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Oxidation rate in the preparation of polyferric sulfate coagulant

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Abstract: The oxidation rate of ferrous sulfate was investigated in the preparation of polyferric sulfate(PFS) coagulant. It was proved that this reaction is zero order with respect to Fe^{2+} , first order with respect to $\text{NO}_2(\text{g})$ and first order with respect to the interface area between gas phase and liquid phase. If the partial pressure of $\text{NO}_2(\text{g})$ in gas phase is increased or the interface area is increased, the time needed to complete the reaction will be decreased.

Key words: coagulant; flocculant; polyferric sulfate; PFS; oxidation rate; water treatment

Introduction

A preparation method of polyferric sulfate (PFS) coagulant was reported by Japanese scientists (Yang, 1986) in the seventies. Since the eighties the preparation and application of PFS have been widely investigated in China because of its high coagulation efficiency in water treatment. But the mechanism of the preparation has not been properly understood so far. There are different opinions on this question at present. Some investigators think ferrous iron can be easily oxidized by oxygen because of the formation of $\text{Fe}(\text{NO})$ complex (Bai, 1996). The other investigators refer the oxidation rate mainly to the transfer of NO_2 across the interface between gas phase and liquid phase (Chen, 1995). Our experiment shows that the latter is reasonable.

1 Experiment

PFS was prepared by the devices in Fig.1. 486 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ along with 32.4 ml concentrated H_2SO_4 (95% - 98%) and 296 ml H_2O were added to a reaction vessel. During the reaction time, temperature was maintained 50 - 60°C, pressure was 101325 ± 666.6 Pa. The solution of NaNO_2 was slowly added to the reaction vessel with a dropping funnel when pure oxygen was being conducted to the vessel and reaction solution was being strongly stirred. After several hours, the reaction was completed and the solution turned red brown. Some properties of the product are shown in Table 1.

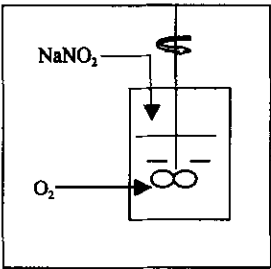


Fig.1 The devices for the preparation of PFS

Table 1 Some properties of the product

pH	Density, g/ml	Fe^{2+} , g/L	Fe^{3+} , g/L	Hydrolysis, $[\text{OH}]/3[\text{Fe}]$	Viscosity, cp
0.5	1.44	0.16	162	16%	11

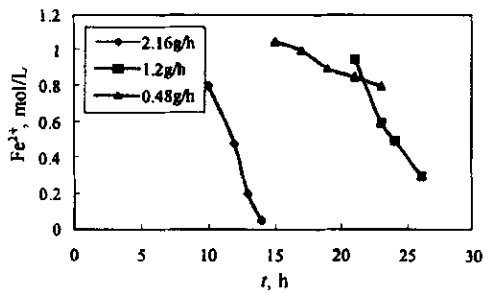


Fig.2 The changes of ferrous concentration with time

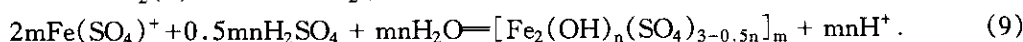
2 Result and discussion

2.1 The result of the experiment

The solution in the reaction vessel was sampled and analyzed by potassium permanganate method and iodimetric method respectively. Fig.2 shows that ferrous iron linearly decrease with time during the entire reaction and the more NaNO_2 is added the more quickly ferrous iron decrease. Fig.3 shows that ferric iron linearly increase during the entire reaction and the more NaNO_2 is added, the more quickly ferric iron increase.

2.2 The mechanism of the reaction

The mechanism of the reaction was suggested according to our experiment as shown in following equations:



Equation (1) - (3) show that NaNO_2 reacts with H^+ producing NO_2 and NO when it is added to the solution. According to Equation (4) - (6), the NO produced in the solution enters gas phase and is oxidized by O_2 becoming NO_2 . The NO_2 produced in the gas phase again enters liquid phase and oxidizes Fe^{2+} to Fe^{3+} , as shown in Equation (7) - (8). The NO_2^- produced in Equation (8) repeats Reaction (1) - (8), continuing the oxidation of Fe^{2+} to Fe^{3+} . Equation (9) shows that the produced Fe^{3+} partially hydrolyze and polymerize becoming product PFS at last.

2.3 The rate equations of the reactions

2.3.1 The transfer rate of NO_2

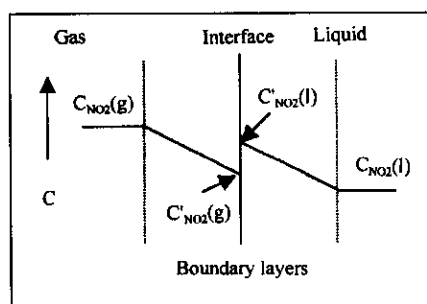


Fig. 4 Double membrane model

The transfer of NO_2 to the liquid phase from the gas phase is the key procedure which controls the rate of whole process. The rate equation of the transfer can be deduced by a "double membrane model" which is shown in Fig. 4. In Fig. 4, C is the concentration of NO_2 in the main body of the gas phase or the liquid phase, C' is the concentration of NO_2 in the interface areas between the gas phase and the liquid phase. Because of turbulence in the gas phase and stirring in the liquid phase, the concentration of every solute is uniform everywhere in the main bodies, but it decreases along the transfer direction of NO_2 in the boundary areas. When the transfer takes place, $\text{NO}_2(g)$ enters the gas boundary layer, then passes through the liquid boundary layer, finally entering the liquid main body. Because NO_2 transfers by diffusion in the boundary layer, the first Fick law is followed:

$$J_g = -D_g A [dC_{\text{NO}_2(g)} / dX_g] = D_g A [C_{\text{NO}_2(g)} - C'_{\text{NO}_2(g)}] / X_g, \quad (10)$$

$$J_l = -D_l A [dC_{\text{NO}_2(l)} / dX_l] = D_l A [C'_{\text{NO}_2(g)} - C_{\text{NO}_2(l)}] / X_l. \quad (11)$$

here, J_g and J_l are the transfer rate of NO_2 ; D_g and D_l are the diffusion coefficients of NO_2 ; X_g and X_l are the thickness of the boundary layers, respectively in the gas boundary layer and the liquid boundary layer; A is the interface area. If Henry's law is followed and the transfer reaches

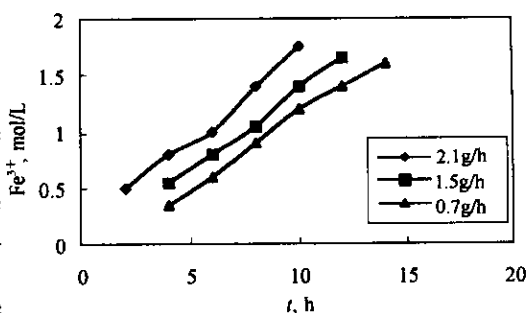


Fig. 3 The changes of ferric concentration with time

stable state, we will have $C'_{\text{NO}_2(\text{g})} = HC'_{\text{NO}_2(1)}$ and $C_{\text{NO}_2(\text{g})} = HC_{\text{NO}_2(1)}^*$, and $J = J_g = J_1$, here H is Henry constant, $C_{\text{NO}_2(1)}^*$ is the concentration of $\text{NO}_2(1)$ in equilibrium with $\text{NO}_2(\text{g})$, so Equations(10) and (11) become:

$$J = DgA[HC_{\text{NO}_2(1)}^* - HC'_{\text{NO}_2(1)}]/X_g, \quad (12)$$

$$J = D_1A[C'_{\text{NO}_2(1)} - C_{\text{NO}_2(1)}]/X_1. \quad (13)$$

Or

$$JX_g/DgAH = C_{\text{NO}_2(1)}^* - C'_{\text{NO}_2(1)}, \quad (14)$$

$$JX_1/D_1A = C'_{\text{NO}_2(1)} - C_{\text{NO}_2(1)}, \quad (15)$$

(14) + (15):

$$J = DgD_1A[C_{\text{NO}_2(\text{g})} - HC_{\text{NO}_2(1)}]/[X_gD_1 + X_1DgH]. \quad (16)$$

Since the solution was strongly stirred, so X_1 is very small and X_1DgH can be neglected, Equation (16) becomes:

$$J = DgA[C_{\text{NO}_2(\text{g})} - HC_{\text{NO}_2(1)}]/X_g. \quad (17)$$

It can be seen that the larger interface areas is, the more quickly NO_2 transfers across the interface; the higher partial pressure of $\text{NO}_2(\text{g})$ is, the more quickly NO_2 transfers across the interface.

2.3.2 The concentration of NO_2 in the solution

As soon as $\text{NO}_2(\text{g})$ enters the solution, it quickly reacts with Fe^{2+} . The concentration of $\text{NO}_2(1)$ in the solution can be obtained by stable state treatment.

$$\begin{aligned} dC_{\text{NO}_2(1)}/dt &= J - VK_8C_{\text{Fe}^{2+}}C_{\text{NO}_2(1)} = DgA[C_{\text{NO}_2(\text{g})} - HC_{\text{NO}_2(1)}]/X_g \\ &\quad - VK_8C_{\text{Fe}^{2+}}C_{\text{NO}_2(1)} = 0, \end{aligned} \quad (18)$$

here V is the volume of the solution, K_8 is the reaction rate constant of Equation(8). From Equation(18), following equation was obtained:

$$C_{\text{NO}_2(1)} = DgAC_{\text{NO}_2(\text{g})}/[X_g(DgAH/X_g + VK_8C_{\text{Fe}^{2+}})].$$

Because the gas phase was not stirred, X_g is relatively large and $DgAH/X_g$ can be neglected, therefore we have

$$C_{\text{NO}_2(1)} = DgAC_{\text{NO}_2(\text{g})}/X_gVK_8C_{\text{Fe}^{2+}}. \quad (19)$$

2.3.3 The rate equation of the reaction

According to Equation(8), the oxidation rate of Fe^{2+} was expressed as follows:

$$-dC_{\text{Fe}^{2+}}/dt = K_8C_{\text{Fe}^{2+}}C_{\text{NO}_2(1)}. \quad (20)$$

Substitute Equation(19) for $C_{\text{NO}_2(1)}$ in Equation (20), we have

$$-dC_{\text{Fe}^{2+}}/dt = DgAC_{\text{NO}_2(\text{g})}/(X_gV) = KAC_{\text{NO}_2(\text{g})}, \quad (21)$$

here $K = Dg/(X_gV)$. It is clear that this reaction is zero order with respect to Fe^{2+} , first order with respect to $\text{NO}_2(\text{g})$, and first order with respect to interface area A . So in order to decrease the time needed to complete the reaction the pressure of $\text{NO}_2(\text{g})$ can be increased as shown in Figures 2 and 3. However, this will make the effects of corrosion on the testing devices more serious, possibly requiring pressure resisting devices. In addition, you could reduce the reaction time by increasing the interface area between the gas and liquid. For this purpose, one factory in China used reaction tower instead of the common reactor, as the result, the time needed to complete the reaction was reduced to 2 hours from more than 10 hours(Chen, 1995).

If the $C_{\text{NO}_2(\text{g})}$ and the interface area are maintained constant, Equation(21) becomes:

$$-dC_{\text{Fe}^{2+}}/dt = K, \quad (22)$$

the integral equation will be

$$C_{\text{Fe}^{2+}} = -Kt + B,$$

here B is the integral constant. This equation is accord with Fig.2 properly.

3 Conclusion

The transfer of $\text{NO}_2(\text{g})$ across the interface between gas and liquid is the key procedure in the oxidation reaction of Fe^{2+} by oxygen. If the pressure of $\text{NO}_2(\text{g})$ or the interface area is increased, the transfer rate of $\text{NO}_2(\text{g})$ will be increased, therefore the rate of whole PFS preparation process will be increased.

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