Study on the Removal of High-concentration Chloride Ion from Desulfurization Wastewater in Thermal Power Plant by Removing Chlorine Extractant

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Abstract. In this study, a dechlorination extractant was used to study the removal rate of high concentration chloride ion in desulfurization wastewater from thermal power plant. The test determined the optimal extraction process parameters of the chlorine removal agent by comparing the extraction of the chlorine extractant, the extraction time, the time of the static phase separation, and the method of dosing. The experiments of back-extraction time and static phase separation time were carried out to determine the optimal back-extraction process parameters of the chlorine removal agent. At the same time, the feasibility of applying the chlorine extraction agent to the cycle was verified.

1. Introduction
Limestone-gypsum wet flue gas desulfurization process is the most widely used flue gas desulfurization process in thermal power plants at present, which has the advantages of mature technology and stable operation [1-2]. Always, the HCl in the wet desulfurization flue gas, the chloride ion in the process water, and the chloride ion in the limestone continuously enter the desulfurization slurry to enrich, so that the desulfurization waste water discharged usually contains a high concentration of chloride ions. High-concentration chloride ions have many hazards such as reducing desulfurization efficiency, accelerating equipment corrosion, and affecting gypsum quality [3-5].

At present, commonly used methods for removing chloride ions at home and abroad include chemical precipitation method [6-8], membrane separation method [9-11], electrolysis method [12-14], and evaporation method [15-17]. The precipitation method has high processing efficiency but high price also. It is difficult to industrially promote because the large-scale application of precipitants is costly [18]. The membrane separation method requires special membrane technology for the desulfurization wastewater containing high chloride salt. The cost has greatly increased [19]. Electrolytic method has good effect on the application of small amount of waste water, but the operation cost is relatively high, generally used after wastewater pretreatment [20]. Although the evaporation method has good treatment effect, it has large energy consumption. The equipment is easily fouled and corroded and is not economical. It can be seen that the commonly used methods of chlorine removal currently have the disadvantages of large one-time investment, high operating costs and many restrictions. Therefore, it is of great economic importance to study an efficient and economical chlorine ion remover.

In this experiment, a chlorine removal agent was used to remove chlorine from the desulfurization wastewater from thermal power plants. Through the extraction and reuse performance evaluation tests
of the chlorine removal agent, the optimum extraction and back-extraction process parameters for the chlorine removal agent were determined. The test results showed that the chlorine removal agent could successfully reduce the chloride ion in the desulfurization wastewater to less than 500 mg/L, which solved the problem that the desulfurization wastewater could not be reused due to the excessive corrosion of the chloride pipeline equipment. The processed desulfurization wastewater can be reused because of the low concentration of the chloride ion, therefore the cost of desulfurization wastewater was further reduced in zero emission system.

2. Test content

2.1 Raw water quality
A large power plant was used as test water with Cl-=15485 mg/L and pH=7.

2.2 Test drugs
A chlorine removal agent, acid, alkali-A, alkali-B, alkali-C, alkali-D

2.3 Test principle
The principle of extractive chlorine removal is that, under the acidic conditions, the chlorine extractant reacts with H+ and Cl- in the desulfurization wastewater, and Cl- is separated from the water by complex extraction. Excluding the extraction of the chlorine extractant, the alkaline substance is used for back-extraction, and the Cl- in the extracted phase is extracted into the solution to achieve the separation of the Cl- and the chlorine extractant. The chlorine extractant can be recycled after back-extraction use.

2.4 Test methods

2.4.1 Continuous Extraction Test
Through laboratory small-scale experiments, supporting small-scale continuous test extraction device, and preliminary determination of extraction chlorine removal process parameters. This type of device was used to achieve continuous operation. During the experiment process, the previously obtained process parameters were improved, and the chlorine removal effect was tracked and evaluated. The small-scale continuous extraction experimental device was shown in Figure 1:

![Figure 1. Continuous extraction device](image)

According to the test of the simulation evaluation equipment, the final extraction method was continuous counter-current extraction, the extraction grade was 4, the extraction ratio was O/A = 1:1, the wastewater treatment capacity was about 5-6L/h, and the chlorine removal effect was obtained, which were shown in Table 1.

| Water sample | Acid Dosage | Extraction ratio | Extraction series | Stable water Cl- (mg/L) | Stable water pH |
|--------------|-------------|-----------------|------------------|------------------------|----------------|
| Raw water    | 50g/L       | 1:1.5           | 4                | 1429                   | 1-2            |
| Outflow      | /           | 3:10            | 4                | 460                    | 5-6            |
After a period of stable operation, the stable effluent water quality was shown in Table 1. After the raw water was acidified, the extraction was performed with an O/A ratio of 1:1.5 compared to the extraction, and the stable effluent Cl=1429 mg/L, the effluent pH=1-2. The extracted water was treated with O/A=3:10 for extraction without acidity adjustment, stable effluent Cl-=460 mg/L, effluent pH=5-6, and effluent Cl<500 mg/L to achieve treatment. Requirements, can enter the desulfurization system for recycling.

2.4.2 Extraction Process Study
After the desulfurization wastewater was acidified, the extraction system was dechlorinated to determine the optimal extractant ratio, the chlorine removal experiment was conducted, and the extraction comparison, mixing time, phase separation time, etc., were explored to clarify the optimum extraction technology package.

2.4.3 Back-extraction process research
Extraction desulfurization wastewater after chlorine removal can be used as reagent dilution water or desulfurization process water and other make-up water systems. After organic phase extraction was saturated, it could be used for back-extraction. For the back-extraction process, back-extraction agent selection, back-extraction comparison, mixing time, the phase separation time and other processes were further explored and the back-extraction process was optimized to determine the best back-extraction technology package.

2.4.4 Recycling Process Study
The back-extraction agent after back-extraction could be used again for recycling, and desulfurization wastewater continued to be dechlorinated. The reuse effect of the back-extraction agent after back-extraction was evaluated. The performance of the extractant, the number of cycles and the loss of the organic phase were explored, and then the entire process system route was determined.

3. Results and discussion

3.1 The best extraction process parameters
A large power plant was used as test water with Cl-=15485mg/L, pH=7. The laboratory studied the extracting process of the chlorine extractant compared to the extracting process, the mixing time and the static phase separation time. The process was tried and tested, and the extraction process was optimized to obtain the best extraction process.

3.2 Saturation extraction capacity
The wastewater was treated with acidification, and several consecutive extractions were performed with O/A = 1:1. 500 mL of a chlorine-removing extractant was continuously contacted with 500 mL of freshly-acidified wastewater. The extraction and mixing time was 5 min. The phase time was 15 minutes, and the chloride ion concentration of each extracted water was detected to obtain the chloride ion amount extracted into the extractant until the chloride ion concentration in the waste water is no longer reduced, and the extractant no longer has the extraction ability, i.e., the extractant reached chlorine saturation. The results reflected the saturated extraction capacity, which were shown in Table 2.

| No. | Outflow Cl–, mg | Extractant Cl–, mg |
|-----|-----------------|--------------------|
| 1   | 1262            | 6480.5             |
| 2   | 3961            | 3781.5             |
| 3   | 6883.5          | 859                |
Table 2 showed that when the extractant was continuously contacted with wastewater after 5 times of fresh acidification, the chlorine ion concentration in the wastewater was no longer reduced, the extractant no longer had the extraction capacity, that was, the extractant reached the saturated state of the extracted chlorine, and the saturated extraction of the extractant was performed. The capacity was 23248mg/L.

3.3 Extraction ratio
The wastewater was acidified and compared with O/A=1:5, 1:3, 1:2, 1:1, 2:1, and 3:1. The extraction and mixing time was 5 min. After the layering was completed, the effluent was tested for chloride ion, and the effect of extraction on the chlorine removal by extraction was determined. The result was shown in Figure 2.

![Figure 2](image2.png)

Figure 2. Effect of extraction ratio on chlorine removal

Figure 2 was shown that with the extraction ratio increased, the chloride concentration in the effluent gradually decreased until it was stable. When the extraction ratio was 1:1, the effluent chloride concentration was 2542 mg/L, and there was little change in the effect of chloride ion concentration on the effluent with the increase of extraction ration. In summary, the extraction ratio was optimally 1:1.

3.4 Extraction time
The wastewater was acidified and extracted once with O/A = 1:1. The extraction and mixing durations were 1 min, 5 min, 10 min, and 20 min, respectively. The effluent was subjected to chloride ion determination after the stratification was complete. Stable ion concentration gives the best extraction stir mixing time. The result was shown in Figure 3.

![Figure 3](image3.png)

Fig 3. Effect of extraction time on chlorine removal by extraction

As can be seen from Figure 3, with the extension of extraction time, the effluent chloride concentration gradually decreased until stable, when the extraction time was 5min, the effluent chloride concentration was 2542mg/L, and continue to extend the extraction time, the effluent chloride
ion concentration did not change much. In summary, 5 min was the optimal extraction time for chloride extraction.

3.5 Static phase separation time
The wastewater was acidified, and the extraction was performed with an O/A ratio of 1:1. Extraction and mixing time was 5 min, and the phase separation time was 5 min, 10 min, 15 min, and 20 min, respectively. The effluent chloride and COD were measured. The initial determination of the phase separation time had an effect on the chlorine removal efficiency of the wastewater. The high COD concentration reflected more entrained extractant in the water. The high concentration of chloride ions in the washing solution reflects more entrained wastewater in the extraction phase, and vice versa. The results of the effluent chloride and COD concentrations were shown in Table 3.

Table 3. Effect of static phase time on chlorine removal efficiency of wastewater

| Static phase separation time, min | Effluent Cl⁻, mg/L | Effluent COD, mg/L |
|----------------------------------|--------------------|--------------------|
| 5                                | 2524               | 15461              |
| 10                               | 2524               | 3548               |
| 15                               | 2524               | 2060               |
| 20                               | 2524               | 2007               |

Table 3 was shown that static phase separation time had no effect on the concentration of chloride ions in the effluent. With the extension of the static time, the effluent COD gradually decreased. When the static phase separation time was 15 minutes, the effluent COD was 2060 mg/L and continued to prolong. The phase separation time had little effect on the effluent COD.

The wastewater was acidified and compared with O/A=1:1 for one extraction. The extraction and mixing time was 5 minutes. The phase separation time was 5 minutes, 10 minutes, 15 minutes, and 20 minutes respectively. O/A = 1:1 water washing, the chlorine ion concentration in the water washing solution was measured, and the influence of the static phase separation time on the extraction phase was initially determined. The results were shown in Table 4.

Table 4. Effect of static phase time on extraction phase

| Static phase separation time, min | Washing solution Cl⁻, mg/L |
|----------------------------------|-----------------------------|
| 5                                | 1685                        |
| 10                               | 530                         |
| 15                               | 145                         |
| 20                               | 133                         |

Table 4 showed that with the standing time prolonged, the concentration of chloride ions in the water-washing solution gradually decreased until stable, and when the static phase separation time was 15 minutes, the chlorine ion concentration of the water-washing solution was 145 mg/L. The phase separation time had little effect on the concentration of chloride ions in the washing solution, with extension continued. In summary, 15 minutes was optimal for the phase separation.

3.6 The optimal back-extraction process parameters
After the wastewater was extracted and dechlorinated, the extracting agent complexed the chloride ions into the extraction phase. The back-extraction was the process of back-extraction the chloride ions in the extraction phase into the aqueous phase. The extraction phase become an extraction agent and could be used in the extraction of the waste water to remove chlorine. Therefore, the back-extraction process was the key to whether the extractant could be recycled. Only when back-extraction was achieved, it was meaningful to extract chlorine.

3.7 Screening agent
Four different inorganic basic substances: alkali-A, alkali-B, alkali-C, and alkali-D were subjected to back-extraction test. Four kinds of back-extraction agents were added in equimolar amounts to 20 mL of water, compared to O/A=5 :1. Perform a single back-extraction with a back-stirring mixing time of...
5 min. After the phase separation was completed, checked the effluent status and the effluent chloride ion concentration. Taken into consideration the back-extraction effect and the chemical cost and obtain the best back-extraction agent. The test results were shown in Table 5.

| Back-extraction agent | Effluent Cl⁻, mg/L | Back-extraction efficiency | Back-extraction effect |
|------------------------|-------------------|-----------------------------|-----------------------|
| alkali-A               | 57539             | 49.50%                      | Water turbidity, extractant precipitation |
| alkali-B               | 66542             | 57.20%                      | Water clarification, extractant emulsification |
| alkali-C               | 69854             | 60.10%                      | Water clarification, extractant emulsification |
| alkali-D               | 69792             | 60%                          | Water clarification, extractant clarification |

Table 5 showed that the use of alkali-A for back-extraction reagents would not only have a relatively low back-extraction efficiency but also caused turbidity in both the back-extraction water and the extractant. At the same time, it would easily cause fouling of the equipment, therefore, it was not suitable for continuous production. The use of alkali-B and alkali-C for back-extraction reagents, although the extractive water was clarified, the extractant was not easily separated by emulsification, so it was not suitable for continuous production. At the time of D, not only the back-extraction efficiency was relatively high, but also the back-extraction water and the extractant were clarified, which was suitable for continuous production.

Using equimolar base-D as a back-extraction agent, compared with O/A=5:1, 100 mL of the extracted phase was continuously contacted with 20 mL of fresh back-extraction solution four times, and the chlorine ion concentration of each outlet water was tested to verify whether it could completely extract the chloride ions in the extraction phase. The experimental results were shown in Table 6.

Table 6. Alkali-D back-extraction effect

| Back-extraction times | Effluent Cl⁻, mg/L | Overall back-extraction efficiency |
|-----------------------|-------------------|---------------------------------|
| Once                  | 69792             | 60.0%                           |
| Twice                 | 44636             | 98.4%                           |
| Three times           | 1511              | 99.7%                           |
| Four times            | 232.5             | 99.9%                           |

Table 6 showed that when 100 mL of the extracted phase was continuously contacted with 20 mL of fresh back-extraction solution twice, the overall back-extraction efficiency reached 98.4%; when the back-extraction solution was continuously contacted four times, the overall back-extraction efficiency reached 99.9%. The results showed that alkali-D was trpped completely as a back-extraction agent.

3.8 Comparison of back-extraction

100mL saturated extraction phase was taken, alkali-D as a back-extraction agent, a single extraction was compared to O/A = 10:1, 10:2, 10:3, 10:4 for a single extraction, and the back-stirring mixing time was 5 min. After the stratification was completed, the effluent was tested for chloride ions. When the amount of chlorine ions extracted was stable, the best back-extraction ratio could be obtained. The result was shown in Figure 4.
Fig. 4. Effect of back-extraction on back-extraction effect

Fig. 4 showed that with the back-extraction ratio increased, the amount of chlorine ions stripped gradually increased until it was stable. When the back-extraction ratio was 10:2, the concentration of chloride ions in the back-extraction water reached the highest. The amount of chloride ions extracted was 2321.9 mg. The effect of continuously increasing the back-extraction amount on the amount of stripped chlorine ions did not change much. The test results showed that the name back-extraction was optimal for the back-extraction ratio of 10:2.

3.9 Back-extraction time

100mL of saturated extraction phase was taken, alkali-D as a back-extraction agent, a single extraction was compared to O/A=5:2, extraction and mixing time was 1min, 5min, 10min, and 20min, respectively. After the determination of the water chloride ion concentration, when the effluent chloride ion concentration was stable, the best extraction and mixing time could be obtained. The result was shown in Figure 5.

Fig 5. Effect of mixing time on back-extraction effect

Figure 5 showed that with the mixing time for back-extraction increased, the concentration of chloride ions in the effluent gradually increased and then stabilized. When the back-extraction time was 5 min, the concentration of chloride ion in the effluent was 56991mg/L. The concentration of chloride ion in the effluent did not change a lot with the time of back-extraction extended. The result showed that 5 min was optimal for back-extraction time.

3.10 Static phase separation time

100 mL saturated extraction phase was taken, alkali-D as a back-extraction agent, a single extraction was compared to O/A = 10:2, back-extraction mixing time was 5min, and the static phase separation time was 5 min, 10 min, 20 min, 30 min respectively. The concentration of chloride ion and COD in
the back-extraction solution was measured, and the effect of the static phase separation time on the back-extraction solution was initially determined. The results were shown in Table 7.

Table 7. Effect of static phase separation time on back-extraction solution

| Static phase separation time | Back-extraction solution Cl⁻ (mg/L) | Back-extraction solution COD (mg/L) |
|-----------------------------|-------------------------------------|-------------------------------------|
| 5min                        | 116095                              | 2649                                |
| 10min                       | 116095                              | 863                                 |
| 20min                       | 116095                              | 183                                 |
| 30min                       | 116095                              | 179                                 |

Table 7 showed that the static phase separation time had no effect on the concentration of chloride ions in the back-extraction solution. With the static phase separation time prolonged, the COD concentration of the back-extraction solution gradually decreased. When the static phase separation time was 20 min, the effluent COD was 183 mg/L. Continued to extend the phase separation time had little effect on the effluent COD.

Another 100 mL of saturated extraction phase was taken, alkali-D was used as a back-extraction agent, a single extraction was performed at a ratio of O/A=10:2, the mixing time for back-extraction was 5 min, and the static phase separation time was 5 min, 10 min, 20 min, 30 min, respectively and the extraction agent compared to water was O/A = 1:1. The results were initially determined the phase separation time of the extractant and were shown in Table 8.

Table 8. Effect of static phase time on extractant

| Static phase separation time (min) | Water-washing solution Cl⁻ (mg/L) |
|------------------------------------|-----------------------------------|
| 5                                  | 9564                              |
| 10                                 | 3349                              |
| 20                                 | 335                               |
| 30                                 | 321                               |

Table 8 showed that with the prolongation of the standing time, the chloride ion concentration of the water-washing solution gradually decreased. When the static phase separation time was 20 minutes, the chlorine ion concentration of the water-washing solution was 335 mg/L. Continued to extend the phase separation time had little effect on the chloride ion concentration in the solution. The result showed that 20 minutes was the optimal static phase separation time.

3.11 Evaluation of extractant recycling effect

The wastewater was treated with acidification to perform several consecutive extractions with O/A = 1:1, and the extraction agent was continuously contacted with freshly-acidified wastewater. The extraction and mixing time was 5 min, and the static phase separation time was 15 min. The concentration of chloride ions, which extracted into the extractant, was measured every time until it was no longer reduced. At that time, the extractant no longer had the ability to be reused, that was, the extractant reached the chlorine saturation state. The results were shown in Table 9.

Table 9. Saturated extraction capacity of recycled extractants

| NO. | Effluent Cl⁻, mg | Extract Cl⁻, mg |
|-----|------------------|-----------------|
| 1   | 1180.5           | 6562            |
| 2   | 3825.5           | 3917            |
Table 9 showed that when the reused extractant was continuously contacted with the wastewater after the fresh acidification for five times, the chloride ion concentration in the wastewater was no longer reduced, and the extractant no longer had the extraction capability, that was, the reused extractant reached the chlorine saturation state. The saturated chlorine extraction capacity was 23156 mg/L, which was not significantly different from the original extraction solvent's saturated chlorine extraction capacity of 23248 mg/L. In summary, the reclaimed extractant obtained by this process still has a high saturated chlorine extraction capacity and can be recycled.

4. Conclusion

4.1 Extraction process parameters
● After desulfurization wastewater was removed by continuous counter-current extraction, chlorine content of original desulfurization wastewater could be reduced from 15485 mg/L to <500 mg/L, which reached the treatment requirements. The treated desulfurization wastewater could enter the desulfurization system for cycle use.
  ● The test results showed that, based on the acidified wastewater, the optimization parameters of the extraction and dechlorination process were as follows: one extraction was performed with a ratio of O/A=1:1, the extraction reaction time was 5 min, and the static phase separation time was 15 min.
  ● The saturated chlorine extraction capacity of the chlorine extractant was 23248 mg/L.

4.2 Back-extraction process parameters
The test results showed that on the condition that saturated chlorine extraction capacity was 23248 mg/L, the optimization parameters for the back-extraction were as follows: the back-extraction agent as alkali-D, the back-extraction ratio was O/A=10:2, back-extraction mixing time was 5 min and the static phase separation time was 20 min.

4.3 Evaluation of extractant recycling effect
The extractive and back-extractive chlorine removal test was conducted at the same process parameters. The saturated extracting chlorine capacity of the reused extractant was 23,156 mg/L, which was not significantly different from the saturated extracting chlorine capacity of the original extractant 23248 mg/L. The test results showed that the reused extractant obtained by this process still had a high saturated chlorine extraction capacity and could be recycled.

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