Study on regeneration and desiliconization purification of pickling waste liquid of building steel

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Abstract. In this paper, Fe₂O₃ power was used to replace the scrap steel in the traditional process, as the medium for removing the free acid in the waste acid solution of the cold-rolled strip pickling. The removal effect of free acid and silicon of the system with Fe₂O₃ addition and crap steel were compared. The results indicated that the system with Fe₂O₃ addition obtained a better effect. Subsequently, the optimum dosage, optimum reaction temperature and time were determined by the orthogonal experiment. The effect of flocculants of polyacrylamide (PAM), PAC, PAM+PAC and MgCl₂ with the desiliconization was explored.

1. Introduction
In the process of building cold rolled strip production, the conventional acid pickling waste liquid recycling process uses the spray roasting method to regenerate the waste acid. Ferrous chloride in pickling waste liquid is decomposed into hydrogen chloride gas and iron oxide powder at high temperature. Hydrogen chloride gas is absorbed to form regenerated acid, which is used for pickling line and iron oxide powder recycling. It is mainly used as raw material for coating and magnetic material industry and powder metallurgy industry [1,2]. In the traditional process, the waste acid solution is heated and a large set of steel scrap soaking tower is set up. The scrap steel sheet reacts with free acid to remove the waste acid. After cooling, ammonia water and coagulant aid are added to form large flocculates to absorb colloidal silicon and other impurities in waste acid, so as to avoid large amount of silica in waste acid, reducing the recovery efficiency of waste hydrochloric acid and cold rolled steel plate quality [3,4]. After the removal of free acid and desiliconization, the waste acid is purified, and iron oxide powder with high purity can be produced after roasting. At present, the prominent problem of this technology is not only the huge equipment, but also the unsafe hidden danger due to the hydrogen generated in the reaction process. In view of the above problems, iron oxide powder produced by acid regeneration unit itself was used as free acid removal agent instead of scrap steel sheet.

2. Experiment
2.1. Reagents and instruments
Main reagents: Fe₂O₃, iron powder, ammonia, polyacrylamide (PAM), HCl etc
Main instruments: stirrer, spectrophotometer etc
2.2. Experimental principle
Firstly, iron oxide powder reacts with free acid in waste acid (as shown in reaction formula 1). After the waste acid with free acid is cooled, ammonia water enters the high-density reaction tank through the metering pump to mix with the return sludge, and adsorbs on the surface of silicon sludge and enters into the reaction tank. By adjusting the pH value, Fe$^{2+}$ and other metal ions are generated into hydroxide. Through the air blown from the bottom of the reaction tank, it oxidizes to form precipitable Fe(OH)$_3$ (reaction formula 2-4).

Fe$_2$O$_3$+6HCl=2FeCl$_3$+3H$_2$O                          (1)
FeCl$_2$ + 2NH$_3$ + 2H$_2$O = Fe(OH)$_2$ + 2NH$_4$Cl                    (2)
FeCl$_3$ + 3NH$_3$ + 3H$_2$O = Fe(OH)$_3$↓+ 3NH$_4$Cl                   (3)
4Fe(OH)$_2$ +O$_2$ + 2H$_2$O = 4Fe(OH)$_3$↓                      (4)

3. Experimental results and discussion

3.1. Comparison of Fe$_2$O$_3$ iron powder and scrap steel sheet

3.1.1. Acid removal effect. In this study, according to the range of normal reaction conditions in actual production, the reaction time was determined to be 12 hours, the reaction temperature was 70 ℃, and the dosage of iron powder and traditional scrap steel sheet were 40 g and 200 g, respectively. The removal of free acid from waste acid by these two materials is shown in Table 1.

| remover          | reaction time (h) | T      | Waste acid removal rate (%) |
|------------------|-------------------|--------|----------------------------|
| iron powder      | 12                | 70℃    | 63.04                       |
| excessive scrap  | 12                | 70℃    | 43.05                       |

It can be seen from Table 1 that under the same reaction conditions, the free acid removal rate with iron powder is 20% higher than that of scrap steel sheet.

3.1.2 Desilication effect. The pH value was controlled at 4.5 and the temperature was controlled at 70 ℃ with ammonia water. PAM (polyacrylamide) was used as coagulant aid, and the dosage was 0.6mg/l. The silicon removal rate of waste acid by iron powder and traditional scrap steel sheet is shown in Table 2 (the silicon content is determined by spectrophotometry).

| remover          | reaction time (h) | T      | Silicon removal rate (%) |
|------------------|-------------------|--------|--------------------------|
| iron powder      | 12                | 70℃    | 63.04                    |
| excessive scrap  | 12                | 70℃    | 43.05                    |

It can be seen from Table 2 that under the same reaction conditions, the silicon removal rate with iron powder is higher than that with scrap steel sheet. Therefore, iron powder as a free acid removal agent in waste acid has great research significance. In the following, the best free acid removal and desilication conditions of iron powder after adding waste acid are explored in depth.

3.2. Optimum conditions for waste acid treatment

3.2.1. Optimal conditions for free acid removal. A certain concentration of waste acid solution is prepared in a 1L beaker. According to the experimental arrangement, iron powder with corresponding content is added, and stirred, heated in a constant temperature water bath for 10 ~ 13 hours. After cooling, the residual free acid concentration was detected at 2cm below the liquid level.
Table 2. Comparison of silicon removal rate between iron powder and scrap steel sheet

| Remover          | PH value | Set the temperature | Residual silicon content (mg/L) |
|------------------|----------|---------------------|--------------------------------|
| Iron powder      | 4.5      | 50℃                 | 116.23                         |
| Excessive scrap  | 4.5      | 50℃                 | 124.56                         |

According to the actual process conditions, the concentration of HCl in the waste acid containing silicon is 50g/L. The three factors affecting the removal rate are reaction time, reaction temperature and iron powder dosage. Each factor has four levels for orthogonal test. The best reaction time for free acid removal is 13 hours, the optimal reaction temperature is 70℃, and the optimal amount of iron powder is 40g.

3.2.2. Optimal desilication conditions. In the actual waste acid treatment, due to the difference of acid pickling process, the acidity, silicon content and metal ion content of acid solution in different acid pickling tanks are different, and different conditions will cause different surface properties of silicate materials (such as chemical composition of dissociation surface, surface electrical properties, solution characteristics and adsorption energy, etc.) and affect their hydrophilicity in waste acid solution. Therefore, in this study, three kinds of acid samples from the actual pickling tank of a steel company in Wuhan were sampled, and the main ion concentrations were shown in Table 4.

Table 3. main ion analysis results of waste acid sample

| acid sample No | [H⁺](mol/L) | [Fe²⁺](g/L) | [Fe³⁺](g/L) | SiO₂(mg/L) |
|----------------|-------------|-------------|-------------|------------|
| acid sample 1  | 1.90        | 161.765     | 40.32       | 2874       |
| acid sample 2  | 1.57        | 121.915     | 48.75       | 1608       |
| acid sample 3  | 1.32        | 99.145      | 45.07       | 1014       |

(1) Natural subsidence
Take 500ml acid sample 1, 2, 3 respectively, and they stand for 10, 20, 30 and 40 minutes without adding chemicals. Samples were taken at 2cm below the liquid surface to detect the SiO₂ content and calculate the silicon removal rate. The results are shown in Fig. 1.

![Figure 1. Natural settlement curve of desilication of three acid samples](image)

It can be seen from Fig. 1 that when the static sedimentation time is 40 min, the silicon removal rate in acid sample 1 is stable at about 69%. Also, in acid sample 2 the value can reach 57%; while in
Acid sample 3, the silicon removal rate can only reach 48%, and with the extension of time, the growth rate of silicon removal rate gradually decreases and gradually tends to be stable. After 40 min of static precipitation, samples were taken at 2cm below the liquid level of the supernatant to detect the silicon content. The silicon content of the three acid samples was more than 500 mg / L. It can be seen that in the actual industrial production process, the natural sedimentation rate of silicon impurities is slow and the settling time is long if the settling tank is set separately. Due to the fine particle size and strong stability of silicon impurities in waste acid solution, it is difficult to remove silicon directly by gravity sedimentation.

Generally, in the actual industrial production process, the appropriate coagulant aid is selected to desiliconize. Therefore, the following content is aimed at the study of desilication rule under different coagulant aid conditions when iron powder is added into waste acid solution for treatment.

(2) Desilication under different coagulant aids

In this part, the silicon removal effects of the above three acid samples were investigated under four working conditions of adding coagulant aid PAM alone, adding PAC alone, PAM + PAC combination and adding MgCl2 alone, so as to explore the influence of dosage on silicon removal under different coagulant aid conditions.

For each acid sample, 4 parts of 500 ml were taken for each acid sample. For each acid sample, PAM with concentration of 40 mg / L, 60 mg / L, 80 mg / L and 100 mg / L (the mass concentration of the solution was 1 ‰) was added to each acid sample, and the sample was taken at 2 cm below the liquid surface for 40 min. the silicon removal rate under different conditions was detected and calculated.

For PAC alone, take 4 parts of 500ml for each acid sample, and change the above PAM dosage to 160mg / L, 180mg / L, 200mg / L, 220mg / L, and other settings are the same.

For the combination of PAM and PAC, 4 parts of 500ml of each acid sample are taken. According to the optimal dosage of PAM and PAC, the dosage of PAM in acid sample 1 is 60mg / L, that of acid sample 2 and 3 is 80mg / L; the dosage of PAC in three acid samples is 160mg / L, 180mg / L, 200mg / L and 220mg / L respectively, and other settings are the same.

Considering that the price of industrial product MgCl2 is relatively cheap, the coagulation aid effect of MgCl2 for acid sample was investigated. For MgCl2, 4 parts of 500ml were taken for each acid sample, and the dosage of MgCl2 in the three acid samples were 200mg / L, 300mg / L, 400mg / L and 500mg / L respectively, and the other settings were the same. The silicon removal rates under the above four working conditions are shown in Fig. 2.
Figure 2. Change of silicon removal rate with different coagulant aid dosage

The comparison of silicon removal rate under the best dosage of coagulant aid under the above four working conditions is shown in Fig. 3.

According to figure 3, for acid sample 1 and acid 2, the comparison of comprehensive silicon removal rate under four working conditions is: PAM + PAC > MgCl₂ > PAM > PAC; for acid 3, the comparison of comprehensive silicon removal rate under four conditions is: MgCl₂ > PAC + PAC > PAM > PAC, which is related to the iron ion and silicon content in the original acid sample. For acid sample 1 and 2, PAM alone has good effect, and the silicon removal rate reaches 96.9% and 84.7% respectively. For acid sample 3, the best effect can be achieved by adding 80 mg / L PAM and 200 mg / L PAC.
4. Conclusion

(1) Through the comparative test of free acid removal and desilication efficiency between scrap steel sheet and iron powder, considering the comprehensive technical and economic factors, the treatment effect of iron powder is better.

(2) The results of orthogonal test showed that the best reaction time was 13 hours, the best reaction temperature was 70 ℃, and the best iron powder dosage was 40 g, the removal rate of free acid was the highest.

(3) Under the optimal dosage of coagulant aid and coagulant aids, PAM alone has good effect on acid sample 1 and 2 (with high iron ion concentration and silicon content), and the silicon removal rate reaches 96.9% and 84.7% respectively; for acid sample 3, when the iron ion concentration and silicon content are low, the combined addition of 80mg / L PAM and 200mg / L PAC can achieve the best effect.

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