Preparation of fly ash-based flocculant and flocculation performance

Junxin Zhang\textsuperscript{a}, Xiumei Duan\textsuperscript{b}\textsuperscript{*}
YingKou Institute of Technology, Yingkou 115014, P.R. China
\textsuperscript{a}877950641@qq.com, \textsuperscript{b}duanxiumeiabc@163.com

Abstract: Using fly ash from a thermal power plant in Yingkou City as raw material, the inorganic polymer flocculant polyaluminum ferric chloride (PAFC) was prepared by sodium carbonate impregnation, high temperature roasting activation, and acid leaching. The influence of activation temperature and activation time on the leaching of aluminum and iron was investigated through single factor test and orthogonal test. The PAFC preparation conditions were optimized, and the prepared PAFC flocculant product was applied to kaolin turbidity water. The test results showed that the content of aluminum in fly ash was 7.08\%, and the content of iron was 4.95\%. The mass ratio of the activator sodium carbonate and fly ash was 10:7, the activation temperature was 800\(^\circ\)C, and the activation time was 2h. The leaching rates of aluminum and iron were the highest, 88.31\% and 53.66\% respectively. The optimal conditions for the preparation of the flocculant were as follows: the molar ratio of aluminum to iron was 5.7:1, and the reaction time was 1.5h. The liquid product obtained under these conditions was yellowish brown, and the solid product obtained after being dried was yellow powder.

1. Introduction
In recent years, the total annual discharge of fly ash in our country has been around 600 million tons, and the historical stockpile is at least 2500 million tons, and it is increasing at a rate of about 150 million tons every year. The open-air stacking not only causes serious waste pollution of land resources, but also poses a serious safety threat to the surrounding water bodies and atmospheric environment. The main oxides contained in fly ash from power plants are: SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, CaO, TiO\textsubscript{2}, MgO, K\textsubscript{2}O, Na\textsubscript{2}O, MnO etc. Statistics show that the four components of SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, and CaO account for nearly 90\%\cite{1}. The Si, Al and Fe elements contained in fly ash are inexpensive raw materials for the preparation of flocculants\cite{2}. In this experiment, fly ash from a thermal power plant in Yingkou City was used as raw material, and the inorganic polymer flocculant PAFC was prepared through sodium carbonate impregnation, high-temperature roasting activation, and acid leaching. The effect of activation temperature and activation time on the leaching of aluminum and iron elements was investigated by single factor test and orthogonal test, and PAFC preparation conditions were optimized. It provides a feasible method for the resource utilization of fly ash and the preparation of fly ash-based polymer inorganic flocculant.
2. Experimental part

2.1 Experimental materials and equipment
The reagents used in this experiment include fly ash, hydrochloric acid, sodium carbonate, aluminum trichloride, ferric chloride, sodium hydroxide, kaolin. Among them, the fly ash was taken from a power plant in Yingkou.

The equipments used in this experiment mainly include electronic balance, electric furnace, plasma emission spectrometer, vibrating screen, scanning electron microscope, desktop centrifuge, digital display electronic constant temperature water bath, digital display speed measurement six-unit synchronous electric stirrer, turbidity meter, magnetic stirrer, pH meter.

2.2 Characterization and activation of fly ash
The image of fly ash was analyzed using scanning electron microscope[3], and the content of aluminum and iron was analyzed following the method and steps described by Zhao[4].

Take dried fly ash and sodium carbonate (the mass ratio 10:7) and mix them evenly in a crucible, and then put them into a furnace under different activation temperatures and different activation times. The level of aluminum leaching rate was used to optimize activation condition. The level of aluminum leaching rate was tested as follows: the roasted fly ash and concentrated HCl was mixed (the ratio of hydrochloric acid volume to fly ash mass is 5:1), heated at 90°C, and continuously stirred for 30 minutes. The reaction product was added some water and filtered, Al concentration in filtrate was detected.

2.3 Preparation of fly ash-based flocculant PAFC and flocculation performance
The fly ash activated under optimal conditions and HCl was mixed, adjusted aluminum and iron concentrations by adding amounts of aluminum chloride and ferric chloride. The mixed liquor was bathed at 90°C and stirred continuously about 1 hour, and put for 18 hours to obtain the desired PAFC product.

A certain concentration of kaolin turbid liquid was prepared, then added some PAFC solution, and stirred quickly for 30 seconds. Then the solution was stirred slowly at a constant speed for 30 minutes, and then settled freely for 30 minutes. Turbidity and turbidity removal rate in the supernatant were measured and calculated.

3. Test Results and Discussions

3.1 Aluminum and Iron Content in fly ash
The test results of the fly ash sample used in the experiment are shown in Table 1.

| element   | fly ash/% | control/% |
|-----------|-----------|-----------|
| aluminum  | 7.08      | -0.0255   |
| iron      | 4.95      | -0.0355   |

From the data in the table, it can be calculated and analyzed that the content of alumina oxide in the ash sample is 13.37%, and the content of iron oxide is 7.1%. However, Gong et al[5] analyzed the composition of fly ash and found that silica content was 50.77%, and the content of alumina and iron oxide were 25.20% and 13.42%, which were nearly twice the results of this experiment. Which showed that the content of fly ash was related to the region. The content of silica in fly ash is very high, and the polysilicate flocculant can be made from fly ash, and the content of alumina and iron oxide is also high, which can be used to prepare the polymer polyaluminum iron silicate flocculant.
3.2. Activation of fly ash
The physical and chemical activation method was used to activate the fly ash: the fly ash was ground first, and then mixed with sodium carbonate activator and roasted at high temperature.

3.2.1. Effect of activation time and temperature on aluminum and iron leaching rate
The dried fly ash and sodium carbonate was mixed with 10:7, the activation temperature was 700℃, and perform the activation operation at different activation times (0.5h, 1h, 1.5h, 2h, 2.5h). Another set of experiments were operated under different activation temperature (500℃, 600℃, 700℃, 800℃, 900℃) with the same activation time 2h. The effect of acid leaching in different time periods was shown in Fig.1a, and the effect of the activation temperature was shown in Fig.1b.

![Graphs showing the effect of activation time and temperature on aluminum and iron leaching rate](image)

(a) Effect of activation time on leaching rate  (b) Effect of activation temperature on leaching rate

Fig. 1 Effect of activation time and temperature on aluminum and iron leaching rate

It was shown from the Fig.1a, the iron and aluminum leaching rate increased as the activation time was more. aluminum leaching rate increased significantly during 0.5h-2h, and the increase was not obvious after 2h. This was because could not be completely broken in a short time, and the aluminum leaching rate during the acid dissolution reaction is not high at the same temperature and the same energy supply. As time prolonged, the silicon-aluminum bond gradually broke, and the amount of dissolved aluminum also increased. When the unbroken silicon-aluminum bond gradually decreased, and the increase of the aluminum dissolution rate was not obvious. Taking into account of the cost of activation time and energy consumption, the activation time was selected as 2h.

It was shown from the Fig.1a, the iron and aluminum leaching rate increased as the activation temperature increased. When the temperature exceeded 800℃, the increase slowed down significantly. In addition, the fly ash calcined product at 500℃, 600℃, and 700℃was fluffy and easy to take out from the crucible; but the calcined product at 800℃ was sintered, and the phenomenon was more serious at 900 ℃, and it was stuck together with the crucible, so it was not easy to take out. The reason was that the energy supply was insufficient at low temperature, and sufficient energy could not be obtained to break the silicon-aluminum bond. When the activation temperature was higher than the melting point of sodium carbonate, the sodium carbonate changed from solid to liquid. However, the sodium carbonate in the liquid phase was more likely to react with the porcelain crucible chemically[6], and after the reaction was over, the temperature of the reaction system dropped, and the phase state of the activation system changed back to the solid-solid system, thereby interacting with the crucible. Since the leaching rates of aluminum and iron were not much different with the two temperature of 800℃ and 900℃, and the energy consumption was higher at 900℃. Combined with the above analysis, the activation temperature is selected here as 800℃.
3.2.2 Orthogonal experiment
To further explore the activation conditions, two factors (temperature and time) were selected and took an orthogonal experiment. There were nine groups of experiments, and the leaching effects of aluminum and iron in each group were shown in Table 2.

Table 2 Optimization results of fly ash activation conditions

| Temperature/℃ | Time/h | Aluminum leaching rate/% | Iron leaching rate/% |
|---------------|--------|--------------------------|---------------------|
| 800           | 2      | 88.31                    | 53.66               |
| 700           | 2      | 48.89                    | 35.95               |
| 600           | 2      | 34.31                    | 35.51               |
| 800           | 1.5    | 85.67                    | 54.46               |
| 700           | 1.5    | 46.03                    | 25.36               |
| 600           | 1.5    | 34.57                    | 34.38               |
| 800           | 1      | 65.50                    | 43.49               |
| 700           | 1      | 41.33                    | 35.25               |
| 600           | 1      | 25.87                    | 28.15               |

It was shown from Table 2 that the optimal activation condition was activated at 800 ℃ for 2h, and the corresponding leaching rate of aluminum was 88.31%.

3.3 Preparation of PAFC and flocculation performance
Adding external iron and aluminum salt to adjust the aluminum iron ratio, and the flocculant was prepared adopting acidification method. The experimental results were shown in Fig. 2a. After the aluminum iron ratio was determined, different reaction time was optimized. The experimental results were shown in Fig. 2b.

Fig. 2 Effect of aluminum/iron molar ratio and time on flocculation effect of PAFC
It was shown from Fig. 2a that the color of the final liquid product gradually deepened and became more and more viscous with the increase of ferric chloride dosage. When the aluminum iron ratio changed from 8.6:1 to 5.7:1, the iron content increased, the turbidity removal rate increased significantly. This was because the addition of iron made the precipitation, adsorption and electric neutralization capacity of the product stronger, which has stronger electro adsorption and bridging
ability, and the flocculation performance of PAFC products was significantly enhanced. When the amount of iron increased a certain extent, the turbidity removal rate did not increase any more but decreased. This was because the iron content was more higher, the branching structure of the product was more obvious, the structure was denser, the product was easy to generate hydroxide precipitation, the stability and the flocculation effect became worse. Combined with the experimental results and analysis, the aluminum iron ratio was selected with 5.7:1.

It was shown from Fig. 2b that the degree of polymerization of the product was not high under short-time reaction and it was impossible to form high molecular weight polymer, which induced the flocculation effect of the product was poor. When the reaction time was too long, the proportion of network structure increased. The phenomenon of intermolecular crosslinking polymerization was more serious, resulting in the poor stability of flocculant products. At the same time, the production efficiency was also affected, and the energy consumption increased and the production cost increased. So, 1.5h was selected in this experiment.

4. Conclusion
Based on the results and discussions presented above, the conclusions are obtained as below:

(1) It is shown that the content of alumina oxide in the ash sample is 13.37%, and the content of iron oxide is 7.1%. Which showed that the content of fly ash was related to the region. The content of silica and iron/aluminum was also high, which can be used to prepare the polymer polyaluminum iron silicate flocculant.

(2) The optimal activation condition was activated at 800 ℃ for 2h, and the corresponding leaching rate of aluminum was 88.31%.

(3) Turbidity removal rate of Kaolin suspension was highest at aluminum/iron molar ratio of 5.7:1 and reaction time 1.5h. The liquid product obtained under these conditions was yellowish brown, and the solid product obtained after drying was yellow powder.

Acknowledgments
This work was financially Supported by Program for Excellent Talents of Science and Technology in Yingkou Institute of Technology (110507002).

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