Treatment Technologies

NO.	Thallium removal technologies	Principle	Advantages	Disadvantages
1	Chemical precipitation method	Removing Thallium from Sediments Formed from Thallium Ions by Using Sulfide and Other Precipitators	Mature,cost effective, , easy to operation	The control requirements are high,easy to cause secondary pollution
2	Pre-oxidation + coagulation sedimentation	Tl+ was oxidized to Tl3+ by oxidant chemicals, using flocculants to settle the floc containing thallium..	High thallium removal efficiency, lower equipment investment	Pre-oxidation is required, the cost of the agent is high, and the effect is sometimes unstable
3	Preoxidation + adsorption method	Tl+ was oxidized to Tl3+ by adding oxidant, and thallium was removed by selective adsorption of thallium trivalent by adsorbent.	simple to operate, the equipment covers a smaller area, easy to be deeply processed	Pre-oxidation is required, and the investment in adsorption equipment per unit of water is relatively high
4	Electrochemistry	The iron or aluminum ions formed during the electrolytic reaction form a relatively stable polymer with thallium ions in the water, which are then removed by flocculation.	high degree of automation , simple operation	The impact load resistance is weak, the energy consumption is large, the effect is unstable
5	Microbiological method	Fixed and removed by active sulfate reducing bacteria and other microorganisms based on adsorption and REDOX action between microorganisms and thallium ions	Low cost, no secondary pollution	less practical application, less engineering application

According to the research literature and the existed environmental protection facilities of the lead and zinc production enterprise, this study intends to use "chemical precipitation" and "pre-oxidation + adsorption" processes to conduct experimental research respectively.

3. Experimental study on thallium removal

3.1 Experimental purpose

In view of the situation that the thallium content in lead-zinc mine wastewater may occasionally exceed the standard, an experimental study on the key technology of advanced treatment of thallium-containing wastewater is carried out, with the aim of developing a stable, efficient, simple and practical key technology for emergency treatment of thallium pollution, and the research results provide technical support for on-site emergency treatment of thallium pollution. The objective of this study is to obtain the total thallium after treatment. 5μg/L.

3.2 Experimental Water quality

The water used in this experiment was on-site sampling at the entrance of a lead-zinc mine waste water treatment station, and the thallium concentration was 13.56μg/L prepared by adding thallium standard solution. The experiments were carried out by lime precipitation method, sulfide precipitation method and adsorption method respectively.

3.3 Experimental research on thallium removal of wastewater

3.3.1 Removal test of thallium by lime precipitation

Take a certain amount of raw water, add lime milk to control the pH value of different reactions, stirring reaction time is 30mins. The experimental results are shown in Table 1.

Table 1 Table of experimental results of thallium removal by lime precipitation.

Numble	Chemicals	Condition	Tl （μg/L）
0	/	/	13.56
1	CaO	pH9	9.9
2	CaO	pH10	8.8
3	CaO	pH11	6.8

As can be seen from Table 3.3-1, the lime precipitation method has a certain effect on the treatment of thallium pollutants, and the removal rate of thallium is also improved with the increase of the lime dosage. When the pH value is 11, the thallium concentration is down to 6.8μg/L, which still cannot reach the treatment target.

3.3.2 Thallium removal experiment by sulfide precipitation method

Take a certain amount of experimental raw water, add the prepared industrial grade sodium sulfide solution, stirring reaction time is 30min. The experimental results are shown in Table 2.

Table 2. Experimental results of thallium removal by sulfide precipitation method

NO.	Chemicals	Dosage	Tl（μg/L）
0	/	/	13.56
1	Na2S	5mg/L	8.1
2	Na2S	10mg/L	5.2
3	Na2S	20mg/L	3.6

It can be seen from Table 3.3-2 that the thallium treatment by sulfide precipitation method has a good treatment effect. When the dosage of sodium sulfide is 20mg/L, thallium can be removed to 3.6μg/L, which can meet the requirements of) modification list " Emission standard of pollutants for lead and zinc industry" (GB 25466-2010).

3.3.3 Thallium removal experiment by pre-oxidation and coagulation precipitation

Raw water with a thallium concentration of 13.56μg/L was prepared by adding a certain amount of T^{l+} standard solution to the wastewater sample at the entrance of a lead-zinc mine sedimentation tank. A certain amount of oxidizing agent was put into 500 mL water sample for stirring reaction, and then a certain amount of flocculant was added to obtain the best oxidation flocculant for removing thallium. OX-A, OX-B, OX-C and OX-D were used as oxidants respectively, and the oxidation reaction time was 30 min. PAC was used as flocculant, and the flocculation reaction time was 10 min. Table 4.5-1 shows the experimental results.

Table 3 Experimental results of removal of different oxidants on thallium

Numble	Oxidant	Dosage	Flocculants	Tl（μg/L）	pH

0	/	/	/	13.56	7.66
1	OX-A	1mg/L	PAC	9.58	8.97
2	OX-A	2mg/L		8.14	7.66
3	OX-A	3mg/L		8.13	8.89
4	OX-A	4mg/L		7.85	7.78
5	OX-B	2ml/L		8.00	9.81
6	OX-B	4mL/L		5.76	11.68
7	OX-B	6mL/L		4.64	11.96
8	OX-B	8mL/L		4.50	12.22
9	OX-C	0.2g/L		5.81	9.66
10	OX-C	0.4g/L		3.87	9.79
11	OX-D	1mL/L		10.65	9.25
12	OX-D	2mL/L		10.16	8.99

As can be seen from Table 3, the experiment using OX-C+PAC has the best removal rate on thallium. When the dosage of OX-C is 0.4g/L and with the flocculants of PAC, the thallium in raw water can be reduced from 13.56 μg/L to 3.87μg/L. Therefore, OX-C was suggested as the oxidizing agent.

After OX-C was found to be the best oxidant for thallium removal, different flocculants were tested, PAC and PFS were used respectively. The experimental results are shown in Table 4.

Table 4 Experimental results of removal of different flocculants on thallium

Numble	OX-C Dosage	Flocculants	Tl（μg/L）
0	/	/	13.56
1	0.4g/L	PAC	3.1
2	0.6g/L	PAC	2.8
3	0.8g/L	PAC	1.1
4	0.4g/L	PFS	4.6
5	0.6g/L	PFS	1.6
6	0.8g/L	PFS	1.9

As can be seen from Table 3.3-4, both PAC and PFS have a good removal effect on thallium. When the dosage of OX-C is 0.6g/L and with the flocculant of PFS, thallium in raw water can be reduced from 13.56 μg/L to 1.6μg/L, and with less dosage of OX-C. Therefore, PFS is selected as the best chemicals of coagulation process.

3.3.4 Experimental study on removal of thallium by catalytic oxidation-adsorption method

The selected catalyst is an iron-zinc series catalyst with Fe as the main body and ZnO as the carrier, which is suitable for oxidation catalytic reaction system in liquid solution to promote the transformation of Tl^{+} to Tl^{3+}. The selected adsorbent is a sodium-type strong acid gel-type cationic adsorption resin with uniform size (monodisperse) particles based on styryl-divinylbenzene copolymer, which has strong chemical stability, permeability stability and mechanical stability. For thallium trivalent ion has a good adsorption effect, The treatment effects of "oxidation + coagulation", "catalysis + oxidation + coagulation" and "catalysis + oxidation + coagulation + resin adsorption" were investigated respectively. The test results are shown in the table below：

Table 5 Results of catalytic and adsorption thallium removal tests.

NO.	Method	Conditions	Tl /μg/L
1	oxidation + coagulation	OX-C+PFS	1.6
2	catalysis + oxidation + coagulation	catalyst +OX-C+PFS	0.83

3	catalysis + oxidation + coagulation + resin adsorption	catalyst +OX-C+PFS+resin	0.53

As can be seen from the above table, when OX-C is the oxidant and PFS is the coagulant, the removal effect of thallium is further enhanced and the thallium content is further reduced after treatment with the addition of catalyst. After the use of the resin adsorption process after catalysis + oxidation + coagulation, the thallium content is much more further reduced, so both the catalysis and adsorption process can enhance the removal of thallium, and the resin adsorption process can reduce the thallium in the wastewater to a lower degree, far below the special limit requirements of " Emission standard of pollutants for lead and zinc industry" (GB 25466-2010) modification list.

3.3.5 Experimental Conclusions

(1) The lime precipitation method has a certain effect on the treatment of thallium pollutants, but the treatment target Tl<5μg/L cannot be achieved;

(2) The sulfide precipitation method has a good effect on the removal of total thallium, and the thallium can be removed to 3.6μg/L in the experiment, which meets the requirements of the " Emission standard of pollutants for lead and zinc industry" (GB 25466-2010) modification list;

(3) OX-C was found to be the best oxidant for thallium removal, PFS is selected as the best chemicals of coagulation process, When the dosage of OX-C is 0.6g/L and with the flocculant of PFS, thallium in raw water can be reduced from 13.56 μg/L to 1.6μg/L

(4) The selected catalyst and resin adsorbent can enhance the removal of thallium, and the combination of the two technologies can reduce the maximum thallium to 0.53μg/L.

4. Comparison of technical proposals on thallium removal

Taking a lead and zinc mine in China as an example, the wastewater treatment station adopts the fifth-grade coagulation and sedimentation process, the treatment scale is 32000m3/d, and no emergency thallium removal treatment facility has been established. The source investigation found that the amount of wastewater that may increase the thallium content is about 20m3/h. According to the experimental results, three treatment schemes are proposed:

Scheme 1: The existing treatment station will build the dosage facility of oxidation reagent, and once the inlet thallium ion concentration exceeds the control value, the oxidizer and coagulant will be added according to the dosage determined by the experiment;

Scheme 2: Build sulfide agent dosing facilities in the existing treatment station. Once the inlet thallium ion concentration exceeds the control value, the sulfide precipitation reagent will be dosed according to the dosage determined by the experiment;

Scheme 3: The wastewater polluted by thallium at the source is treated separately and discharged directly after reaching the standard by the new built catalytic oxidation + adsorption process facilities.

The comparison of technical and economic indicators of the three schemes is shown in the following table

Table 6 Comparison of technical proposals

Items.	Scheme 1	Scheme 1	Scheme 1
design scale / m3/d	32000	32000	480
operation	complex	simple	simple
investment cost /10KRMB	~65	~45	~96
investment cost / RMB/m3	~2.249	~0.656	~0.7
Running cost/ RMB/d	~71968	~20992	~336
Outlet Tl / μg/L	~1.5	~1.5	~0.5
Environmental risk Of Tl pollution	medium-	medium-	low

Remarks: The above estimation is based on Tl content of raw water 10μg/L and influent Tl content of resin adsorption method 20μg/L.

As can be seen from above table, taking the lead-zinc ore investigated as an example, scheme 3 is the best treatment effect with highest investment cost. The effect of thallium removal in Scheme 2 and Scheme 1 is similar, but the investment in scheme 2 is lower than that in scheme 1. scheme 3 has the lowest environmental risk due to source treatment, and the lowest overall operating cost once environmental risks occur. It can be seen that the resin adsorption method can greatly reduce the operating costs of enterprises and avoid risks from the source if it can be processed at the source. In view of the large amount of water treated, the investment and operating cost of sulfide precipitation method facility are lower.

5. Conclusions and recommendations

If the waste water contaminated at source can be separated, the resin adsorption method can greatly reduce the operating costs of enterprises and avoid risks from the source. In view of the large amount of water treated, the investment and operating cost of the sulfide precipitation method facility are low. According to the results of the experiment and the comparison of technical schemes, it is suggested that the overall idea of emergency treatment of thallium-containing wastewater in the lead and zinc industry should be "mass separation and mass treatment" to reduce the risk of thallium pollution from the source as far as possible. Lead and zinc enterprises can consider two thallium pollution treatment facilities according to their own conditions to deal with the environmental risk of thallium pollution:

1) If the thallium content of a wastewater at the source is high (recommended value >10μg/L) and the diverting conditions are available, the wastewater containing thallium can be separately raised to the resin adsorption treatment system and up-to-standard discharge which can remove the risk of thallium pollution to the environment at the source.

2) An emergency treatment system for thallium removal by terminal sulfide precipitation was added to the existing wastewater treatment station. It is recommended to strengthen the monitoring of thallium concentration at the inlet of the daily treatment station. When the inlet thallium index of the wastewater treatment station is high (such as >5μg/L), the newly added sulfide agents dozing system of the wastewater treatment station is started. By adding sulfide chemicals, the concentration of thallium pollutants in the effluent is controlled to ensure that the effluent can meet the standard and avoid environmental risks.

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