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www.elsevier.com/locate/watres

Wat. Res. Vol. 35, No. 14, pp. 3418–3428, 2001
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Printed in Great Britain
0043-1354/01/\$ - see front matter

PII: S0043-1354(01)00034-3

MODIFIED INORGANIC POLYMER FLOCCULANT-PFSi: ITS PREPARATION, CHARACTERIZATION AND COAGULATION BEHAVIOR

DONGSHENG WANG and HONGXIAO TANG*

State Key Laboratory of Environment Aquatic Chemistry, Research Centre for Eco-Envir. Sci.,
Academia Sinica, P.O. Box 2871, Beijing 100085, People's Republic of China

(First received 7 April 2000; accepted in revised form 27 December 2000)

Abstract—As a new kind of water and wastewater treatment reagents, inorganic polymer flocculants (IPFs) are in a trend of rapid development. Among them, iron-based IPF without any toxic problems is greatly expected. In this paper, a new protocol for preparation of iron-based IPF is investigated. Three kinds of silica, named silicaA, silicaB and silicaC, are prepared and used as modifiers to tailor-make polyferric silicate (PFSi), denoted PFSiA, PFSiB and PFSiC, respectively, in accordance to the above silica. Based on several direct and indirect speciation methods, the species distribution and characteristic of three kinds of PFSi are investigated in detail. The experiment results show that the species distribution of PFSi is mainly decided by the kinds of silica introduced and Si/Fe ratio adopted. SilicaA and silicaB function as precipitation preventing reagents during the hydrolysis of Fe(III). At certain amount of basicity, Fe_a (monomers) increases with increase of Si/Fe ratio, while Fe_c (colloidal species) decreases markedly. Although the formation of Fe_c is inhibited, the stabilization of Fe_b (oligomers or polymers) can still not be achieved. SilicaC on the other hand exhibits little effect on the species distribution of modified Fe(III) solutions. The coagulation behavior of above PFSi is also examined. The different effect of silica is then discussed with respect to the chemical species. © 2001 Elsevier Science Ltd. All rights reserved

Key words—coagulation, inorganic polymer flocculant (IPF), Fe(III), modifier, silica

INTRODUCTION

Inorganic polymer flocculants (IPFs) are a new kind of water and wastewater treatment reagents, which have been developed worldwide since the 1960s (Tang and Stumm, 1987; Tang, 1990). Because of their superior efficiency and relatively lower cost compared with traditional coagulants such as aluminum or iron salts, IPFs are becoming the main water and wastewater treatment reagents, with production and applications on a large scale in Japan, Russia, West Europe and China presently. The USA has also paid much attention to it in recent years (Tang, 1990; AWWA, 1989; Dentel, 1991; Gray *et al.*, 1995).

Being tailor-made to contain desired more powerful coagulating species, pre-produced IPFs are successful in surpassing the effectiveness of inorganic metal salts and in remedying certain difficulties experienced with seasonal changes in surface water quality (Tang and Stumm, 1987; Gray *et al.*, 1995; Bottero, 1990; Dempsey *et al.*, 1984; Van Benschoten and Edzwald, 1990a,b). Since the application of aluminum-based coagulants was questioned for their potential toxicity (Lewis, 1989), the needs of iron-

based coagulants both on their quality and quantity are increased. However, compared with aluminum-based IPFs, they are still in the development stage and remain in laboratory tests. Although there is commercial polyferric sulfate (PFS) product available, which is manufactured by utilization of industrial wastes or byproducts and therefore at a lower cost, its efficiency remains in a common level. While PFS has been produced in a limited extent, polyferric chloride (PFCI) is still in a state of controversy (Tang and Stumm, 1987; Mikami *et al.*, 1980). LePrince *et al.* (1984) reported the partially neutralized iron(III) chloride prepared at r_{OH} ($= OH/Fe$) 2.5 exhibited the best capability for turbidity removal, especially at low temperatures. Tang and Stumm after detailed examination of PFCI solutions at various B^* ($= OH_{bound}/Fe_{total}$) values, classified PFCI into five types and considered the type C at the intermediate B^* values to contain the largest portion of high charged polycations (Tang and Stumm, 1987). Recently, Tang *et al.* (1994) improved markedly the stability and efficiency of PFCI by using phosphate as stabilizer.

In this investigation, we tried to prepare iron-based IPF-PFSi by adding other modifiers of several kinds of silica. The species distribution and transformation properties were characterized by combining direct

*Author to whom all correspondence should be addressed.

Fax: +86-10-6292-3563; e-mail: wgds@mail.rcees.ac.cn

and indirect speciation methods. The coagulation behavior of preformed PFSi was then examined and discussed in respect of different chemical species.

BACKGROUND OF MODIFIER SELECTION

In aqueous solution, the trivalent Fe(III) ions readily undergo hydrolysis, complexation/polymerization and precipitation. In general, the Fe(III) monomers and polymers generated by hydrolysis have a stronger tendency to precipitation than aluminum. How to stabilize the iron polymers in the optimum form for coagulating function is always a key problem for preparing high level flocculants and commercial products. Typically, the study of hydrolysis of Fe(III) is carried out on partially neutralized solution prepared by slow addition of base. The extent of hydrolysis and polymerization is characterized with the operation parameter B ($=\text{OH}/\text{Fe}$) and more precisely by hydrolysisity B^* (Tang and Stumm, 1987; Tang, 1990). Four regions can be distinguished from a typical titration curve, which can be roughly related to the types of polymeric ferric solutions by combining with the comprehensive chemical model of Tang and Stumm (1987). Obviously, to preform stable Fe(III) polymers, it needs to cross the first precipitation zone (roughly $0.2 < B^* < 0.5$) and prevent homogeneous amorphous precipitation ($B^* > 1.5$). Despite numerous investigations, the mechanism of hydrolysis-polymerization-precipitation of Fe(III) and the quantitative principles are still not perfectly clear (Van De Woude and De Bruyn, 1983; Melikov, 1987; Khoe and Robins, 1989). The nature and behavior of hydrolysis products are controlled by many factors, such as the components and concentration of the primary Fe(III) solution, pH, components of co-existing anions, temperature, time of aging, traces of contaminants including dust particles, which can seed the precipitation of the solid, preparation methods and other topchemical transformation. Generally speaking, with physical conditions established, the salient deciding factor is anion components.

In view of this, to prevent iron species from precipitating, the following three kinds of materials might act as modifiers: (1) inorganic anions such as sulfates, phosphates, or silicates; (2) organic anions such as various organic acids, surfactants; and (3) artificial or natural organic polyelectrolytes such as polyalcohol, polyose. The mechanism of their hydrolysis-precipitation inhibition might be attributed to their coordinate effects with iron monomers to influence the subsequent polymerization process as result, or direct combination with iron polymers to prevent further polymerization. Anyway, the modifiers chosen to prepare flocculant should satisfy the following conditions: (1) no deterioration on the efficiency of PFCl as flocculant; (2) without toxicity, and other after effects during water treatment;

(3) convenient to be applied and with low cost. According to these, inorganic anions may be of first choice. Besides phosphate, the silica species are in preference for their strong coordinate and aggregating effects and they also possess a few particular different aqueous behaviors (Iler, 1979).

In aqueous solutions, a variety of polymeric silica species can be formed. By the silica-molybdate acid analysis method (Iler, 1979), they can be classified into three categories as Si_a (monomers), Si_b (oligomers) and Si_c (polymers and colloids) like the ferron method (Hsu and Cao, 1990) performed with hydrolyzed Al(III) and Fe(III) species. Since the separation and purification of these species are very difficult, three kinds of silica, named silicaA, silicaB and silicaC, are first prepared containing different amounts of the above silica species. The significance of various silica on hydrolysis and polymerization of Fe(III) and their subsequent effect on coagulation become the focus of this study.

MATERIALS AND METHODS

Preparation of modifiers

All reagents used were of analytical reagent grade except those being pointed out. Before the preparation of PFSi, three kinds of modifiers, silicaA, silicaB and silicaC, were first prepared. SilicaA and silicaB were prepared by acidification of reagent Na_2SiO_3 and industrial water glass solutions, respectively, using HCl. SilicaA was prepared first as 0.6 mol/L stock solution of Na_2SiO_3 . Before use, a certain amount of stock solution was titrated into diluted HCl solution at a rate of 0.5 ml/s under rapid stirring using 665Dosimat Titrprocessor (Metrohm, Sweden). The final pH was 1.80, and the concentration of Si was 0.40 mol/L. SilicaB was prepared using the same procedure, except that 0.6 mol/L (Si) diluted water glass solution was prepared in-situ and used immediately. SilicaC was traditional activated silica, prepared from industrial water glass by neutralizing 83% of its alkalinity and aged for 1 h. The main characteristic and results of speciation as characterized using Si-Mo assay are summarized in Table 1.

In summary, silicaA contains mainly monomer and low polymer with Si_a 71.4%, Si_b 13.3% and Si_c 15.3%. The species distribution in silicaB is Si_a 26.6%, Si_b 9.40 and Si_c 64.0%, and silicaC contains mainly Si_c , >96%. It must be pointed out that the Si_c component in the above silica differentiates significantly. The reaction rate constant, k_c , was 0.0244, 0.0094 and 0.0002 for silicaA, silicaB and silicaC respectively. Only in silicaC, the Si_c component can be detected by photon correlation spectroscopy (PCS).

Table 1. Species distribution of three kinds of silica

Silica	Si_a (%)	Si_b (%)	Si_c (%)	k_c	d (nm) ^a
Stand. Si	100	0	0	0.294	UD ^b
Silica(A)	72.1	13.8	14.1	0.0279	UD
Silica(B)	26.6	9.4	64.0	0.0095	UD
Silica(C)	1.4	0.0	98.6	0.0001	47.3

^a Measured by PCS using Cumulants analysis.

^b Undetectable by PCS.

Preparation of PFSi(A, B, C)

Three kinds of PFSi (A–C) were prepared from silica (A–C) respectively. A stock solution was prepared as 3.1 mol/L FeCl_3 . The prepared silica solution was quickly added into a certain amount of diluted FeCl_3 stock solution under vigorous stirring at the predetermined Si/Fe ratio, i.e. 2.0, 1.0, 0.5 and 0.2. Under rapid stirring at room temperature, 0.5 mol/L NaHCO_3 was titrated micro-dropwise at a flow rate of 0.6 ml/min into above solution. The volume of NaHCO_3 was varied depending on the desired basicity B at 0, 0.6, 1.0 (corresponding to type A and C of PFCI, Tang and Stumm, 1987), respectively. The final Fe(III) concentration was 0.3 mol/L. The serial numbers of samples are explained in Table 2. The pH evolution was recorded immediately after sample preparation was finished.

Characterization methods

Two main kinds of speciation methods, i.e., the timed complexation spectroscopy method and PCS analysis, were applied. The timed complexation spectroscopy methods were ferron methods to differentiate Fe(III) species, and Si–Mo methods to differentiate silica species, respectively. The experiments were run on Beckman DU650-UV-Visible Spectrometer. The PCS measurements were performed on a Brookhaven Model BI-200SM servomotor-controlled light scattering goniometer with a Model BI-9000AT autocorrelator (Wang *et al.*, 2000). The incident light source was a 35 mW He–Ne laser operating at a 632.8-nm wavelength with vertical polarization. The instrument alignment was checked by the BI-IST software, the deviations were less than 2% over the angular range.

Coagulation experiments

A stock suspension of clay particles was first prepared by dispersing powder kaolin in deionized water to a concentration of 50 g/L and preserved in refrigerator. The stock suspension was finely mixed prior to use. Then under rapid stirring a certain quantity was transferred to test water, which contained 5×10^{-4} mol/L NaHCO_3 and NaNO_3 , respectively. Therefore, the effect of bicarbonate ion was controlled at a constant range (Letterman *et al.*, 1979). A total amount of 20 L suspension was prepared for batch experiments. The size distribution of the kaolin suspension was measured by a particle counter (Multisizer II, Coulter Electronics, Hialeah, FL, USA). The results showed that the particles in the suspension had a mean volume diameter of 2.28 μm with a relatively narrow size distribution. The specific surface area of kaolin was 30.2 m^2/g measured by an accelerated surface and porosity system (2000AP, Micrometrics, USA). Electrophoretic mobility (EM) of the kaolin particles was measured by a laser zeta potential analyzer (Zetaplus, BIC, NY, USA). It was found that the particles

were negatively charged at all pH values measured (from 3.0 to 11.0).

For the purpose of evaluating the coagulation efficiency, the conventional jar test was applied using a standard bench-stirrer (PB-700 JarTester, Phipps & Bird, Richmond, VA, USA). The jar test was carried out in beakers of 600 ml. The target pH was adjusted by adding predetermined amounts of 0.1 and 0.02 mol/L HCl or NaOH to the suspension. Coagulation experiments with a 0.3 mol/L ferric chloride solution, which has been classified as type A based on the analysis of Tang and Stumm (1987) was also conducted for comparisons. During the rapid mixing the coagulants were dosed by a milli-injector. The initial rapid mixing with 200 rpm was used to obtain swift homogeneous dispersion. The rapid mixing of 30 s was followed by slow mixing for 15 min at speed of 40 rpm. Then the suspension was left to settle for 10 min. After settling, the sample was collected at 2.0 cm beneath the surface for residual turbidity (RT) measurement using a model turbidimeter (NDH-20, Japan). EM was measured just after the rapid mixing using the BIC-Zetaplus.

RESULTS AND DISCUSSION

pH evolution and stability

The pH values were monitored immediately after sample preparation. It is found that the silica (A, B, C) modified ferric chloride (PFSi at $B = 0$), all maintain steadily the same pH value. With PFSi samples at $B = 0.6$, the pH value decreases with aging but at a different range for the different kinds of silica and Si/Fe ratio applied (Fig. 1). Silica(A) and silica(B) show similar pattern of decreasing the pH with increasing of Si/Fe ratio. However, silica(C) shows little effect of Si/Fe ratio on pH. The PFSi samples at $B = 1.0$ appear to have the same trend as $B = 0.6$.

The stability of the samples was observed under the same room temperature, and the results are shown in Table 3. With silica modification at moderate Si/Fe ratio (0.2–1), the stability of solution is markedly improved. Some of the samples stand above 1 year without precipitation. However, with Si/Fe ratio increases more than 1, the stability of sample deteriorates again. Some of the samples finally become gel.

In order to understand further the effect of different kinds of silica on the hydrolysis of Fe(III), the first precipitation zone for different silica at Si/Fe

Table 2. The serial numbers of samples

B	Silica	Si/Fe ratio				
		2.0	1.0	0.5	0.2	0
0	A	0PFSiA20	0PFSiA10	0PFSiA05	0PFSiA02	0PFC (FeCl_3)
	B	0PFSiB20	0PFSiB10	0PFSiB05	0PFSiB02	
	C	0PFSiC20	0PFSiC10	0PFSiC05	0PFSiC02	
0.6	A	06PFSiA20	06PFSiA10	06PFSiA05	06PFSiA02	06PFC
	B	06PFSiB02	06PFSiB10	06PFSiB05	06PFSiB02	
	C	06PFSiC02	06PFSiC10	06PFSiC05	06PFSiC02	
1.0	A	10PFSiA20	10PFSiA10	10PFSiA05	10PFSiA02	10PFC
	B	10PFSiB20	10PFSiB10	10PFSiB05	10PFSiB02	
	C	10PFSiC20	10PFSiC10	10PFSiC05	10PFSiC02	

ratio of 1 was investigated as shown in Fig. 2. It is interesting to note that the precipitation region is significantly narrowed with modification of silica(A) and silica(B), while silica(C) exhibits only limited effect.

Fig. 1. The pH evolution of PFSi at $B = 0.6$.

Speciation by ferron assay

The speciation of all samples was run after 24h aging. Results obtained from ferron assay are summarized at Table 4. Along with the increase of B , the amount of Fe_a decreases, while the amount of Fe_c increases markedly. However, the Fe_b species are still the minor components, existing only between 2% and 10%. The maximum is not more than 15%. It increases only slightly with increase of B . Compared with the results of PFCI (Gray *et al.*, 1995; Tian and Tang, 1989), the same trend of species distribution is observed. The increase of basicity promotes mainly the amount of Fe_c with little yield of Fe_b .

Table 4 illustrates simultaneously the effect of types of silica and Si/Fe ratio. At $B = 0$, the only species existing are Fe_a . Silica exhibits no effect. With the increase of B to 0.6 and 1.0, the effect of silica becomes obvious. Silica(A) shows a similar effect as silica(B). By increasing the Si/Fe ratio, Fe_a and Fe_b increase, however, Fe_c decreases significantly. Thus, at certain amount of silica(A) and silica(B), the further hydrolysis of Fe(III) can be inhibited. But with silica(C), to the contrary, the increases of Si/Fe ratio has little effect on the species distribution, which is almost similar as the sample of PFCI. Hence, the kinds of silica introduced have significant effect on the species distribution of PFSi corresponding with Si/Fe ratio. Silica(A) and Silica(B) are more active than silica(C) in preventing the hydrolysis of Fe(III), through strong complexation or stereo combination with Fe(III) species by interaction of type $-Fe(OH)_2^+ + -SiO(OH)_3 \rightleftharpoons -FeOSi(OH)_3 + H_2O$. However, silica(C) appears inert to the hydrolysis of Fe(III) and this may contribute to its bigger particle size and with little amount of surface active SiOH group available in comparison with silica(A) and silica(B). By increasing the Si/Fe ratio, more quantity of Fe(III) is complexed as indicated from the increase of Fe_a and this may interfere with subsequent polymerization and particle growth. As shown previously in Fig. 2, the first precipitation zone is

Table 3. The stability of samples

No.	Si/Fe	Stability	No.	Si/Fe	Stability	No.	Si/Fe	Stability
0PFSiA20	2.0	Gel	06PFSiA20	2.0	70 ^a	10PFSiA20	2.0	85
0PFSiA10	1.0	/ ^b	06PFSiA10	1.0	/	10PFSiA10	1.0	/
0PFSiA05	0.5	/	06PFSiA05	0.5	152	10PFSiA05	0.5	167
0PFSiA02	0.2	/	06PFSiA02	0.2	141	10PFSiA02	0.2	138
0PFSiB20	2.0	Gel	06PFSiB20	2.0	118	10PFSiB20	2.0	/
0PFSiB10	1.0	/	06PFSiB10	1.0	/	10PFSiB10	1.0	/
0PFSiB05	0.5	/	06PFSiB05	0.5	/	10PFSiB05	0.5	/
0PFSiB02	0.2	/	06PFSiB02	0.2	149	10PFSiB02	0.2	152
0PFSiC20	2.0	64	06PFSiC20	2.0	84	10PFSiC20	2.0	/
0PFSiC10	1.0	102	06PFSiC10	1.0	/	10PFSiC10	1.0	/
0PFSiC05	0.5	/	06PFSiC05	0.5	/	10PFSiC05	0.5	/
0PFSiC02	0.2	/	06PFSiC02	0.2	87	10PFSiC02	0.2	94
0PFC	0	/	06PFC	0	55	10PFC	0	70

^aDestabilized time (day).

^bNo precipitation observed.

markedly modified in presence of silica(*A*) and silica(*A*). However, the species distribution and transformation mode has not been changed. The main species generated are Fe_a and Fe_c , no significant increase of Fe_b is observed. It is found that the subunits of iron hydroxide sols influenced by the type of anions present are in the size range of 16 Å in chloride solution (a model of polymer containing 24 Fe atoms is also proposed) or vary from 7 up to 13.5 Å in nitrate solution (Bottero *et al.*, 1991; Tchoubar *et al.*, 1991). It seems thus that these polymers once formed lack enough stability and quickly undergo aggregation or coalescence. The function of silica is mostly on retarding the formation of these subunits and also Fe_c as result. The stabilization of these subunits could still not be achieved in chloride and nitrate solutions. It is noteworthy that with the presence of silica, the species of Fe_a , Fe_b and Fe_c in PFSi samples are no longer the same as that in single PFCl solutions. They are all in a state of complexation or combination with silica species.

Speciation by molybdc acid assay

Due to the analytical limitation, only suitable samples aged for 24 h were analyzed using Molybdc

Fig. 2. Effect of silica on the first precipitation zone of Fe(III).

acid method, and PCS determination is described as follows. The results of PFSiA and PFSiB are summarized in Table 5. For comparison, the results of aged silica(*A*) and silica(*B*) are also displayed.

It can be seen also that *B* value has important effect on the existing state of silica species in PFSi. At *B* = 0, the characteristic of species distribution of samples remains similar mode of silica introduced, while the species of original silica sample change quickly after 24 h aging. Obviously, complexation with Fe(III) inhibits further polymerization of silica. However, as *B* increases, the species distribution of silica in PFSiA changes markedly, and differentiates with Si/Fe ratio. By increasing Si/Fe ratio, the amount of Si_b and Si_c increase, indicating the combination between silica and hydrolyzed Fe(III) species is reinforced with alkalinity addition.

Speciation by PCS

The lowest limit of detection for the PCS instrument is the particle size of about 1–5 nm. However, only those with scattering intensity above 1 kcps were reliable. All the samples of 0PFSiA, 0PFSiB, 06PFSiA20, 06PFSiA10, 06PFSiB20 and 10PFSiA20 do not have enough scattering intensity. As shown from Tables 4 and 5, the mainly existing species in above samples are Fe_a and Si_a . Therefore the PCS diagram represents mainly the particle size distribution of Fe_c and Si_c . Figure 3 shows some of the results of PCS measurements of PFSiB at *B* = 1.0.

The PCS diagrams show that along with the increase of Si/Fe ratio, more complicated polymers are formed and the particle size distribution is of range and multidispersed. It is evident that some of copolymerized species or aggregates between silica and iron(III) polymers are formed. By decreasing the Si/Fe ratio, the particle distribution becomes typically that of PFCl (Bottero *et al.*, 1991; Wang *et al.*, 2000), i.e., exhibiting a narrow distribution with particle diameter at several nm.

Table 4. The speciation of PFSi(*A, B, C*): ferron assay

No.	Fe_a (%)	Fe_b (%)	Fe_c (%)	No.	Fe_a (%)	Fe_b (%)	Fe_c (%)	No.	Fe_a (%)	Fe_b (%)	Fe_c (%)
0PFSiA20	100	0	0	06PFSiA20	97.8	2.2	0.0	10PFSiA20	85.0	11.6	3.4
0PFSiA10	100	0	0	06PFSiA10	95.7	4.3	0.0	10PFSiA10	77.7	15.9	6.4
0PFSiA05	100	0	0	06PFSiA05	89.3	4.0	6.7	10PFSiA05	72.2	7.6	20.2
0PFSiA02	100	0	0	06PFSiA02	81.0	3.1	15.9	10PFSiA02	64.5	4.9	30.6
0PFSiB20	100	0	0	06PFSiB20	98.1	1.9	0.0	10PFSiB20	87.8	6.7	5.5
0PFSiB10	100	0	0	06PFSiB10	96.7	3.3	0.0	10PFSiB10	77.1	7.6	15.3
0PFSiB05	100	0	0	06PFSiB05	83.8	2.7	13.5	10PFSiB05	71.9	5.5	22.6
0PFSiB02	100	0	0	06PFSiB02	81.3	2.4	16.3	10PFSiB02	67.9	5.5	26.6
0PFSiC20	100	0	0	06PFSiC20	78.2	1.3	20.5	10PFSiC20	58.4	8.9	32.7
0PFSiC10	100	0	0	06PFSiC10	77.4	2.5	20.1	10PFSiC10	60.2	8.0	31.8
0PFSiC05	100	0	0	06PFSiC05	79.7	1.9	18.4	10PFSiC05	62.4	7.0	30.6
0PFSiC02	100	0	0	06PFSiC02	77.4	2.4	20.2	10PFSiC02	63.4	4.0	32.6
0PFC	100	0	0	06PFC	79.4	2.5	18.1	10PFC	64.7	2.8	32.5

Coagulation efficiency

The coagulation results and change of particle charge with dosage of PFSi at $B = 0$ are shown in Fig. 4. Although the samples are all prepared at basicity of 0, the capability of charge neutralization is distinguished from each other and differentiates markedly with the kinds of silica used and the

Table 5. The speciation of PFSi by Si-Mo assay

No.	Si _a (%)	Si _b (%)	Si _c (%)
Silica A 0 h	72.1	13.8	14.1
Silica A 24 h	14.3	1.8	83.9
0PFSiA20	74.4	10.2	15.4
0PFSiA10	72.4	14.3	13.3
0PFSiA05	71.8	13.8	14.4
0PFSiA02	71.8	12.6	15.6
06PFSiA20	25.2	9.9	64.9
06PFSiA10	30.1	15.7	54.2
06PFSiA05	39.4	10.3	50.3
06PFSiA02	72.8	11.2	16.0
10PFSiA20	6.7	22.8	70.5
10PFSiA10	14.9	31.6	55.5
10PFSiA05	50.4	17.3	32.3
10PFSiA02	80.9	9.2	9.9
Silica B 0 h	26.6	9.4	64.0
Silica B 24 h	18.2	0.4	81.4
0PFSiB20	24.8	7.4	67.8
0PFSiB10	22.5	8.9	68.6
0PFSiB05	23.2	4.1	72.7
0PFSiB02	30.6	2.5	66.9

increase of Si/Fe ratio. It can be seen from Fig. 4(a) and (b) that for the increase of PFSiA and PFSiB dosage, the EM of particles increases and turns into positive gradually. However, the trend decreases quickly with increase of Si/Fe ratio, indicating that the charge-neutralization capability of PFSi decreases significantly with the increase of Si/Fe ratio. The effect of silica and Si/Fe ratio on change of RT can also be observed clearly from Fig. 4. At low dosage, the higher the Si/Fe ratio, the higher residual turbidity, since the particles remain colloidal stable being highly negatively charged. By increasing the dosage, the charge of particles becomes gradually neutralized, thus, particle destabilization takes place. The coagulation efficiency changes then. It is interesting to note that better turbidity removal is observed for PFSi at moderate Si/Fe ratio with particles still negatively charged. Accordingly, during experiment it is observed that the flocs formed are larger and precipitate rapidly.

For PFSiC as shown in Fig. 4(c), the change of EM shows a similar trend of the effect of Si/Fe ratio. The higher Si/Fe ratio, the lower charge-neutralization capability is exhibited. However, the scale of EM decrease is exhibited only limitedly, while the coagulation behavior is significantly modified with the increase of Si/Fe ratio. From the result of RT curves as shown in Fig. 4(c), it can be seen that turbidity removal is best for samples at high Si/Fe

Fig. 3. The typical PCS diagram of PFSi.

Fig. 4. The coagulation behavior and particle EM change of PFSi at $B = 0$.

ratio. The flocs appear again fast, tight and larger, and undergo rapid precipitation.

A similar trend has been found on the other PFSi with higher B values. The typical results of PFSi at $B = 1.0$ are shown in Fig. 5. With the increase of coagulant dosage, the EM of particle increases also from negative to positive depending on the kinds of silica and Si/Fe ratio. Silica(A) and silica(B) exhibit a remarkable effect on the charge neutralization ability of PFSi, while silica(C) has only moderate effect.

However, the effect of kinds of silica and Si/Fe ratio on the coagulation efficiency becomes more obvious. As shown in Fig. 5, the coagulation of clay particles is greatly inhibited for PFSiA and PFSiB at high Si/Fe ratio. While at moderate Si/Fe ratio, an enhancement of coagulation is observed with the increase of dosage even if particles remain negatively

charged. Note that such a modification is still very limited. However, for PFSiC a remarkable effect of silica(C) is found. Increase of the Si/Fe ratio results in efficient coagulation and significant lower residual turbidity.

Mechanism of coagulation with PFSi: Effect of silica

With the chosen experimental conditions, the difference of coagulation results will mainly be dependent on the composition of coagulants. Based on the ferron assay, the species in PFSi samples can be classified similarly as Fe_a , Fe_b and Fe_c , which differs markedly with those in pure PFCI solutions. The main species, Fe_a and Fe_b , in the PFCI solutions at low basicity are highly positive charged monomers and oligomers, such as dimers and trimers (Gray

Fig. 5. The coagulation behavior and particle EM change of PFSi at $B = 1.0$.

et al., 1995). When added to suspension, they undergo rapid hydrolysis and adsorption, the further hydrolysis species formed are still positively charged and cause efficient charge-neutralization with the negative kaolin particles. In PFSiA and PFSiB, the main species, Fe_a , are in a state of complexation with silica by interaction of type $-Fe-OH_2^+ + Si(OH)_4 \rightleftharpoons -Fe-O-Si(OH)_3 + H_3O^+$. When added to suspension, they also readily undergo hydrolysis and precipitation, since the solution is supersaturated with respect to ferric hydroxide under the experimental conditions. However, the charge of precipitation formed is depended largely on the Si/Fe ratio. At high Si/Fe ratio, a weaker charged hydrolytic product might be formed with low charge-neutralization capability, resulting in thus deteriorated turbidity removal. By decreasing the Si/Fe ratio, the charge of hydrolytic product increases so that charge reversal can then be observed. At higher coagulant dosage, the negatively

charged clay particles become gradually neutralized. Particle destabilization is observed. An enhancement of turbidity removal takes place for PFSi at moderate Si/Fe ratio even when particles are still negatively charged. Recent study of the effect of soluble silica on the alum coagulation has also shown such a phenomenon (Duan, 1997). Similar improvement of coagulation has been found also with sulfate ion (Letterman, 1983). Although it becomes difficult to interpret the coagulation result with EM, the enhancement is involved closely with the kinetics of precipitation. With the charge effect by the above complexation interaction, the formation of precipitation is kinetically accelerated compared with coagulation of $FeCl_3$. In the meantime, the primary particles formed are in a moderate particle size level (of a few nm as shown in PCS analysis) and their aggregates are fractal objects with rather open structures (Jullien and Bottet, 1987). Therefore, such

an enhancement takes place only in higher coagulant dosage. A mechanism of electrostatic patch (Gregory, 1973) can also be invoked for such an enhancement. However, in the respects of turbidity removal, it is not economical for high dosage needed.

For PFSiC, the modifier silica(C) is mainly composed of colloid particles, which has little effect on the hydrolysis of Fe(III). The species in PFSiC remain highly positively charged and the effect of charge-neutralization is then maintained. In addition to charge-neutralization coagulation, another mechanism might be taken into effect, where the colloidal silica particles act as the core of hydrolysis products and function as the bridge between clay particles. Therefore, the better turbidity removal is observed at high Si/Fe ratios for PFSiC.

At higher basicity, the effect of silica become more evident. As shown previously, by increasing the basicity, Fe_c is increased with little increase of Fe_b . Therefore, the drop of charge-neutralization capability becomes more significant for PFSiA and PFSiB. It needs to be pointed out that the low basicity chosen here does not affect much the species distribution, and as result a similar coagulation trend is observed.

Indication on the improvement of stable iron-based IPF with high efficiency

During 1960s and 1970s (Tang and Stumm, 1987; Tang, 1990), PACl, PAS and other sorts of Al-based IPFs were produced and applied on an industrial scale gradually. From the history of development of IPF, it is found that Fe(III), the same trivalent metal ions as Al(III), is considered first to have a similar behavior of hydrolysis. Therefore, it is assumed that iron salts could be developed similarly into pre-formed IPF. This point of view became the initial basis for PFCl preparation. As result, PFCl with high basicity ($B = 2.5$) similar to that of PACl was considered to own the best coagulation capability.

However, it is important to pay more attention to the difference rather than the similarity of hydrolysis behavior between Al(III) and Fe(III). It is noticed gradually that the hydrolysis trend of Fe(III) is much stronger than that of Al(III). Under higher pH situation, the hydrolysis products of Fe(III) could no longer maintain their charge neutralization ability while aluminum species may be more refractory to hydrolysis and remain markedly positively charged. Furthermore, the primary hydrolysis products, the monomers, differentiate significantly both on their behavior and stereo structure. In a recent report, Martin (1991) considered that the iron monomers remained to be octahedral, while the monomer of Al(III) underwent a regular reduction from six through five to four-coordinate in the aluminate, $Al(OH)_4^-$. The four successive deprotonations from Fe^{3+} were spaced at about two pH units while the four Al^{3+} deprotonations occurred cooperatively

and squeeze into an interval of less than one pH unit. Hence, the Keggin structure as in Al_{13} polymers can be formed with Al(III) during alkalinity titration and similar structure for iron is impossible. Even if it might be possible for iron to form the same Keggin structure, the stronger hydrolysis trend would lead to the lower charge of this polymer causing it to become unstable for further polymerization or aggregation. However, the possibility of tetrahedral Fe has been suspected to be present in ferrihydrites (Cardile, 1989; Combes *et al.*, 1989).

The improvement of coagulation with PACl may due to the specific characteristic of Al_{13} both on its union structure and chemical behavior. Recent characterization of acid-base properties of Al_{13} (Furrer *et al.*, 1992) and coagulation behavior of PACl (Van Benschoten and Edzwald, 1990a,b; Bottero *et al.*, 1981; Parathasarathy and Buffle, 1985; Tang and Luan, 1996) showed that Al_{13} was quite stable from hydrolysis. It is interesting to note that with tetrahedral Al present in the center of the structure, the basicity of Al_{13} maintain is more than 2.0. Thus, it is possible to prepare PACl at high basicity with large yield of Al_{13} . Under normal slow alkalinity titration, polymer iron species could not exist in a stable state, although many studies revealed that the particles in the stable Fe(III) sols were consisted of subunits in the range of several Å (Bottero *et al.*, 1991; Tchoubar *et al.*, 1991). Even with the addition of modifiers such as silica, the readily occurring nucleation-precipitation of Fe(III) is slowed down due to the complexation effect. However, no higher yield of stable polymers is achieved. From these results, it seems impossible to prepare stable iron(III) polycations in large amount by partially neutralizing with alkalinity titration. However, the improved coagulation efficiency by silica modification indicates other methodology to tailor-make iron-based IPF. With the enhancement by the patch coagulation effect and the general bridge effect, the modified IPF-PFSi exhibits some special merits. Especially for silica(C), a much more efficient and economical turbidity removal could be reached with only slight decrease in charge-neutralization ability. Therefore, a general consideration on the aspects of charge-neutralization capability, precipitation formation, stability and bridge function will be needed for the further development and design of IPFs.

CONCLUSIONS

Several conclusions can be drawn from the above results:

The property and speciation of modified-PFSi depend significantly on the basicity, the kinds of silica introduced and the Si/Fe ratio adopted. Silica(A) and silica(B) function as precipitation preventing reagents during the hydrolysis of Fe(III).

At certain amount of basicity, Fe_a increases with increase of Si/Fe ratio, while Fe_c decreases markedly. Although the formation of Fe_c is inhibited, the stabilization of Fe_b can still not be achieved. Silica(C) on the other hand exhibits little effect on the species distribution of modified Fe(III) solutions. However, the trend of species distribution observed is similar as that of PFCI. It seems that iron polymers once formed lack enough stability and undergo quickly aggregation or coalescence. The function of silica is mostly on retarding the formation of these subunits and also Fe_c as result.

The coagulation efficiency of PFCI is markedly modified with introduction of silica. The charge-neutralization ability is deteriorated for silica(A) and silica(B) modified PFSi. At certain dosage, an enhancement of coagulation can be achieved through a mechanism of electrostatic patch effect. With the introduction of silica(C), slight decrease on charge-neutralization is observed, while significant enhancement of coagulation is obtained. However, it seems impossible to prepare stable iron(III) polycations in large amount by partially neutralizing with alkalinity as that of PACI. Preparation of IPF with higher efficiency may be approached by increasing the bridge effect. It should also be pointed out that due to the complicated nature of quality from water to water, a scientific design and application is needed based on the primary water quality conditions.

Acknowledgements—The help and discussion of Prof. Luan in this laboratory during experiments are greatly acknowledged. This research is supported by CNSF 59778019 and 29807004.

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