韓國環境科學會誌 第4卷(第2號), 181～194, 1995
J. of the Korean Environmental Sciences Society

Effects of Temperature on Flocculation Kinetics Using Fe(III) Coagulant in Water Treatment

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(Manuscript received 17 November, 1994)

Abstract

Flocculation kinetics using ferric nitrate as a coagulant to coagulate kaolin clay in water was examined as a tool to investigate the effect of low temperature under tightly controlled treatment conditions. Both the particle size distribution data obtained from Automatic Image Analysis (AIA) system and the on-line measurement of the degree of turbidity fluctuation in a flowing suspension by Photometric Dispersion Analyzer (PDA) were used to measure flocculation kinetics. Results show that cold water temperature had a pronounced detrimental effect on flocculation kinetics. For improving flocculation kinetics at low water temperature, maintaining constant pOH to adjust water chemistry for temperature changes was found to be partially effective only in the more acidic pH range studied.

Key Words : Flocculation kinetics, Fe(III) coagulant, Temperature effect, Particle size distribution, Turbidity flutuation.

1. INTRODUCTION

The study of flocculation kinetics is of fundamental interest in the field of water treatment, because rational study of the factors affecting the coagulation process should be based on the rate of particle growth. However, there has been little work done concerning direct measurement of flocculation kinetics spanning the full range of coagulation domains encountered in public water treatment. This research focuses on the use of Fe(Ⅲ) salt to make quantitative studies of the rate at which flocculation processes occur, the factors on which these rates depend, and the mechanisms involved. Fe(Ⅲ) salts are receiving attention as alternative coagulants to alum for several important reasons; (1) concerns about aluminum concentration in treated waters (AWWA, 1990), (2) possible cost savings comparing to other alternative coagulants, and (3) better coagulation efficiency at low water temperature and more efficient removal of color-causing organic materials than alum (Knocke *et al.*, 1986; Crozes *et al.*, 1995).

Although the treatment of cold water is encountered in the temperate regions of the world, published information on the impact of cold water temperature on flocculation is both scarce and contradictory. In particular, very little data are available on flocculation kinetics at low temperature covering the adsorption-destabilization (A/D) and sweep floc coagulation domains encountered in public water treatment. Therefore, it is necessary that the impact of low temperature on flocculation should be investigated to ensure the applicability of coagulation theory to water treatment practice on a year-round basis.

There are reports of decreased turbidity removal efficiency and deteriorated effluent quality at very low temperature. Water temperature can apparently affect fluid and particle motion, particle-particle interaction, hydrolysis reaction of metal salt coagulants, and adsorption and precipitation rates. Although these physical and chemical factors have been considered to be affected by varying water temperature in the process of flocculation, the system chemistry involving metal salt coagulants and water has been known to be an important factor (Hanson and Cleasby, 1990; Van Benschoten and Edzwald, 1990). The changes of chemistry in Fe(Ⅲ) salts and water due to cold temperature would affect the kinetics of flocculation through the influence of the temperature upon the rate of hydrolysis and precipitation of Fe(Ⅲ) salts, the change on the solubility product of iron, and the ion product of water (pK_w). The net effects of temperature would include lowered solubility product of water, retarded rate of hydrolysis of Fe(Ⅲ) salts, and larger pK_w at lower temperature.

Accordingly, an increase in optimum coagulation pH with a decrease in temperature was noted by several investigators (Camp *et al.*, 1940; Mohtadi and Rao, 1973; Hanson and Cleasby, 1990; Van Benschoten and Edzwald, 1990). The authors noted that some of adverse effects due to cold water temperatures were offset by an increase in the coagulation pH. Also, the differences in size and strength of flocs formed by using metal salt coagulants were reported at varying temperature. For example, the reduction in the apparent floc size and the formation of weaker flocs were noted at cold water temperatures (Morris and Knocke, 1984; Haarhoff and Cleasby, 1988; Hanson and Cleasby, 1990). In addition, under low temperature conditions, good treatment of particulates and natural organic matters with a Fe(Ⅲ) coagulant in comparison with alum has been reported (Knocke *et al.*, 1986; Haarhoff and Cleasby, 1988; Hanson and Cleasby, 1990; Crozes *et al.*, 1995). The authors ascribed the better performance of Fe(Ⅲ) salt to the faster rate of precipitation with Fe(Ⅲ). Recently, Hanson and Cleasby(1990) and Van Benschoten and Edzwald (1990) introduced the use of constant pOH for correcting system chemistry for temperature effects. The constant pOH, in effect, is maintaining hydroxyl ion concentration constant as the temperature changes. The authors noted that flocculation performance at low temperatures was improved with an increase in the coagulation pH, by using pOH as the independent variable rather than pH.

2. EXPERIMENTAL MATERIALS AND METHODS

These experiments were conducted using the experimental conditions selected from conventional jar test results. From the jar tests the optimum pH and coagulant dosages were chosen for the comparison of flocculation kinetics when utilizing either of the two main coagulation mechanisms, namely, the A/D and the sweep flocculation mechanisms. The experimental parameters are summarized in Table 1.

Kaolin clay (Kentucky Ball Clay), with a log mean diameter of 1.8 ㎛, was used as the primary particulate system. A stock clay suspension of 800 mg/L was prepared in a 60

Table 1. Summary of experimental conditions

Parameter	Description
Primary particle	Kaolin clay (1.8 ㎛ avg. equiv. circular dia.)
Particle concentration	25, 50, and 100 mg/L of kaolin clay (Turbidity: 24, 53, and 106 NTU)
Dilution water	distilled water with 0.005 M $NaNO_3$
Coagulant	stock solution: 0.25 M as $Fe(NO_3)_3.9H_2O$ dosing solution of 10 mg/mL as $Fe(NO_3)_3.9H_2O$
Temperature	room temperature (23 ± 0.5℃) and 5 ℃
Rapid mixing	250 rpm (G = 455 sec^{-1} at 23℃) for 1 or 2 min
Slow mixing	30, 45, 60 rpm (G = 20, 37, 56 sec^{-1} at 23℃)
Suspension	pH 6.0, 6.5, 6.8, and 8.0

L plastic tank equipped with a mixing device and brought to pH 7.0 with 0.1 N NaOH. The stock clay suspension was added to the dilution water to achieve the desired clay concentration. The dilution water used to make a desirable concentration of clay suspension from the 800 mg/L stock clay solution was distilled water. The distilled water was stored in a 300 L polyethylene tank before use, while it was being brought to equilibrium with atmospheric CO_2 and temperature. When diluting clay suspension, a desired amount of 1 M $NaNO_3$ was added to maintain 0.005 M of $NaNO_3$, which gives 0.005 M ionic strength in the diluted suspension. The choice of 0.005 M $NaNO_3$ was based on the results obtained from preliminary tests. According to the result of the preliminary tests, the ionic strength used, 0.005M did not give any sign of aggregation of clay particles due to destabilization caused by double layer compression and facilitated consistent measurements of the zeta potential (ZP). In addition, the ions, Na^+ and NO_3^- are known to be the indifferent electrolytes which do not form any complex with metal salt coagulants (Hunter, 1989).

Ferric nitrate was used as a coagulant to allow sulfate concentration to be controlled as an independent variable. The stock solution containing 0.25 M $Fe(NO_3)_3.9H_2O$ was stored at room temperature. The dosing solution of 10 mg/mL as $Fe(NO_3)_3.9H_2O$ was prepared volumetrically from the stock solution the day before each experiment was to be conducted, and was stored overnight to avoid coagulation differences due to a potential aging, and to ensure consistent speciation in the coagulant dosing solution. The pH of stock and dosing solutions were checked periodically to check for potential aging of Fe(Ⅲ) in the solution.

The suspension pH was adjusted to the desired target pH by using 0.02 to 0.05 N NaOH or 0.01 N HNO_3 as necessary. As shown in Table 1, a minimum pH of 6.0 was selected for one pH value on the basis of preliminary jar tests because coagulation at this pH can be expected to be mainly caused by the A/D mechanism. Stated another way, the formation of highly positive charged Fe(Ⅲ) species is expected to be predominant and the formation of hydroxide precipitate is expected to be very slow or none at this pH and at the dosages used. A pH of 8.0 was selected for the highest pH level on the basis of preliminary jar tests that showed the aggregation of particles mainly caused by the interaction between clay particles and rapidly formed hydroxide precipitate. In addition, $Fe(OH)_{3(S)}$ is least soluble at around pH 8.0.

The flocculation tests were conducted in an 18 L square batch reactor system which was equipped with a two-blade turbine impeller, electric motor and speed controller, and a tachometer. The stirring power input to the reactor was determined experimentally by direct measure of the torque on the impeller shaft at various rotational speeds. From the relation between torque and the rotational speed, the root mean square velocity gradient (G) was calculated from the power input (P) to the fluid and the viscosity as follows:

$$G=(P/\mu V)^{1/2}=(\tau\omega/\mu V)^{1/2}=(2\pi N\tau/\mu V)^{1/2} \quad (1)$$

where P is the power input, τ is the torque, ω is the angular velocity of the rotating impeller (radians/sec) with rotating speed, N (revolutions/sec). μ is the dynamic viscosity, and V is the reactor volume being mixed. From the measurement of torque in 18 L reactor, the G was found to be related to the rotating impeller speed by

$$G=0.135N^{1.471} \text{(at 23℃, with N in rev./min)} \quad (2)$$

At the lower temperature, the impeller speed was maintained constant resulting constant power input but with a lower resulting G value.

The quantitative measure of change in aggregate size or, alternatively, the change in number of primary particles due to the growth of aggregates can be used to assess the kinetics of flocculation. In this research, two methods were used to assess flocculation kinetics. The one was the direct quantitative measure of the changes in the particle size distribution by use of automatic image analysis system (AIA). The other was the rather indirect qualitative measurement by use of an Photometric Dispersion Analyzer (PDA) in which the degree of turbidity fluctuation due to the continuous changes in the average number concentration and the size of the suspended particles can be obtained and related to the rate of flocculation.

The AIA can measure and analyze the number of particles in several discrete sizes, ranging from 0.5 to 300 ㎛, depending on a magnification power selection for the microscope used. The AIA system was coupled directly to an Olympus BH-2S upright, transmitted light microscope via a video camera. The image to be analyzed by the AIA was input to the system through a TV/video camera mounted on the microscope and digitized. From the digitized image, the AIA can then measure geometric parameters of particles (i.e., size and shape) and entire field parameters (i.e., reference area and counts). The particle size distribution is illustrated graphically with Figure 1 being typical of the raw data collected from the AIA. Each particle size

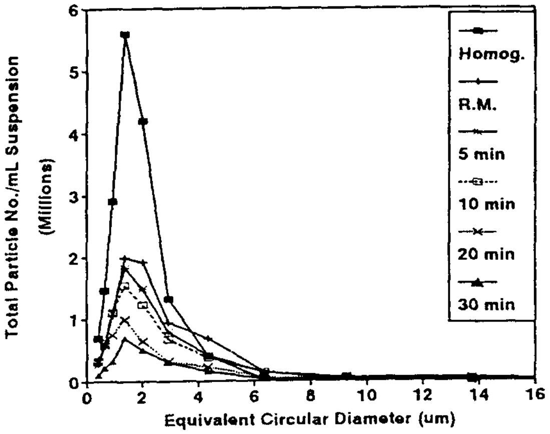

Fig. 1. Changes in particle size distribution as a function of flocculation time (pH 6.8 at 23 ℃, clay: 25 mg/L, dose: 5 mg/L as $Fe(NO_3)_3 \cdot 9H_2O$, flocculation: 30 rpm)

distribution in the figure represents a sample taken from a reactor at a different flocculation time. In this graph, the number of particles per mL of sample in each size class is plotted against the equivalent circular diameter of each size class. As shown in Figure 1, the number of particles with equivalent circular diameter in the 1 to 3 μm is gradually decreased as flocculation proceeds. The different size distributions indicate that a significant change was occurred over the course of the 30 min of flocculation, with substantial disappearance of smaller particles.

The state of aggregation of kaolin particles in flowing suspensions was monitored with the PDA. A fiber optical sensor in a cell of the PDA, which is connected through a tubing to a flocculation reactor directly, is sensitive to fluctuations in the flowing suspension's turbidity caused by random variations in the number concentration and the size of the suspended particles in the light beam. The essential point is that when aggregation of particles occurs, the turbidity fluctuations increase markedly, and provide a simple and effective method of on-line monitor of the rate of flocculation. It has been shown that the root mean square (rms) value of the fluctuating signal varies with the square root of the particle concentration and with the size of the suspended particles in a rather complex manner (Gregory, 1985). Assuming that variation in particle number follows Poisson distribution, Gregory (1985) derived formulas as expressed in Eq.(3) for the relationship between the PDA output, and the number concentration and the size of suspended particles using a modified Lambert-Beer law

$$V_{rms} / V = (L/A)^{1/2} (\Sigma NiCi^2)^{1/2} \qquad (3)$$

where, V is the voltage corresponding to the intensity of light after passing through a suspension and V_{rms} is the standard deviation of the voltage about the mean value, V. L and A

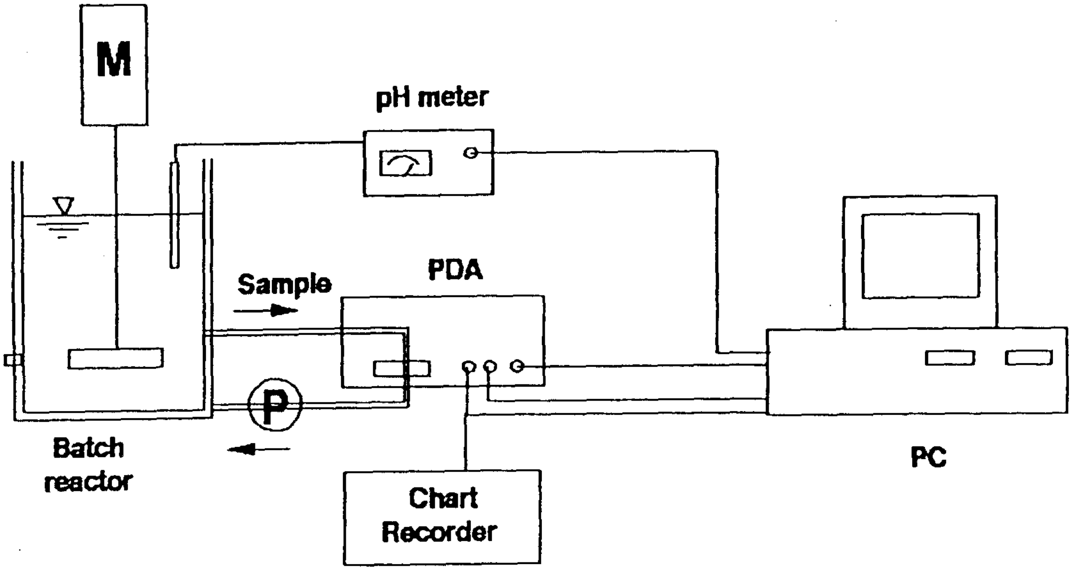

Fig. 2. Schematics of experimental setup

are optical path length and effective cross-sectional area of the light beam. Ni and Ci represent the number concentration and scattering cross-section of particles of type i and the sum is taken over all types of particles. The nature of the sum in Eq.(3) is such that high number of smaller sized particles contributes relatively little to the ratio value (V_{rms} / V) and that, in an aggregating system, the larger aggregates have a greater influence on the ratio value.

The experimental setup is shown schematically in Figure 2. During the flocculation processes, a sample stream was withdrawn at a rate of 15 mL/min through a glass tube of 2.5 mm internal diameter by a peristaltic pump. The glass tube was passed through a cell of the PDA and the output signal of the PDA was monitored directly by a personal computer based data acquisition system. Also, during the flocculation period, 1 mL of samples were collected at each different mixing time using 1 mL syringe with a needle through a sampling port for the analysis of the particle size distribution using the AIA.

3. RESULTS AND DISCUSSION

3.1 Flocculation kinetics

Figures 3(a) and (b) show the comparison of experiments to represent the effect of pH on flocculation kinetics. A comparison of particle count measurements by the AIA and the growth of aggregates expressed as the signals of the PDA was made to assess the reliability of both kinetics measuring techniques. The kinetics of flocculation was measured simultaneously by using the AIA and PDA. First, the particle size distribution obtained from the AIA, previously as shown in Figure 1, was manipulated to plot the total particle count fraction which was obtained as the ratio of the total particle number per mL of suspension at any given time to the total particle number per mL of suspension measured in the homogenized sample. In the X-axis, the zero time in this figure refers to the beginning of flocculation period immediately following the 1 min rapid mixing, thus the negative time represents the rapid mix time duration. Generally, Figure 3(a) shows the decrease in the total number of particles in suspension during the flocculation

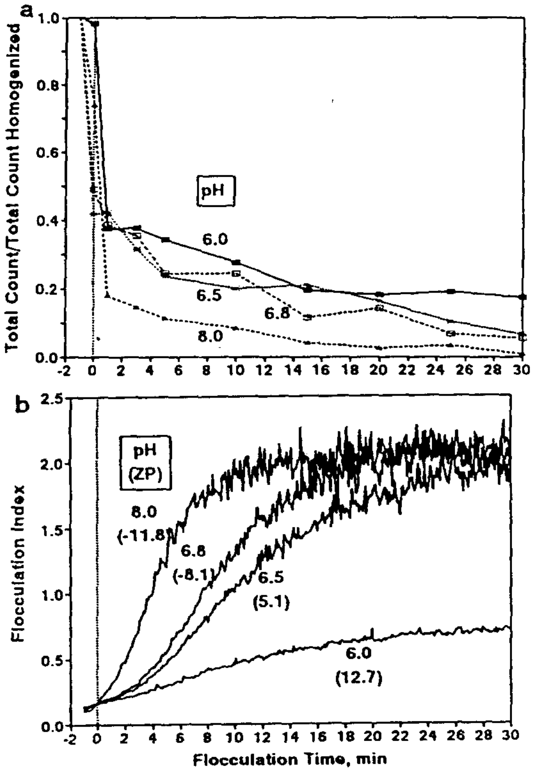

Fig. 3. Effect of pH on the rate of flocculation (clay: 25 mg/L, dose: 5 mg/L, flocculation: 60 rpm, at room temperature): (a) total particle count fraction vs. time using the AIA; (b) flocculation index vs. time using the PDA

time owing to aggregation of primary particles into flocs. Second, Figure 3(b) shows the PDA monitor responses collected at every 5 seconds. The ratio, V_{rms}/V, was plotted as a function of flocculation time. In this study, the ratio value was referred as flocculation index for the sake of illustration and discussion. Figure 3(b) indicates that the ratio, V_{rms}/V, always increases in the course of aggregation until a limiting value is reached. Thus, the flocculation rate evidenced by the flocculation index shows a rapid increase in the rate of flocculation, especially at the higher pH levels. Figures 3(a) and (b) demonstrate the dramatic impact of suspension pH on the rate of flocculation, as evidenced by both the decreases of total particle count fraction and marked increase of flocculation index, respectively. Overall, under the same coagulant dose, the curves in Figs. 3 show marked increases in the rate of flocculation as the suspension pH increases from pH 6.0 to 8.0. The higher pH favors the faster rate of flocculation. The ZP value at each pH indicates that the surface charge resulting from the addition of coagulant is more negative at the higher pH; whereas, at lower pH, complete charge neutralization and even charge reversal are achieved with a 5 mg/L of coagulant dose. To some extent, the faster rate of flocculation at higher pH relative to the rate at lower pH may be attributed to a general effect of precipitate of iron hydroxide which forms more rapidly at higher pH, and hence enhances particle collision frequency resulting in faster rate of flocculation.

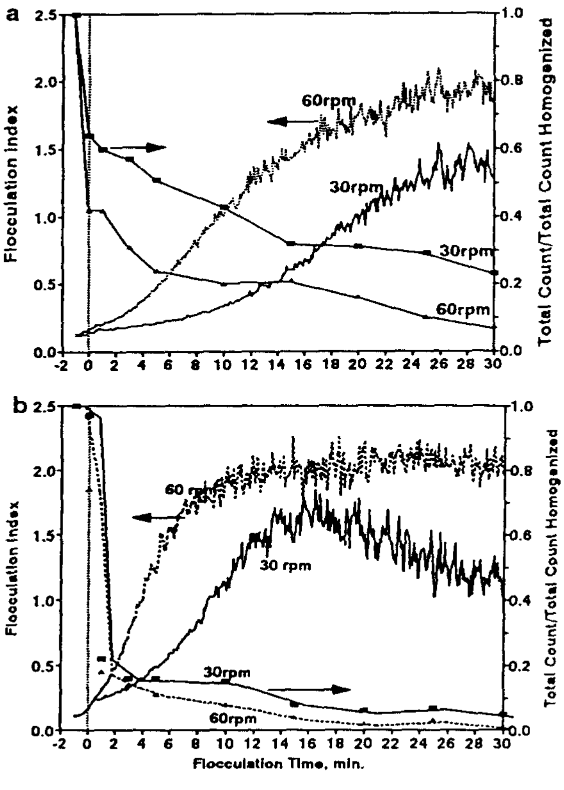

Fig. 4. Effect of flocculation mixing intensity on the rate of flocculation (clay: 25 mg/L, dose: 5 mg/L, flocculation: 30 rpm, at room temperature): (a) at pH 6.5; (b) at pH 8.0

Figures 4(a) and (b) are comparisons of flocculation rate at different mixing intensities under experimental conditions of pH 6.5 and 8.0, respectively. The mixing intensities applied during flocculation are 30 and 60 rpm, which correspond to G=20 and 56 sec^{-1} at 23 ℃, respectively. These minimum and maximum mixing intensities were selected based on preliminary tests not to cause either significant settling or break-up of flocs during slow mixing process. The results produced at pH 6.5 and 8.0 as shown in Figures 4(a) and (b) demonstrate that a substantial difference in process kinetics is evident under the different mixing intensities. That is, higher mixing intensity results in a more rapid disappearance of primary particles and rapid formation of aggregates, as indicated by the plots made from the AIA and PDA, respectively. However, at pH 8.0, the observed differences of the rate of flocculation expressed by the disappearance of primary particles are less evident. The flocculation kinetics data, thus far presented, as shown in Figures 3 and 4 demonstrate that both the particle size distribution data obtained from the AIA and the on-line measurement of turbidity fluctuation by the PDA provide reliable and sensitive indications of flocculation kinetics, as evidenced by the rate of disappearance of primary particles and the rate of aggregation of particles. The AIA gave the best indication of the rate of primary particle disappearance; whereas, the PDA flocculation index gave the best indication of the rate of larger floc formation.

3.2 Effects of Temperature

Most of the experimental results for flocculation kinetics at two different temperatures to be presented compare the flocculation kinetics while maintaining a constant pH in the experiments at two temperatures, or while maintaining a constant pOH in the experiments at two temperatures. Figures 5 and 6 present the experimental results for flocculation kinetics at 23 ℃ versus 5 ℃ including the effect of altering system chemistry at 5 ℃ by maintaining constant pH or constant pOH. Included in these figures are baseline data at pH 6.8 and 8.0 at 23 ℃ compared with data collected at 5 ℃. Maintaining a constant pOH at 5 ℃ results in different pH values at different temperatures due to a change in the ion product of water (pK_w). For example, the pH of 6.8 at 23 ℃ results in a pH of 7.5 at 5 ℃ to maintain constant pOH at the two temperatures (i.e., at 5 ℃, $pH = (pK_{w,\ 5\,℃}) - pOH = 14.73 - 7.26 = 7.5$). For comparison, once again, the rate of flocculation process was evaluated by determining the changes in total particle count fraction and the changes in flocculation index in the flocculating suspension at various times during the course of process. Overall, Figures 5 and 6 show that low temperature had a detrimental kinetic effect on flocculation process, slowing the disappearance of primary particles and the growth of aggregates. When comparing flocculation kinetics as evidenced by the rate of disappearance of primary particles at a baseline pH 6.8, as shown in Figure 5(a), the low water tempera-

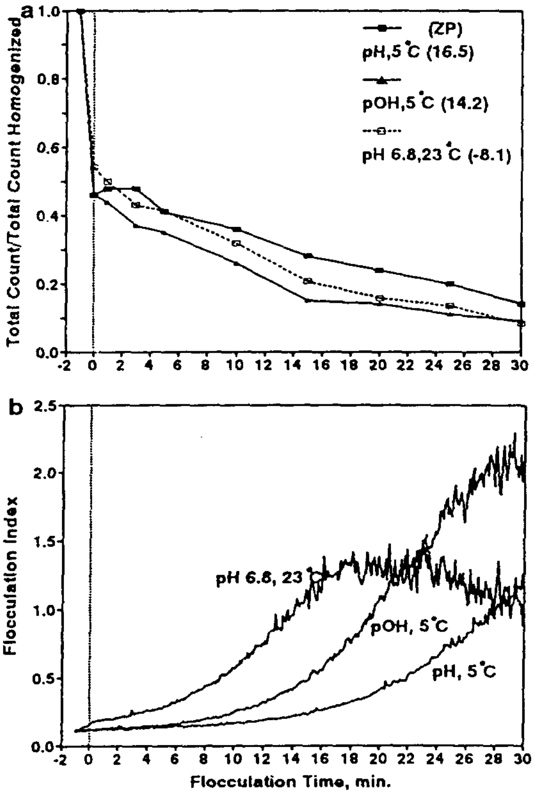

Fig. 5. Effect of temperature and system chemistry on the rate of flocculation (baseline 23 ℃ at pH 6.8, other curves at 5 ℃ with either const. pH (6.8) or const. pOH (i.e., pH 7.5), clay: 25 mg/L, dose: 5 mg/L as $Fe(NO_3)_3.9H_2O$, flocculation: 30 rpm): (a) total particle count fraction vs. time; (b) flocculation index vs. time

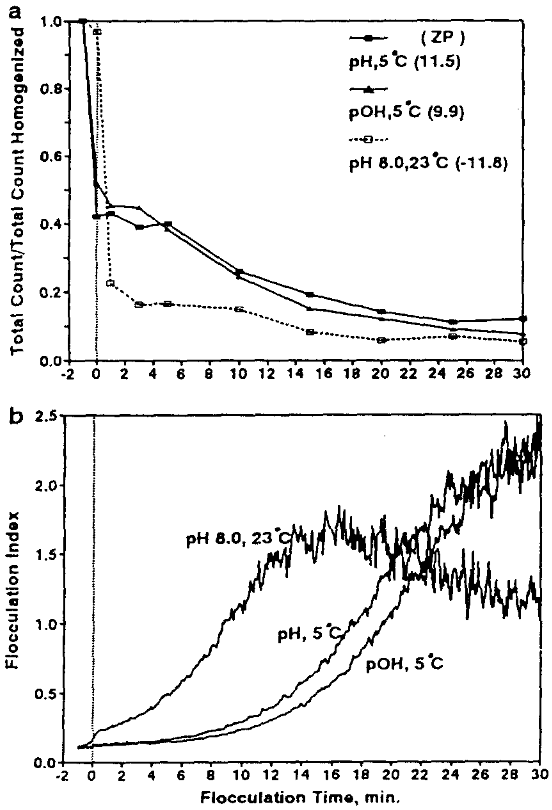

Fig. 6. Effect of temperature and system chemistry on the rate of flocculation (baseline 23 ℃ at pH 8.0, other curves at 5 ℃ with either const. pH (8.0) or const. pOH (i.e., pH 8.7), clay: 25 mg/L, dose: 5 mg/L as $Fe(NO_3)_3.9H_2O$, flocculation: 30 rpm): (a) total particle count fraction vs. time; (b) flocculation index vs. time

ture did not impair the kinetics of flocculation substantially when holding pOH constant. However, Figure 5(b) indicates a significant detrimental effect on flocculation kinetics at low temperature, even when maintaining constant pOH. At pH 8.0, as shown in Figures 6(a) and (b), it is noted that Fe(Ⅲ) coagulant at 5 ℃ did not result in flocculating clay particles as well as 23 ℃, and altering system chemistry by adjusting pH was not capable of improving flocculation kinetics. Comparison of the results at pH 8.0 with those at pH 6.8 shows a different effect of using constant pOH at low temperature on flocculation kinetics. Thus, use of constant pOH was favorable for the aggregation of particles below a certain pH level, in the more acidic pH range. The ZP values for each curve show that Fe(Ⅲ) coagulant at lower temperature is much more effective at charge neutralization of the negatively charged clay particles than at higher temperature. The significant changes in ZP with temperature suggest that the low temperature played an important role in the manner in which the Fe(Ⅲ) coagulant hydrolyzes, apparently production of more highly positive charged Fe(Ⅲ) species.

The results obtained under the same experimental conditions, except using 50 mg/L of clay, are plotted at pH 6.8 and 8.0 in Figures 7(a) and (b), respectively. As shown in these figures, again, low temperature had a pronounced detrimental effect on flocculation kinetics at both pH 6.8 and 8.0. Also, under this higher particle concentration, it is apparent at the more acidic pH that there was only a slight benefit for holding pOH constant at the lower temperature. At the higher pH, as evident in Figure 7(b), maintaining constant pOH at cold temperature was detrimental to the growth of flocs. It is noteworthy that at low temperature, the increase in the flocculation index is very slow, particularly during the first 5 min, indicating slower flocculation in the early phase of flocculation. In this case, it may be explained that the formation of Fe(Ⅲ) precipitates becomes slower at low temperature, resulting in slowing aggregation of particles. Again, the slowing precipitation reaction of Fe(Ⅲ) coagulant in lower temperature water might be evidenced by the attainment of the higher

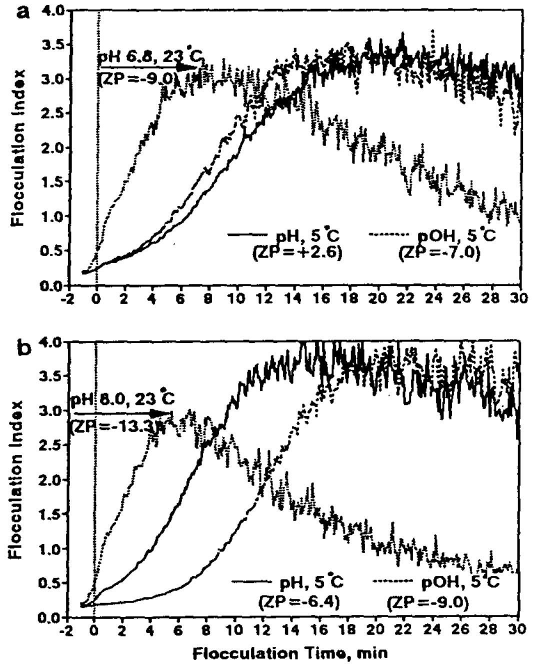

Fig. 7. Effect of temperature and system chemistry on the rate of flocculation, (clay: 50 mg/L, dose: 5 mg/L as $Fe(NO_3)_3 \cdot 9H_2O$, flocculation: 30 rpm): (a) baseline 23 ℃ at pH 6.8, other curves at 5 ℃ with either const. pH (6.8) or const. pOH (i.e., pH 7.5); (b) baseline 23 ℃ at pH 8.0, other curves at 5 ℃ with either const. pH (8.0) or const. pOH (i.e., pH 8.7)

positive charge (or less negative charge) of flocs at low temperature. Francois and Bekaert (1986) also reported that the slowed floc growth at low temperature (5 ℃) might be due to slowing the formation of insoluble Al hydroxides or poor homogeneous distribution of the insoluble hydroxide throughout clay suspension. As investigating the impact of cold water temperature on flocculation kinetics by means of measuring the rate of disappearance of primary particles, Hanson and Cleasby (1990) also noticed that an increased lag phase in the rate of disappearance of primary particles was evident at cold temperature, and poorer flocculation kinetics were observed at 5 ℃ compared with than at 20 ℃.

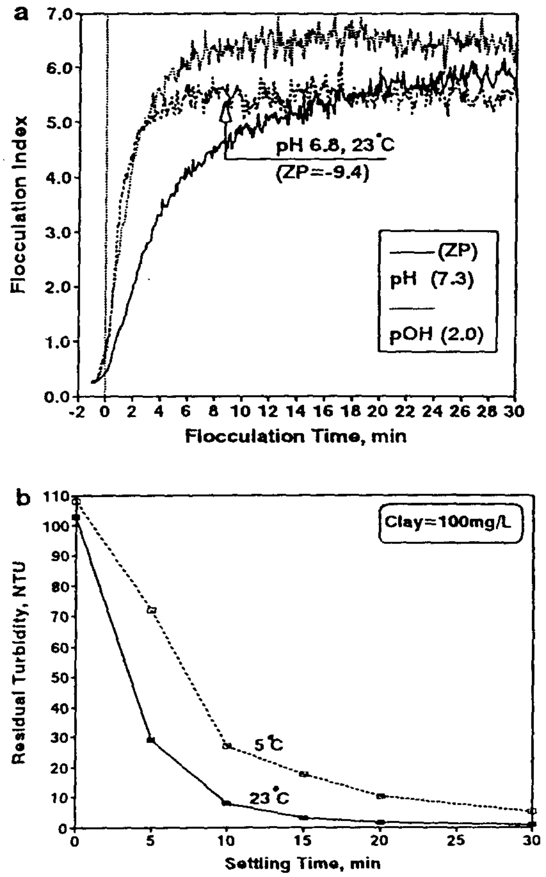

Fig. 8. Effect of temperature and system chemistry on the rate of flocculation, (clay: 100 mg/L, dose: 10 mg/L as $Fe(NO_3)_3 \cdot 9H_2O$, flocculation: 45 rpm): (a) flocculation index vs. flocculation time (baseline 23 ℃ at pH 6.8, other curves at 5 ℃ with either const. pH or const. pOH); (b) residual turbidity vs. settling time (23 ℃ vs. 5 ℃ at constant pH)

Figure 8(a) presents the impact of low temperature on the rate of flocculation for 100 mg/L clay concentration using 10 mg/L of coagulant dose. For 100 mg/L clay concentration, the coagulant dose was increased to 10 mg/L to avoid possible underdosed condition for the higher clay concentration of 100 mg/L. As shown in Figure 8(a), again, a decrease in temperature has a significant effect on the rate of flocculation, increasing the time of formation of aggregates. The adverse impact on the flocculation rates was most severe at constant pH. However, Figure 8(a) shows that when maintaining constant pOH at low temperature did not impair the rate of flocculation. The ZP values shown in Figures 8(a) also indicate that the effect of low temperature on the surface charges of particles was significant at this high clay concentration, too. Comparison of these results for 100 mg/L clay suspension with those for 25 and 50 mg/L clay concentrations shown previously (all at the pH 6.8 baseline condition) indicates that at higher clay concentration, the adverse impact of cold temperature on flocculation kinetics can be significantly reduced by using constant pOH. Especially, the initial slow growth phase of flocs, which was apparent at lower clay concentrations, was appreciably diminished. Gregory and Lee (1990) also observed that under favorable coagulation conditions, such as optimum polymer dose and higher molecular mass of cationic polymer, the initial lag time for the flocculation index became shorter. The supernatant turbidity data as shown in Figure 8(b) would serve as an indirect evidence of the difference in flocculation kinetics expressed by flocculation index. The data in Figure 8(b) were obtained from the measurement of the supernatant turbidity during a sedimentation period following 30 min of flocculation, which was the same test as presented in Figure 8(a). This settling data show that the flocs formed at 23 ℃ is settled much faster than the flocs formed at 5 ℃. Even though the decreased settling rate at 5 ℃ was influenced by an increase in the viscosity of water, it could also be due partly to the characteristic of flocs. Thus, higher number concentration of smaller flocs formed at 5 ℃ could cause the slow settling rate.

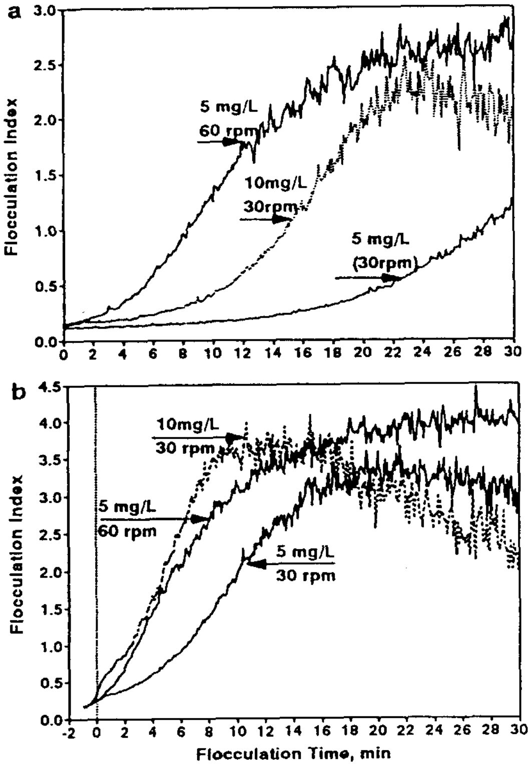

Fig. 9. Effect of flocculation mixing intensity and coagulant dose on the rate of flocculation at 5 ℃ with pH 6.8: (a) clay: 25 mg/L; (b) clay: 50 mg/L

To find out how to improve the rate of flocculation at cold temperature, some tests were carried out by increasing either coagulant dose or slow-mixing intensity. Figures 9(a) and (b) show the experimental results for flocculation kinetics at 5 ℃ by presenting the effect of applying higher intensity of slow mixing and the effect of increasing coagulant dose. Figures 9(a) and (b) represent the data at pH 6.8 for 25 and 50 mg/L clay concentration at pH 6.8, respectively. For discussion, the data obtained at 5 ℃ using 5 mg/L coagulant dose are used as a baseline, and the data obtained only at constant pH are presented. All of these data for 25 and 50 mg/L clay concentration show that when either excess of coagulant is added or increased slow mixing intensity is applied, the rate of flocculation improves significantly. These results suggest that increasing either coagulant dose or mixing intensity at low temperature can partially overcome the detrimental impact of cold temperature on the process of flocculation. Probably, the improvement in flocculation was accomplished by the increased interparticle collision rate which can be caused by the additional formation of Fe(Ⅲ) precipitate at higher coagulant dosage and by the enhanced particle transport at higher mixing intensity. Comparison of the data for 25 mg/L clay concentration with the data for 50 mg/L clay concentration indicates that at higher particle concentration, the improvement of flocculation kinetics is less dramatic by either alternative method. Thus, the increased interparticle collision rate seemed to be more beneficial to enhancing flocculation kinetics at the lower clay concentration.

Figures 10(a) and (b) present another way to improving the rate of flocculation at low temperature by extending the rapid mixing period up to 2 min at pH 6.8 and 8.0, respectively. Comparison of the results at pH 6.8 with those at pH 8.0 indicates different effect of extending rapid mixing period. For example, at pH 6.8, the flocculation kinetics at low temperature was substantially improved by extending the rapid mixing period using either constant pH or pOH. But, at pH 8.0, extending rapid mixing period at low temperature was beneficial to the aggregation of particles only when pH was maintained constant. The adverse effect of using constant pOH on flocculation kinetics at pH 8.0 became even greater when using the extended rapid mixing period. It is noteworthy at pH 6.8 that the initial lag, which was evident at 5 ℃ with 1 min of rapid mixing, was substantially shortend with 2 min of rapid mixing.

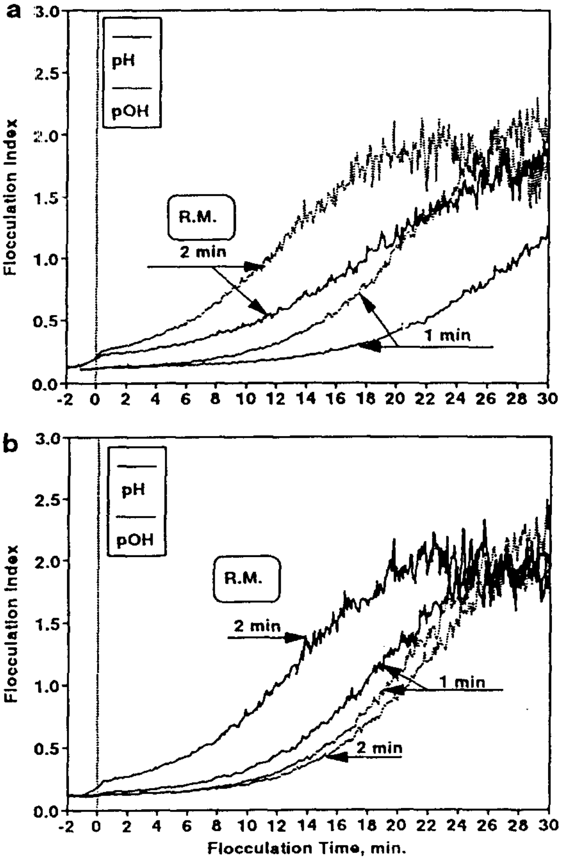

Fig. 10. Effect of rapid mixing duration and system chemistry on the rate of flocculation at 5 ℃ (clay: 25 mg/L, dose: 5 mg/L, flocculation: 30 rpm): (a) at pH 6.8; (b) at pH 8.0

4. CONCLUSIONS

1. Both the particle size distribution data

obtained from the AIA and the on-line measurement of turbidity fluctuation by the PDA provided reliable and sensitive indications of flocculation kinetics, as evidenced by the rate of disappearance of primary particles and the aggregation of particles. The AIA gave the best indication of the primary particle disappearance; whereas, the PDA index gave the best indication of the larger floc formation.

2. There was marked increases in the speed of flocculation with pH increase in experiments between pH 6.0 and 8.0. In addition, there was a significant difference in flocculation kinetics under the different mixing intensity applied.

3. Low water temperature had the pronounced effects on flocculation kinetics over the range of clay concentration studied from 25 to 100 mg/L, slowing the rate of flocculation and enhancing charge neutralizing ability of Fe(Ⅲ) coagulant. The detrimental effect was most notable at lower clay concentrations and with the pH held constant at the cold temperature, and in the formation of larger aggregates as revealed by the PDA analysis.

4. The use of constant pOH at 5 ℃ to adjust water chemistry for temperature change was found to be partially effective for reducing the impact of low temperature on flocculation kinetics, but only in the acidic pH range studied (pH 6.8). But the improved performance did not reach the performance at room temperature.

5. Three experimental provisions were found to partially offset the detrimental effect of low temperature on the rate of flocculation; (1) increasing the coagulant dosage, (2) moderately increasing the slow mixing intensity, and (3) extending the rapid mixing period at acidic pH level studied (pH 6.8).

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정수처리시 Fe(III) 응집제를 사용한 응집동력학에 대한 온도의 영향

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(1994년 11월 17일 접수)

여러가지 다양한 상수처리 실험조건하에서 응집제로 Ferric Nitrate를 사용하여 수중의 카오린 점토입자를 응결하는 과정중의 응집동력학을 조사하기 위하여 본 연구는 수행되었다. 응집동력학을 측정하기 위한 방법으로서 AIA 시스템으로 부터 얻어진 입자크기분포와 Flowing suspension에서의 PDA에 의한 탁도증가 정도의 측정이 사용되었다. 결론으로서, 저온에서의 응집은 그 효율이 상당히 저하 되는것으로 발견 되었으며 저온에서의 응집을 향상시키기 위하여 수중의 pH 보다는 pOH를 일정하게 유지하는 것이 부분적으로 응집효율향상에 도움이 되는 것으로 나타났다.