The removal of fluosilicic acid ions in acid wastewater silicon etched by potassium salt

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Abstract. A Silicon material is widely used in various industries, especially in the field of aerospace and solar energy. But a lot of acidic wastewater from silicon etched is produced by machining process of silicon core during polysilicon production process of modified Siemens process, which contains nitric acid, flu silicic acid, and hydrofluoric acid. The waste acid will cause environmental pollution. This research developed a way to make a chemical precipitation reaction of fluorosilicic acid, with precipitant (potassium nitrate, potassium sulphate) in the waste acid. The dilute nitric acid filtrate non-fluorinated is gotten after filtrated the precipitate. The results showed: (1) Potassium nitrate as precipitating agent, the remove flu silicic acid in waste acid and the utilization of the metal ion is the maximum ;( 2) The optimal precipitant is potassium nitrate.

1. Introduction
At present, to solve the problem of environmental pollution and energy shortage is significant to the development of nation [1, 2]. The solar energy as a renewable energy, and its rational use is the best solution to solve the two problems [3]. In the next 50 years, silicon will become the main material of the electronic and photovoltaic industry [4].

The main production process of polysilicon includes metallurgical method [5], modified Siemens method [6], and fluidized bed method [7], etc [8]. The modified Siemens method is the main way, in the process of polysilicon preparation, the oil, and oxide and metal impurities on the surface of silicon core is removed by the chemical etching method [9]. The residual highly corrosive acidic wastewater from silicon etched contains nitric acid, flu silicic acid, and a very small amounts of hydrofluoric acid. If it is discharged into environment, acidic wastewater will cause incalculable damage [10, 11]. With strong acid, the flu silicic acid decomposed the fluoride under the heating condition, which has a negative impact on humans and plants [12, 13].

The treatment method of acidic wastewater is mainly divided into: the formation fluosilicate precipitation [14]; the generation fluoride precipitation; the preparation white carbon black product [15]. The formation fluosilicate precipitation is low cost and effective recycling.

As investigated subject, the acidic wastewater produced by the production process of a polysilicon enterprise in Yunnan. With potassium salt as the precipitating agent, the removal of the flu silicic acid ion in acidic wastewater is achieved by the chemical precipitation method, and gotten fluorosilicate. The approach is simple, and open up a new road to treatment flu silicic acid wastewater.
2. Materials and methods

2.1. Chemical precipitation reaction mechanism
The chemical precipitation method: certain chemical substance to be added wastewater, and it directly react with dissolved substance, then get salt precipitation, and eliminate pollutant in wastewater. The way is simple operation, quick reaction, economic, and it is a conventional way to treat the fluoride-containing water.

The reaction of calcium salt and barium salt with the fluoride silicate in wastewater is not obvious and cannot be achieved precipitating separation in screening trial. However, potassium salt added to the acidic wastewater can lead to precipitation action and the filtering process is easy. So the experiment of chemical precipitation of potassium nitrate, potassium sulfate is used in this research, fluorsilicate ion in the acidic wastewater can be react with metal ion of the two salt, and generate the fluorsilicate precipitation.

2.2. Method
The different content of potassium nitrate, potassium sulfate solid as precipitant were added in the acidic wastewater from silicon etched. After the reaction to be completed, the filtrate was obtained after filter by medium-speed filter paper, then determine the concentration of flu silicic acid in filtrate. The precipitation of the filter was dried until the constant weight, and measured the mass of the sediment. The concentration of metal ions in the solution, the removal rate of fluorine acid and the utilization ratio of metal ions in the reaction process was obtained by calculating.

3. Results and discussion

3.1. The relationship between precipitant dosage and filtrate composition
As it would be seen, with the raising molar ratio of between the added metal ions in two precipitant with fluorsilicic acid, the concentration of total acid, nitric acid and fluorsilicic acid in filtrate gradually decreased.

With the raising amount of KNO₃ added, the concentration of flu silicic acid almost no longer reduce. At this point, the addition amount of potassium nitrate is the maximum, and the condition of utilization rate is the highest.

![Figure 1. The effect of addition amount of precipitating agent on each substance concentration of the filtrate](image-url)
It can be seen that the concentration of fluorosilicic acid in filtrate is about 0.5403mol/L when the molar ratio is 1.92. Continuing to increase the amount of additive, the concentration of flu silicic acid almost no longer reduce, the concentration of total acid in solution is 8.9375mol/L, and the concentration of nitric acid is 8.9338mol/L. This moment, the addition amount of potassium sulfate is the maximum, and the condition of utilization rate is the highest.

The exothermic reaction of precipitating agent and SiF62 resulted in fluoilicic acid decomposition. The SiF62- is decreased, since it occurred hydrolysis reaction in acidic solution. These both lead to the reduce of hydrogen ion in solution, so that the concentration of total acid is low. The reduce of nitric acid, which is associated with the thermal decomposition behaviors. The generation of potassium flu silicate precipitate by the reaction between precipitating agent and fluorosilicic acid radical ion in solution, which is insoluble in water. Hence the content of flu silicic acid in solution is decreased.

In summary, it is certain that the partial decomposition of fluoride acid can be caused by the addition of solid precipitating agent into the concentrated acid solution.

3.2. The relationship between the amount of precipitating agent and precipitate

![Figure 2. The effect of addition amount of precipitating agent on the amount of the precipitate](image)

When KNO3 was added, the precipitation amount of potassium flu silicate increased significantly with the increase of moral ratio. However, the molar ratio reached 1.48, the upward trend began to slow down, and the precipitation reaction was also decreased. It suggested that the utilization rate of potassium nitrate began to decline and the test would make no sense to further prolong.

When used potassium sulfate for precipitating agent, the precipitation increased gradually with increase the molar ratio of potassium sulfate to flu silicic acid in solution. When the molar ratio is 1.92, precipitate flu silicate presented linear upward trend. But it is over 1.92, the upward trend has slowed. This result showed that, when the molar ratio exceeded 1.92, the reaction of precipitation has slowed, and the utilization rate of potassium sulfate began to decrease.

It can be seen that the metal ions in filtrate is not completely react with flu silicic acid to generate fluorosilicate, from the addition amount of precipitating agent and precipitation of fluorosilicate. Potassium nitrate as a precipitating agent, for example, when the mole ratio reached 1.48, the formation of potassium flu silicate precipitation obtained 0.00929mol. According to the stoichiometric ratio, it should be 0.01088mol. The results showed the 85% of metal ion in addition amount is generated precipitation, and the rest of 15% is no changed in filtrate.
3.3. The relationship between dosage and utilization ratio of precipitating agent

Potassium nitrate as the precipitating agent, a rapid increase in concentration of potassium ions occurred after the 1.62. When the molar ratio of 1.08 to 1.62, the utilization of potassium ions is maximum. The removal rate reached 100% in the 1.48 of molar ratio, indicating that there is no fluor silicic acid in filtrate and the addition amount of potassium nitrate is the maximum.

The experiment was added potassium sulfate. The molar ratio exceed 1.76, the amount of the filtrate added potassium ions significantly increased. It is observed that the maximum utilization of potassium ions would reached with the molar ratio of 1.08 to 1.62. The removal rate reached 97% in the 1.92 of molar ratio.

![Figure 3](image3.png)  
**Figure 3.** The effect of molar ratio of between adding metal ions and fluosilicic in the waste acid on the metal ions in the filtrate

![Figure 4](image4.png)  
**Figure 4.** The effect of molar ratio of between adding metal ions and fluosilicic in the waste acid on the removal of the fluosilicic

The maximum utilization rate of the metal ion of two different precipitating agent in the precipitation process: potassium nitrate < potassium sulfate. This phenomenon occurred can be explained by the colossal stability: Schulze-Hardy Rule: the coagulation capacity is mainly decided by
the electrolytic ionic valence of opposite charge in colloidal particle. It illustrate that sulfate coagulation values greater than nitrate, sulfate stability less than nitrate, so precipitating agent of sulfate more easily reaction with flu silicic acid in waste acid, and utilization rate of metal ion in sulfate precipitation agent higher than nitrate in chemical precipitation process.

4. Conclusion

It should choose potassium nitrate as precipitating agent, from the viewpoint of the removal of flu silicic acid in solution. Because the addition amount is the lowest, the molar ratio of between the addition amount of metal ions and fluorosilicic acid in the waste acid is the minimum, and the concentration of metal ions in solution is the lowest.

If the utilization of metal ions is considered, it could select potassium sulfate as the precipitating agent, the utilization of the metal ion during the chemical precipitation process is the maximum. But with potassium nitrate precipitation agent compared, the molar ratio of between the addition amount of metal ions and fluorosilicic acid in the waste acid is relatively high, the concentration of metal ions in solution is relatively high.

Therefore, from the economic benefit of chemical plant, the use of potassium nitrate as precipitating agent is appropriate.

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