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Research Article

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Experimental Study on the Control of Wire Pickling Solution Concentration

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Abstract

Using diffusion dialysis technology, hydrochloric acid pickling solution from wire surface treatment is recovered. By adding new hydrochloric acid, the pickling solution maintains the concentration necessary for regular production, allowing continuous recycling in wire pickling to reduce the consumption of new hydrochloric acid. This study investigates the effects of the water-to-acid flow ratio, hydrochloric acid concentration, ferric chloride concentration, and receiving solution on the acid recovery rate and ferric chloride retention rate. The results indicate:

- *The water-to-acid flow ratio and receiving solution have little impact on acid recovery;*
- *As the hydrochloric acid concentration increases, the recovery rate gradually decreases from 92% to about 85%, while the retention rate conversely increases from 75% to around 83%;*
- *As the ferric chloride concentration increases, the recovery rate slowly rises, peaking at 92% when the ferric chloride concentration reaches 150 g/L, then slightly decreases, while the retention rate shows the opposite trend*
- *Recovered acid with a concentration of 238 g/L effectively treats rusted wire. The experiment confirms that diffusion dialysis technology can effectively reduce production costs and improve efficiency.*

1. Introduction

In the metal products industry, hydrochloric acid pickling is generally used to remove the oxide layer from the surface of wire rods, which generates a large amount of waste pickling solution. Direct discharge of waste pickling solution can cause serious water and soil pollution. Many researchers at home and abroad have carried out extensive research on the recovery and utilization of waste hydrochloric acid. Conventional methods for treating waste hydrochloric acid include neutralization, evaporation separation and spray roasting [1,2]. In recent years, new techniques such as membrane distillation and diffusion have been proposed for treating waste hydrochloric acid [3-5]. The diffusion dialysis method is based on the principle of concentration gradient diffusion, which is a spontaneous separation process in which ions pass through an ion-exchange membrane from a high-concentration area to a low concentration area.

Due to factors such as the rust condition of the wire rods, the concentration of hydrochloric acid in the pickling solution, and the pickling time, it is inevitable that over-pickling will occur during the process to ensure the cleanliness of the wire rods. Therefore, controlling the concentration of hydrochloric acid in the pickling process is especially important. The diffusion dialysis technique is used to treat the pickling solution in a centralized pickling tank online, retaining ferrous chloride and recovering hydrochloric acid. By adding new hydrochloric acid, the concentration is maintained for normal production use, and the acid is recycled for wire rod pickling. This not only reduces the consumption of new hydrochloric acid and lowers the cost of treating waste acid, but also prevents resource waste and reduces environmental pollution. Additionally, controlling the concentration of hydrochloric acid during the pickling process helps to avoid over-pickling. Compared to existing pickling processes and outsourced waste acid treatment methods, the economic and social benefits are significant.

This study investigated the effects of water-acid flow ratio, hydrochloric acid concentration, ferrous chloride concentration, and receiving liquid on the recovery and retention rates of the diffusion dialysis unit. By preparing a pickling solution with a specific concentration for wire rod pickling experiments and designing the concentration control process through material balance calculations, this research provides a basis for online control of hydrochloric acid concentration.

2. Test Section

2.1 Principle of Diffusion Dialysis Method

The principle of diffusion dialysis is shown in Figure 1. It operates using the concentration gradient as the driving force, where small solvent molecules in the solution diffuse toward the water side. The anion-exchange membrane's framework is positively charged, which attracts negatively charged hydrated ions while repelling positively charged hydrated ions. As a result, under the influence of concentration, the anions on the waste acid side are drawn through the membrane's channels to the water side. To maintain electrical neutrality, positively charged ions are also carried along. Since H+ ions have a smaller hydration radius and fewer charges, while the hydrated ions of metal salts are larger and often have higher valency, H+ ions preferentially pass through the membrane. In this way, the acid in the waste solution is separated out [6].

2.2 Test Equipment and Chemicals

• Experimental Equipment

Ultrafiltration membrane filter GUJPF-12-79-3-BL-30 (Jiangyin Jinshui Membrane Co., Ltd., pore size 30 nm); diffusion dialysis unit HKY-001 (Shandong Tianwei Membrane Technology Co., Ltd., membrane area 0.08 m²).

• Experimental Materials

Rusty wire rod with a diameter of Φ 6 mm (Zhangjiagang Shagang Group, steel grade 82B, length 6 cm, weight 31.2 g).

• Chemicals Required for the Experiment are listed in Table 1, all of analytical grade.

3. Method

Collect the acid wash liquids of different concentrations used in the acid wash tank, filter them with an ultrafiltration membrane filter, and pass the filtered acid wash liquid and the receiving liquid into the diffusion dialyzer at a certain water-acid flow ratio at room temperature, measure the flow of the recovered acid and dialysate, titrate the hydrochloric acid concentration and ferrous chloride concentration of the recovered acid and dialysate, calculate the hydrochloric acid recovery rate (hereinafter referred to as the recovery rate) and the ferrous chloride retention rate (hereinafter referred to as the retention rate) to examine the treatment effect of the equipment. The calculation formula for the hydrochloric acid recovery rate and the ferrous chloride retention rate is:

$$Hydrochloric\ acid\ recovery\ rate = \frac{Q_1C_1}{Q_1C_1 + Q_2C_2} \times 100\% \quad (1)$$

$$Ferrous\ chloride\ retention\ rate = \frac{Q_2C_1}{Q_1C_3 + Q_2C_1} \times 100\% \quad (2)$$

In formula (1) and formula (2), Q1 and Q2 are the flow rates of the recovered acid and dialysate, respectively; C1 and C2 are the hydrochloric acid concentrations of the recovered acid and dialysate, respectively; C3 and C4 are the ferrous chloride concentrations of the recovered acid and dialysate, respectively.

The hydrochloric acid concentration was determined by titration, and 1.0 mol/L sodium hydroxide was prepared, with methyl orange as the indicator. The ferrous chloride concentration was determined by potassium dichromate redox titration, and 0.033 3 mol/L potassium dichromate was prepared, and sodium diphenylamine sulfonate was used as the indicator for titration.

4. Results

4.1 Effect of Water-Acid Flow Ratio on Recovery and Retention Rate

By conducting a diffusion dialysis test on a pickling solution with a known hydrochloric acid concentration of 220 g/L and a ferrous chloride concentration of 58.2 g/L, the recovery rate and retention rate data under different water acid flow rate ratios were plotted and shown in Figure 2.

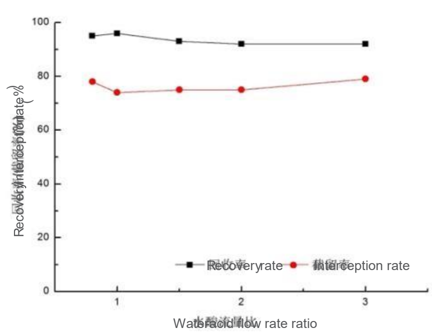

Figure 2: Effect of Different Water-Acid Flow Ratios on Recovery and Retention

As can be seen from Figure 2, as the water-acid flow ratio increases, the recovery rate slowly increases. When the water-acid flow ratio is 1, the recovery rate reaches 92%, and then slowly decreases, while the retention rate is the opposite. But in general, at different water-acid flow ratios, the recovery rate is above 90%, and the retention rate is between 75% and 80%. This is because the water-acid flow ratio will affect the solute diffusion rate and solution concentration in the equipment, but it has little effect within the test flow rate of 7~14 mL/min, and its range of variation is within 5%. Taking into account the recovery rate, retention rate and equipment operating capacity, the water-acid flow ratio was set to 1.5 when conducting the next test.

4.2 Effect of Hydrochloric Acid Concentration on Recovery and Retention Rate

In the pickling solution with a known ferrous chloride mass concentration of 58.2 g/L, the water-acid flow ratio is 1.5, and the recovery rate and retention rate of different hydrochloric acid concentrations measured in the experiment are shown in Figure 3. The experimental design simulates the hydrochloric acid mass concentration of 50 ~ 250 g/L.

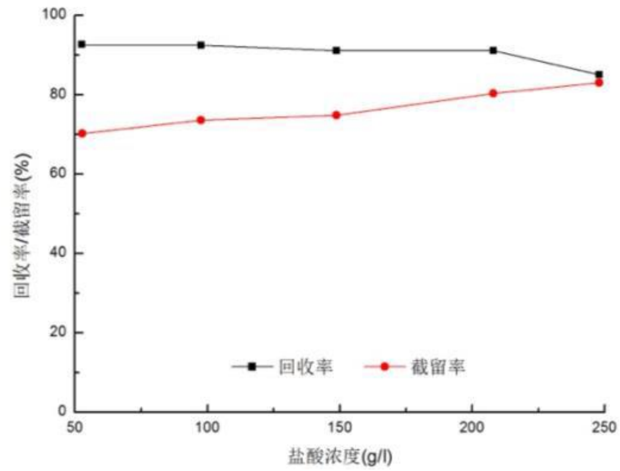

Figure 3: Effect of Different Hydrochloric Acid Concentrations on Recovery and Retention Rate

As can be seen from Figure 3, with the increase of hydrochloric acid concentration, the recovery rate gradually decreases from 92% to about 85%, while the retention rate increases slowly from 75% to about 83%. In order to obtain high recovery rate and retention rate at the same time, it is better to control the mass concentration of hydrochloric acid at 150~200 g/L.

4.3 Effect of Ferrous Chloride Concentration on Recovery and Retention Rate

In the pickling solution with a known hydrochloric acid concentration of 190 g/L, the water-acid flow ratio is 1.5, and the experimentally measured recovery and retention rate data of different ferrous chloride concentrations are shown in Figure 4. The experimental design simulates the waste acid ferrous chloride concentration of 50 ~ 200 g/L.

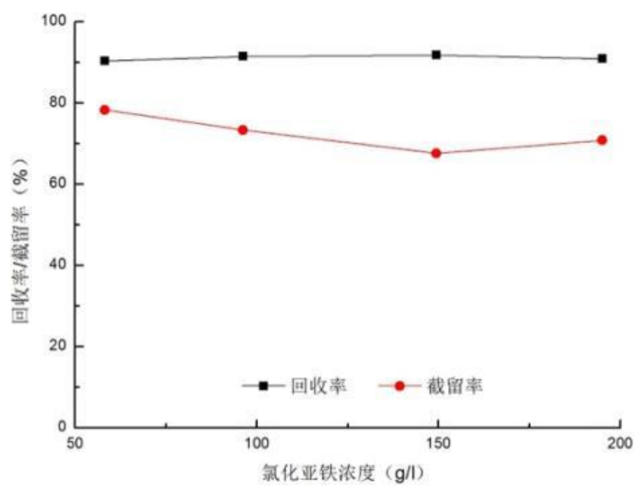

Figure 4. Effect of Ferrous Chloride Concentration on Recovery and Retention Rate

As can be seen from Figure 4, with the increase of ferrous chloride concentration, the recovery rate slowly increases, reaching 92% when the ferrous chloride mass concentration is 150 g/L, and then slightly decreases; the retention rate is the opposite. Considering the recovery rate and retention rate comprehensively, when the ferrous chloride mass concentration in the original acid wash solution is 80 ~ 120 g/L, the diffusion dialysis effect is better.

4.4 Effect of Receiving Solution (Tap Water/Acidic Water) on Recovery and Retention Rate

In the experiment, the effects of tap water and acidic water on the recovery rate and interception rate were studied, with the hydrochloric acid mass concentration of 198.8 g/L, the ferrous chloride mass concentration of 58.2 g/L and the water-acid flow ratio of 1.5, as shown in Figure 5.

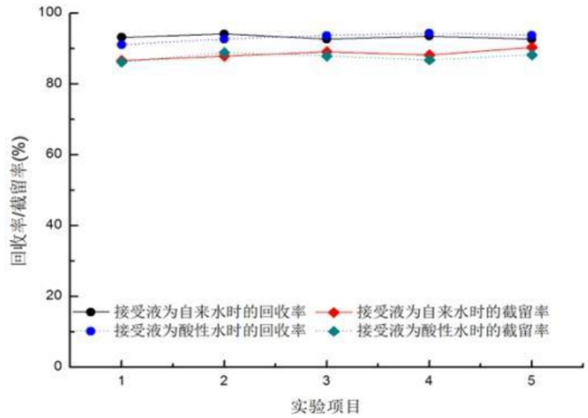

Figure 5: Effects of Different Receiving Solutions on Recovery and Retention Rates

As can be seen from Figure 5, the overall difference between the recovery rate and the interception rate of the two different receiving solutions is not much. It can be seen that using acidic water instead of tap water as the receiving solution has little effect on the recovery rate and the interception rate. Therefore, in actual production applications, it can be considered to use acidic flushing water instead of tap water to reduce costs.

5. Discussion: Experimental Study on Pickling Process with Recycled Acid

5.1 Comparison of Pickling Test between Recovered Acid and Concentrated Hydrochloric Acid

In order to observe the pickling effect of the recycled acid, 50 mL of recycled hydrochloric acid with a mass concentration of 160-200 g/L was used to pickle the Φ6 mm rusty wire rod. The test results are shown in Figure 6.

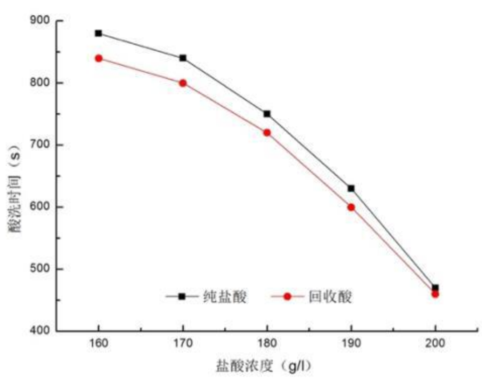

Figure 6: Pickling time of Wire Rod with Different Concentrations of Hydrochloric Acid

As can be seen from Figure 6, within the test range, the recovered acid has a better pickling effect than pure hydrochloric acid at the same concentration, and the pickling time is shortened by about 60 s. This is because the ferrous chloride in the recovered acid has a certain promoting effect on pickling.

5.2 Comparison of Pickling Time of Hydrochloric Acid Washing Solution with Simulated Mass Concentration of Recovered Acid of 238 G/L

In order to meet the requirements of the pickling process in the centralized pickling workshop, the hydrochloric acid concentration is usually controlled at 95~238 g/L in normal use. In order to investigate the pickling effect of the pickling solution after online acid concentration control, the dilute hydrochloric acid concentration of 238 g/L prepared by diluting the concentrated hydrochloric acid with a mass concentration of 428 g/L was used as the pickling solution reference object, and the recovered acid with different concentrations produced by the existing diffusion dialyzer was prepared with the concentrated hydrochloric acid with a mass concentration of 428 g/L to prepare the test hydrochloric acid with a hydrochloric acid concentration of 238 g/L, as shown in Table 2. The pickling process environment of the workshop was simulated, and the wire rod pickling test was carried out on various prepared acids. The pickling effect of the pickling solution with the same concentration under this method and the current pickling process was compared, and the pickling time of the cleaned wire rod was compared. The results are shown in Figures 7 and 8.

Project	Recovered acid mass concentration/(g•L-1)	V (recovered acid) /V(428g/L HCl)	Pickling liquid mass concentration/(g•L-1)
1	190	1:0.25	
2	202	1:0.187 5	
3	214	1:0.125	238
4	226	1:0.062 5	
5	238	——	

Table 1: Preparation of 238g/L Pickling Solution

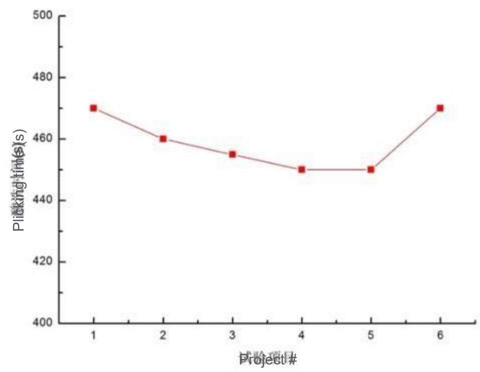

Figure 7: Pickling time of Each Pickling Solution At 238g/L Hydrochloric Acid Concentration

Figure 8: Effects of Various Pickling Solutions on Wire Rod Pickling At a Mass Concentration of 238 G/L Hydrochloric Acid

As can be seen from Figure 8, the pickling effect of the pickling solution under the simulated state is similar to that of the dilute hydrochloric acid with a mass concentration of 238 g/L prepared with concentrated hydrochloric acid with a mass concentration of 428 g/L. The pickling time of a single wire rod can be saved by about 20 s.

The test treats the residual liquid by adding alkali to neutralize it. The calculated cost can be reduced by 3,800 yuan per day compared with the technical cost of the existing pickling process. See Table 3 for details.

Techniques	Types of consumables	Fee	Total fee
Existing pickling process	30% new acid	7 500	9 772.5
	Tap water	22.5	
	Waste acid treatment	2 250	
Diffusion dialysis technology	30% new acid	3 500	5 960.5
	Tap water	40.5	
	Equipment loss	420	
	Residue treatment	1 350	
	Residual waste acid treatment	650	

Table 2: Comparison of the Cost of Treating Waste Acid Using the Current Pickling Process and Diffusion Dialysis Technology / (Yuan/Day)

6. Conclusion

The diffusion dialysis technology is used to treat the pickling liquid of the centralized pickling tank. When the hydrochloric acid concentration in the pickling liquid is controlled at 100-150 g/L and the ferrous chloride concentration is controlled at 80-120 g/L, the recovery rate of the recovered acid can be above 90% and the interception rate can be 75%-88%. The diffusion dialysis effect is significant. In the experimental study of acid recovery by diffusion dialysis, the water-acid flow ratio and the receiving liquid have little effect on the recovery rate and interception rate, while the hydrochloric acid concentration and the ferrous chloride concentration have a greater impact on the recovery of hydrochloric acid. The recovered pickling liquid is used for wire rod pickling production after being prepared according to production requirements. The pickling effect is good, with obvious social and economic benefits.

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