

[Article ID] 1003- 6326(2002) 05- 0983- 04

Comparisons of species and coagulation effects of PFS solution and solid PFS from pyrite cinders^①

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[Abstract] Pyrite cinder is a kind of solid waste of sulfuric acid industry. After mixing pyrite cinders with sulfuric acid, ferric sulfate was obtained by heating, maturing, dissolving and filtrating. Suitable amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and NaClO_3 were added into ferric sulfate solution and polyferric sulfate (PFS) solution was produced. Solid PFS was made by concentrating and drying PFS solution. Time-dependent complex colorimetric tests were done while ferron agent reacted with Fe^{3+} in the solution. The results show that the proportion of transitional low polymeric species and high polymeric species are increased after PFS solution is transferred into solid PFS. It was discovered by jar tests that solid PFS has very good coagulation effects relevant to the increase of transitional lower polymeric species.

[Key words] pyrite cinders; PFS solution; solid PFS; species; coagulation

[CLC number] X 705

[Document code] A

1 INTRODUCTION

Polyferric sulfate (PFS) was successfully prepared in Japan in the mid-1970s and was produced and applied in industries in 1980s. PFS as a coagulant, has many advantages, such as a large floc, fast floc, little consume, good coagulation effects, no poison and a wide range of pH adoption. Among many production methods, the most common method for PFS production is to use NaNO_2 as a catalyst to oxidize FeSO_4 with oxygen^[1~3]. The above catalytic oxidation method has many disadvantages^[4, 5], for instance low Fe content, long reaction time and generation of nitrogen oxide gases which pollute the air. Because Fe content is low in PFS solution, it consumes a large amount of energy and takes long production period to change PFS solution into solid PFS. In this paper, ferric sulfate solution^[6] was obtained by mixing pyrite cinders with sulfuric acid and later by heating, maturing, dissolving and filtrating. A qualitative amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ made by ourselves^[7] and NaClO_3 are added into the ferric sulfate solution, and then PFS solution is produced, which has 14% Fe or more. Solid PFS is easily manufactured by means of concentrating and drying in several hours. The species of PFS solution and solid PFS and coagulation effects are also studied in this paper.

2 EXPERIMENTAL

2.1 Materials

The materials used in experiments are: pyrite cinders (63.7% Fe), sulfuric acid (A. R.), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (prepared by ourselves), NaClO_3 (A. R.), Diatomite (C. P.), ferron agent (7-iodo-8-hydroxyquinoline-5-sulfonic acid, A. R.), 0.2 mol/L NaOH

and 0.1 mol/L H_2SO_4 solution.

2.2 Apparatus

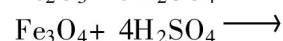
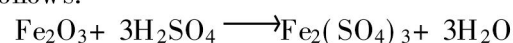
The apparatus used in experiments are: an oven, an agitator, a vacuum pump (SHB-III Zhengzhou Changcheng Science-industry-trade Corporation, China), a Super thermostat (501, Shanghai Experimental Instrument Plant, China), a micro sampler (Beijing Qingyun Science and Technology Corporation, China), a spectrophotometer (722, Shanghai the Third Analytical Instrument Plant, China), a turbid meter (GDS-3S, Wuxi Keda Instrument Plant, China), a pH meter (PHS-25, Shanghai Leici Instrument Plant, China), a 6-link stirrer (JJ-4, Jingtan Fuhua Electric Limited Corporation, China).

3 RESULTS AND DISCUSSION

3.1 Preparation of PFS

3.1.1 Preparation of ferric sulfate solution

Pyrite cinders contained 74.1% Fe_2O_3 and 15.96% Fe_3O_4 were evenly mixed with 65% ~ 85% H_2SO_4 in an earthen bowl, then the mixture was put in an oven and heated to 200 ~ 300 °C for 1 ~ 2 h. The heated mixture was transferred into a three-neck flask, then a quantitative amount of water was poured in the flask stirring for 1 h at 80 °C. The solution in the flask was filtrated. Fe content in the solution was above 3 mol/L^[6]. In this process, the reactions are as follows:

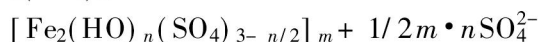
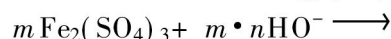
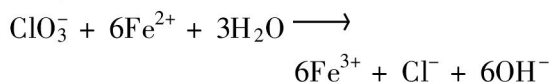
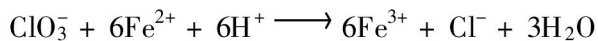


3.1.2 Preparation of PFS solution

A PFS solution was prepared by putting a suitable amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and NaClO_3 in the above

ferric sulfate solution, and reacted at 60 °C for 0.5 h. A different basicity of PFS could be obtained by different ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to NaClO_3 .

The reactions are as follows:



where $[\text{Fe}_2(\text{HO})_n(\text{SO}_4)_{3-n/2}]_m$ is PFS formula.

From these reactions, we can see how H^+ is consumed and OH^- is produced. The basicity (B) of PFS was measured and calculated according to the National Standard of P. R. China for PFS (GB14951-93). The formula of basicity is as follow:

$$B = \frac{[\text{OH}^-]}{3[\text{Fe}]} \times 100\%$$

3.1.3 Preparation of solid PFS

PFS concentrated solution was obtained by evaporation at above 100 °C, then the concentrated solution was dried at 60 °C in a water bath with stirring slowly. After several hours, the yellow solid PFS was obtained.

3.2 Species of solid PFS

A Ferron agent solution was prepared by dissolving analytical reagent-grade Ferron in distilled water to a concentration of 0.2%, and preserved in low temperature. The procedure of special measurement is as follows: before 10 mL of 0.2% Ferron solution was added, 4 mL of 1:1 HCL solution and 8 mL of 20% solution sodium acetate solution were taken accurately in 100 mL-vessel by a pipette, and the mixed solution was shaken immediately, then the pH value of solution was adjusted to a range of 4.80~5.20^[8] by adding 2 mol/L NaOH solution; after all these being done, a certain amount of a solid PFS or liquid PFS was added into the vessel, to keep the Fe concentration in a range of $10^{-4} \sim 10^{-5}$ mol/L^[8], shaking the solution immediately. At the same time, the time was counted, then, the adsorption of the mixture was measured on 722-spectrophotometer and its adsorption was recorded timely at a certain interval later. At every set of test, the above-mentioned Ferron mixture not containing Fe^{3+} was taken as a reference. The results are shown in Fig. 1 and Fig. 2.

Comparing Fig. 1 with Fig. 2, it shows that the time-dependent coordination colorimetric change of liquid PFS is obvious, while the difference of solid PFS is smaller. But the total change tendency is that the higher the basicity of PFS is, the smaller the change of its adsorption. Because the higher the basicity is, the more the hydroxyl group or oxygen-bridge group, and the slower the coordinating speeds of Fe^{3+} with Ferron solution, the smaller the time-dependent coordination colorimetric change.

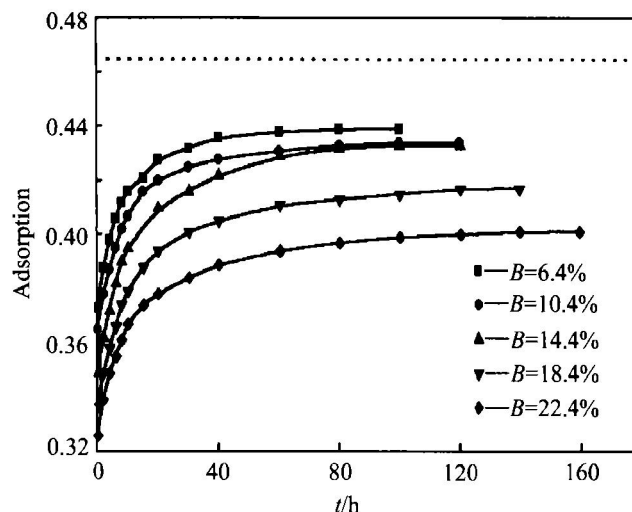


Fig. 1 Curves of time vs dependent coordination colorimetric of liquid PFS with different basicities

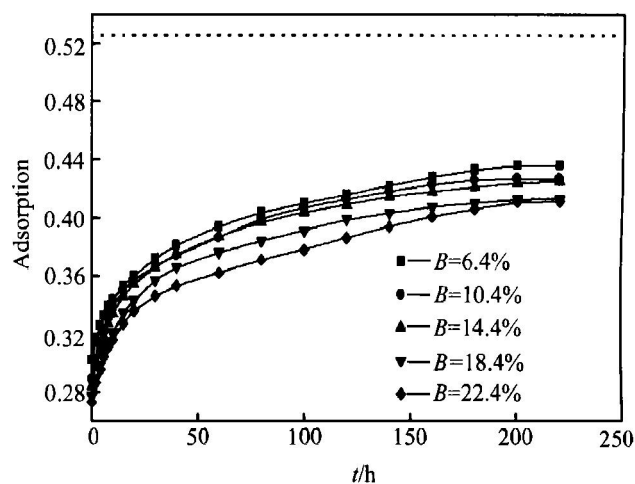


Fig. 2 Curves of time vs dependent coordination colorimetric of solid PFS with different basicities

There are two kinds of classifications for PFS species. One kind of them proposed by Murphy, et al^[9] divided the species of PFS into three species of Fe(a), Fe(b) and Fe(c), by which Fe(a) standards for the species reacted with Ferron within 1 min, Fe(b) standards for the species reacted with Ferron in the next 12 h, and Fe(c) standards for the species not reacted with Ferron within 12 h. Obviously, this classification couldn't reflect the reaction kinetics characterization of various species of PFS with Ferron. The other kind proposed by Tian, et al^[8] and Tang, et al^[10, 11] classified the Fe(III) species of PFS into three species of Fe(a), Fe(b) and Fe(c), namely, monomeric ferric ion, transitional low polymeric species and high polymeric species. According to this classification standard of Fe(a), Fe(b) and Fe(c), the points of the curves when $t=0$ correspond to Fe(a), the time-dependent change parts of the curves correspond to Fe(b), and Fe(c) is able to calculate by the difference between total ferric and both Fe(a) and Fe(b). The dot line in Fig. 1 and Fig. 2 represent

the adsorption of total ferric. The total ferric of them are 8.70×10^{-5} mol/L and 9.50×10^{-5} mol/L respectively. According to the standard curves of Fe-Ferron coordination shown in Fig. 3, the percentages of three species calculated are shown in Table 1 and Table 2.

As shown in Table 1 and Table 2, it can be concluded that the species of the same PFS sample had changed greatly after the liquid PFS was transformed into the solid PFS, namely the amount of Fe(a) reduced greatly, while the amounts of Fe(b) and Fe(c) increased doubly. It indicates that the process of hydrolysis-polymerization still continued in the processes of concentrating and solidifying, and the Fe(a) species were transformed into Fe(b) and Fe(c) species.

Table 1 Distribution of different species of liquid PFS/ %

Basicity	6.40	10.40	14.40	18.40	22.40
Fe(a)	79.57	77.85	74.41	72.04	69.89
Fe(b)	14.83	15.48	18.71	17.63	16.34
Fe(c)	5.60	6.67	6.88	10.33	13.77

Table 2 Distribution of different species of solid PFS/ %

Basicity	6.40	10.40	14.40	18.40	22.40
Fe(a)	56.76	54.48	53.14	52.19	51.62
Fe(b)	26.29	26.86	27.81	26.48	26.67
Fe(c)	16.95	18.67	19.05	21.33	21.71

3.3 Coagulation effects

A certain concentration solution of solid PFS was prepared by dissolving the solid PFS with different basicities in distilled water. All coagulation experiments were carried out in a beaker of 500 mL with a 6-link stirrer, the volume of the diatomite suspension with turbidity of 53.3 NTU was 500 mL. A certain PFS solution was dosed directly into the suspensions by a microinjector. The initial rapid mixing was carried out at 160 r/min for 3 min to obtain swift homogeneous dispersion, followed by a slow agitation for 9 min with 50~60 r/min. Then the suspension was left to settle for 21 min and the sample was collected at 2 cm beneath the surface for measuring residual turbidity. The results are shown in Fig. 4.

Fig. 4 shows that the residual turbidity decreased gradually with the dosage of Fe increasing, while overdosage, the turbidity removal efficiency is reduced. Because the positively charged ferric precipitates formed in the dissolving process of PFS in aquatic solution can neutralize the negatively charged diatomite and make it coagulate; when Fe is overdosage, the positively gel is surplus and make it difficult to coagulate.

Moreover, as shown in Fig. 4, the residual turbidity removal efficiencies are nearly close to each other for solid PFS with different basicities. But the turbidity removal efficiency is bad when the basicity is

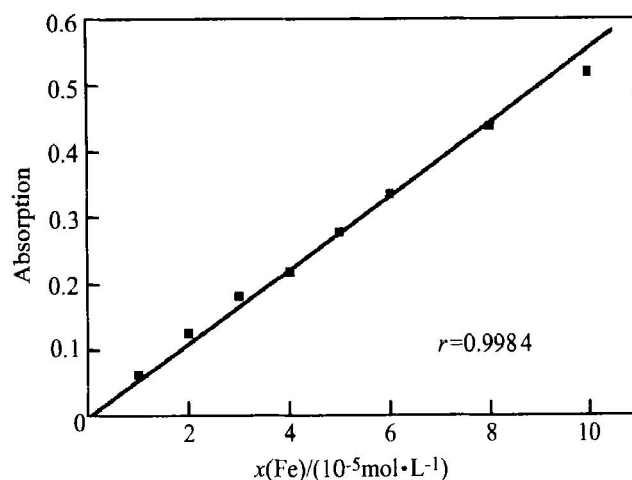


Fig. 3 Standard curve of Fe-Ferron coordination

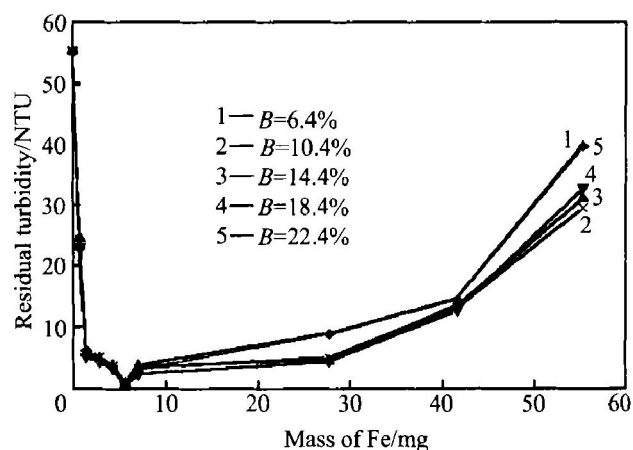


Fig. 4 Effects of coagulant solid PFS dosage on residual turbidity

too high. This coincides with the turbidity removal regulation of liquid PFS with different basicities in the author's another study^[12], i.e. in liquid PFS the turbidity removal efficiency of PFS with much moderate basicity is better than that of PFS with higher or lower basicities.

PFS, a good coagulant, has not only the action of charge neutralization, but also the action of coagulation and "sweep-floc". As shown in Table 1 and Table 2, the rate of Fe(b) species of liquid PFS with basicity of 14.40% is the largest, while the rates of Fe(b) species of various solid PFS with different basicities are nearly the same. Combining the former discussion with the turbidity removal results, it can be concluded that the more the rate of transitional low polymeric species(Fe(b)) is, the stronger the coagulation efficiency.

4 CONCLUSIONS

1) Ferric sulfate solution was obtained after mixing pyrite cinders with sulfuric acid, heating, maturing, dissolving and filtrating. PFS solution was prepared when a proper amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and NaClO_3 were added into the ferric sulfate solution.

PFS solution was transferred into solid PFS by means of concentrating and drying.

2) The coordination species of PFS were greatly and obviously changed after PFS became solid. A lot of free Fe^{3+} ions (Fe(a)) in PFS solution were transferred to transitional low polymeric species and high polymeric species after drying.

3) Solid PFS had very good coagulation effects in diatomite suspension liquid. The removal rate of turbidity was up to 98.73%. The increase of transitional low polymeric species enhanced the coagulation effects.

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(Edited by HE Xue-feng)