

Study on closed recycling regeneration process of FeCl₃ waste etching solution and recovery of Copper

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Abstract. FeCl₃ etching solution is widely used in etching processes due to its strong oxidation and corrosion properties. However, significant amounts of waste etching solution is produced, which pollutes the environment and wastes materials. Aiming to address problems related to the use of recycled FeCl₃ waste etching solution containing Cu, the crystallization regeneration process in an enterprise was improved and the copper element was recovered in the form of copper chloride crystal. Based on the original process, a hydrocyclone was added to pre-separate the slurry. By investigating the change of the inlet flow rate and separation efficiency of the hydrocyclone with inlet pressure under different concentrations, the optimal inlet pressure was determined to be approximately 0.25Mpa. Experimental results indicated that the workload of the centrifuge was reduced by approximately 80%, the average specific surface area of the copper chloride crystal was decreased by 50%, the production of copper chloride crystal byproducts after washing process was increased by approximately 20% and regeneration of FeCl₃ waste etching solution was also realized.

1. Introduction

FeCl₃ etching solution has strong oxidative and corrosive effects on metals such as Fe, Cu, etc. Additionally, it is lower in price and provides a faster etching speed than other etching solutions such as cupric chloride etching solution [1]. Therefore, FeCl₃ etching solution is widely utilized in the etching process of Printed Circuit Boards (PCBs) [2]. However, there is a large amount of FeCl₃ waste etching solution produced during the etching process, which has strong corrosiveness and contains significant amounts of Fe³⁺, Cu²⁺ and other metal ions. If directly discharged, this will cause serious pollution to the environment and waste metal resources. In recent years, with the rapid development of PCB and the increasing scarcity of metal resources in China, the use of recycled FeCl₃ waste etching solution has become a major topic in the field of metal resource recycling and environmental protection [3].

At present, the iron powder replacement method, the ferrous sulphide precipitation method, the crystal electrolysis method, the solvent extraction method and the ionic membrane electrolysis method are frequently used to regenerate FeCl₃ waste etching solution, but many problems exist in the use of these methods. For example, the purity of copper recovered by the iron powder replacement method is not high and the first reduction and second oxidation process not only wastes expensive iron powder but also increases the consumption of chlorine [4]. The ferrous sulphide precipitation method requires iron powder and sulphur powder to generate ferrous sulphide, but the reaction is violent and easily results in secondary pollution [5]. The purity of metal recovered by the crystal electrolysis method is very high, while the energy consumption of the electrolysis process is quite high and results in a large amount of chlorine generated near the anode, resulting in severe equipment corrosion [6]. The solvent



extraction method achieves good separation of Fe and Cu, however the process is complicated, and the introduction of the extraction solvent reduces the purity of the regeneration liquid [7]. In the ionic membrane electrolysis method, FeCl_3 waste etching solution can be generated in the anode chamber, and the cathode liquid can be returned to the anode chamber after removal of Cu^{2+} . Although the ionic membrane electrolysis method is environmental friendly, it is very difficult to match the selection of the ion exchange membrane and electrolytic process [8]. Additionally, the processing cost is so high that it cannot be extended to large-scale industrial applications. Therefore, it is of great significance to determine a method of waste etching solution which possesses higher processing capacity, higher added value of recycled products, lower energy consumption and is less polluting to the environment.

Considering that the crystallization technology does not introduce additional substances, has low operating temperature and can improve the operating environment [9], this work primarily investigates the crystallization method to process FeCl_3 waste etching solution containing Cu, in order to achieve the regeneration of waste and the recovery of the copper element.

2. Regeneration process and equipment of FeCl_3 waste etching solution containing Cu

2.1. Regeneration process of FeCl_3 etching solution containing Cu

The common concentrations of Fe^{3+} , Fe^{2+} , Cu^{2+} are 30%, 0.5%, 2.6%, respectively, in FeCl_3 waste etching solution containing Cu, while in standard etching solution, the Fe^{3+} concentration is at least 38%, the Fe^{2+} concentration is less than 0.4% and the Cu^{2+} concentration is less than 2.6% [10]. Therefore, the removal of Cu^{2+} from the waste solution is the key to realizing the regeneration of FeCl_3 waste etching solution. This work analysed the original treatment process of waste etching solution of an enterprise. The solubility of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in water is shown in Table 1 [11]. The solubility of ferric chloride changes remarkably with temperature while the solubility of copper chloride increases slightly as temperature increases. Additionally, the crystallization temperature of ferric chloride is greater than that of copper chloride.

Table 1. The solubility of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in water.

Temperature (°C)	0	10	20	30	40	50	60	70	80	90	100
Solubility $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (g)	74.4	81.8	91.9	107	—	315	—	—	526	—	536
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	67.7	70.8	73.7	77.3	80.8	84.2	87.6	92.3	96.1	104	110

The copper element is recovered in the form of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ by decompression-evaporation and concentration crystallizing. When the concentration of Cu^{2+} in solution is less than 0.5%, the remaining of Cu^{2+} is removed completely by cooling crystallization. Finally, water and chlorine are added to the waste etching solution to regenerate the FeCl_3 waste etching solution. The process flow chart before modification is shown in figure 1.

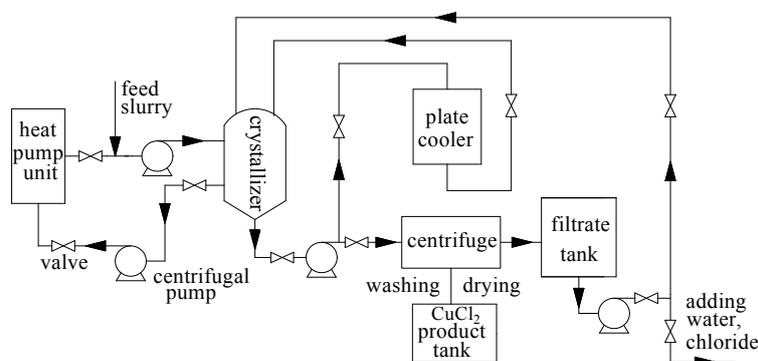


Figure 1. Process flow chart before modification.

However, when the enterprise prepared copper chloride crystals, the crystal slurry after evaporative crystallization was directly transported to a centrifuge for solid-liquid separation. The original process had many deficiencies, the main points of which are summarized as follows. First, the capacity of the centrifuge was limited, thus the evaporative crystallization system was unable to operate continuously. When the copper chloride reached saturation, the slurry became thick and sticky. If the crystals stayed in the crystallizer for a long period of time instead of being separated in a timely manner, the crystal stuck to the wall of tubes, affecting the heat transfer efficiency of the heat exchanger [12]. Secondly, grains were large enough to induce wear on the impeller of the pump, shortening its service life. In addition, the centrifuge separation process did not belong to the closed operation and small crystals often dissipated into the air with vapor, which not only increased the heat loss, but also aggravated the powder pollution. Finally, nearly half of the copper chloride crystals obtained from the centrifuge were less than 70 microns in diameter, increasing the specific surface area of the crystals, making it more possible for them to stick to ferric chloride crystals and diminish during the washing process. Based on these problems, this work improved the separation process of copper crystals and the mother liquor achieved by the centrifuge alone. The process flow chart after modification is shown in figure 2.

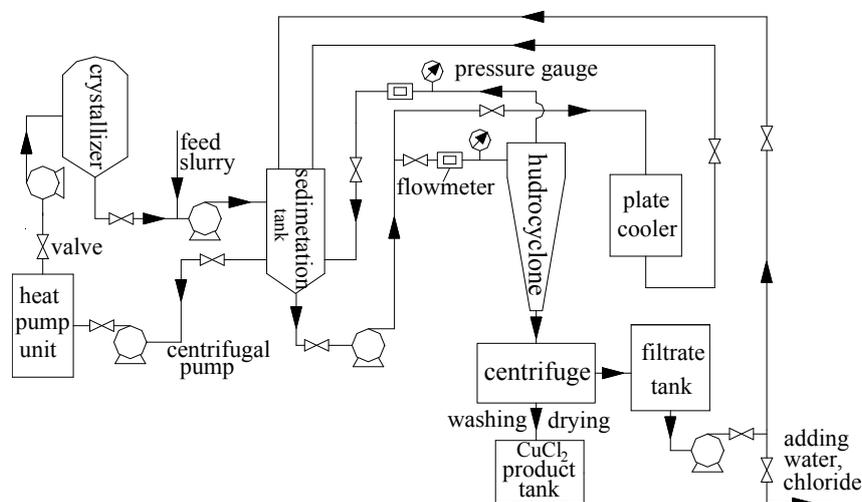


Figure 2. Process flow chart after modification.

2.2. Regeneration equipment of $FeCl_3$ waste etching solution

Based on the original equipment, a sedimentation tank and a hydrocyclone were added to pre-separate the crystal slurry, and then the centrifuge was employed to separate the thick slurry from the underflow. The crystal slurry was separated in a hydrocyclone [13] in a closed environment. Most of the fine slurry passed through the overflow tubes and returned to the setting tank, and approximately 20% of the thick slurry passed through the underflow tube into the centrifuge. This could reduce the processing capacity of the centrifuge and relieve heat loss and powder pollution. Furthermore, there were many crystals in the overflow liquid of the hydrocyclone. These were returned to the setting tank as crystal seeds to promote the secondary nucleation [14], which could result in a more uniform particle size.

This equipment primarily included one water source heat pump unit with a heat supply of 455KW and a power of 144.4KW, one vortex air cooled water chilling unit with a cooling capacity of 119.1KW and a power of 41.7KW, one root water jet vacuum pump unit with a power of 14KW, a hydrocyclone with a nominal diameter of 75mm, one three-foot centrifuge with a rotating speed of 1200r/min and a motor power of 5.5KW, five centrifugal pumps with 11KW of power, one crystallizer, regulating valves, pressure gauges, flow meters, pipelines, etc.

3. Industrial trial operation of regeneration of $FeCl_3$ waste etching solution

3.1. Materials of industrial trial operation

Before the FeCl₃ etching solution was treated, the concentration of Fe³⁺, Fe²⁺ and Cu²⁺ were 31.5%, 0.6%, and 3%, respectively. The copper chloride crystal size distribution before process modification is shown in table 2. The average size of the crystals was approximately 70 microns; therefore, it was necessary to separate particles smaller than 70 microns and return them to the setting tank to continue their growth in order to obtain high quality crystals.

Table 2. The size distribution of copper chloride crystal separated directly by the Centrifuge.

Size (μm)	Distribution (%)						
1.19	0.1	20	1.38	63.25	5.82	200	2.87
1.74	0.27	22.44	1.71	70.96	5.74	224.40	2.32
2.69	0.3	25.18	2.13	79.62	5.69	251.79	2.01
4.26	0.59	28.25	2.73	89.34	5.34	282.51	1.75
6.02	0.96	31.70	3.21	100.24	4.73	316.98	1.06
8.45	0.95	35.57	3.59	112.47	4.38	355.66	0.74
10.62	1.22	39.91	4.12	126.19	4.19	399.05	0.49
13.39	1.54	44.77	4.63	141.59	3.65	447.74	0.36
15.00	0.83	50.24	4.85	158.87	3.44	533.03	0.57
17.83	1.22	56.37	4.97	178.25	3.25	671.04	0.3

3.2. Process of industrial operation

During system operation, 0.65 tons of waste etching solution was treated per hour with a vacuum pressure of 0.08Mpa and a heating temperature of 55 °C. If the temperature was too low, ferric chloride would crystallize and reduce the purity of the copper chloride crystals; if the temperature was too high, copper chloride crystals would dissolve and production would be reduced. Regulating the valve opening allowed the inlet flow rate to be controlled at 6-10m³/h and the inlet pressure ranged from 0.15-0.30Mpa.

As the structural parameters of the hydrocyclone had been determined, its operating parameters primarily influenced the quality of the products. The change of inlet flow rate and separation efficiency with inlet pressure were investigated under three different inlet concentrations. As shown in figure 3 and figure 4, the inlet flow rate increased continuously while the separation efficiency first increased and then decreased as inlet pressure increased. However, the influence of inlet concentration on the inlet flow rate and separation efficiency was very complicated. When the inlet pressure was approximately 0.25Mpa and the concentration was 10%, the separation efficiency reached its maximum at 72.4%. Meanwhile, the inlet flow rate was 6.926m³/h with a split ratio of 20.6% and the concentration of the underflow liquid was 28.6%. The average output of crystals from the underflow reached 350kg/h, significantly satisfying the requirements of copper crystal production.

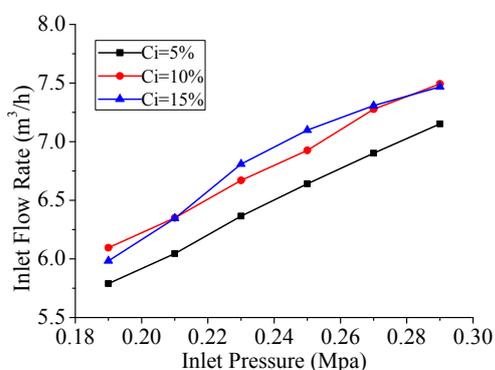


Figure 3. Relationship between inlet flow rate and inlet pressure.

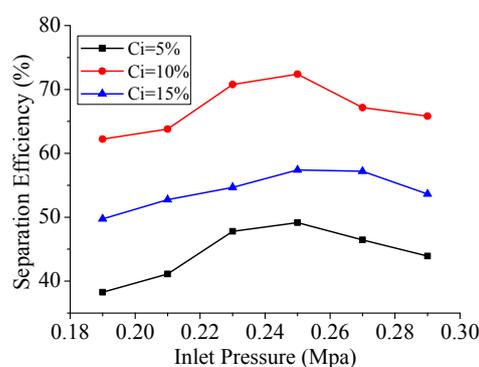


Figure 4. Relationship between separation efficiency and inlet pressure.

4. Data analysis of trial operation

In the experiments, 16 tons of waste etching solution were treated in 25 hours to obtain two tons of copper chloride crystals and approximately nine tons of regenerated FeCl₃ etching solution. Under the inlet concentration of 10% and an inlet pressure of 0.25Mpa, the size distribution of crystals in overflow slurry and underflow slurry were conducted by Mastersizer 2000. The results are depicted in Figures 5(a) and 5(b). The particle size in the overflow slurry was generally approximate to 40 microns and particles greater than 90 microns only accounted for 10%, which effectively decreased the possibility that circulating mother liquor would become stuck on the heat exchange tubes. In addition, the particle size in the underflow slurry generally consisted of 105 microns, and particles less than 40 microns only accounted for 8%. Therefore, the slurry after hydrocyclonic separation achieved an obvious thickening effect, which helped to improve the separation efficiency of the centrifuge and decreased the possibility that fine crystals could block the filter cloth. The following section primarily compares the cost and the quality of products before and after process optimization.

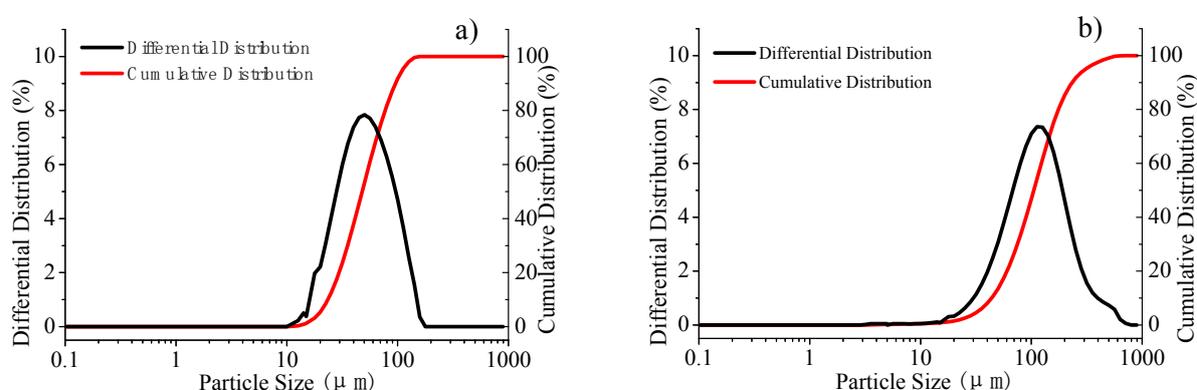


Figure 5. Particle distribution under the inlet concentration of 10% and inlet pressure of 0.25Mpa: (a) overflow particle; (b) underflow particle.

4.1. Analysis of product quality

After the slurry was concentrated by the hydrocyclone and then separated by the centrifuge, the particle mainly consisted of 105 microns and the surface area of the copper chloride crystals decreased by 50%. Therefore, after the washing treatment, production increased by 20% and its concentration increased from 95% to 98%. In the regenerated FeCl₃ etching solution, the concentrations of Fe³⁺, Fe²⁺, Cu²⁺ were 44.27%, 0.07%, 0.13%, respectively, and its density was 1454kg/m³, which meets the concentration requirements regenerated etching solution. Consequently, the closed recycling regeneration process of FeCl₃ waste etching solution and copper extraction successfully achieved the resource utilization.

4.2. Analysis of operating cost

After the process was modified, the waste etching solution was treated as a capacity of 0.65 tons per hour. According to the actual situation, the average utilization rate of the water source heat pump unit, the vortex air cooled water chilling unit and the root water jet vacuum pump unit reached nearly 90% per hour. The utilization rate of the electric motor connected to the hydrocyclone and the centrifuge was approximately 50%. Therefore, the total power per hour of the system is approximately equal to $(144.4+41.7+14+3\times 11) \times 90\% + (11+5.5) \times 50\% = 218\text{kW/h}$.

Since the capacity of the centrifuge and the heat loss of separation was reduced, the treatment of the waste etching solution per ton could save approximately 10% of electric energy as compared to the unmodified process.

4.3. Analysis of resources consumption

In terms of resource consumption, if one ton of waste etching solution was treated, considering the instability of Fe^{2+} , hydrolysis of Cu^{2+} , density and oxidation of recycled etching solution, the process required only three cubic meters of chlorine, 2.5 kilograms of hydrochloric acid and 100 kilograms of water.

The reaction of iron powder replacement of sponge copper not only consumes a large amount of expensive iron powder, but also emits significant heat, requiring high heat resistance of equipment. Additionally, the price of copper chloride crystals is approximately two times that of copper powder. Taking the consumption of chemical resources and the benefits brought from by-products into consideration, the process proposed in this work is a better choice for the processing of FeCl_3 waste etching solution containing Cu.

5. Conclusion

The significance of the closed recycling regeneration process of FeCl_3 waste etching solution is primarily the result of the following conclusions.

- After the process was modified, the evaporation and crystallization system can be run continuously, the crystal slurry flows fluently and the faults from heat pipe fouling and impeller erosion are greatly reduced.
- Crystal slurry concentration and classification are conducted in the closed environment of the hydrocyclone. Less than 20% of the concentrated slurry is separated by the centrifuge, which greatly reduces the workload of the centrifuge and thus decreases the heat loss and crystal loss caused by vapour dissipation. Simultaneously, because the average surface area of copper chloride is reduced, the surface adhesion of ferric chloride crystals and loss during the washing process are also decreased. As a result, the production of copper chloride crystals is increased by 20% and the concentration after washing is increased by 3%.
- Adopting the combination method of evaporation crystallization and cooling crystallization has many advantages compared to other methods. The production process is conducted in a closed environment and no irritating gas leakage and toxic liquid discharge is produced, which achieves zero discharge of the waste etching solution and increases the recovery of metal resources.

Acknowledgments

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