1995

Flocculation kinetics using dual coagulants: effects of temperature, addition sequence, rapid mixing, and sulfate

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Flocculation kinetics using dual coagulants: Effects of temperature, addition sequence, rapid mixing, and sulfate

by

Bashaar Yakoub Ammary

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Civil and Construction Engineering
Major: Civil Engineering (Environmental Engineering)

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

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1. INTRODUCTION

The coagulation process, which consists of a rapid mixing step followed by a slow mixing step (flocculation) is one of the essential unit processes in conventional and direct filtration water treatment plants. The efficiencies of the downstream unit processes (sedimentation and/or filtration) are largely dependent on the coagulation process efficiency. Reporting on the results of a pilot plant direct filtration study, McBride et al. (1977) stated that the single most important parameter evaluated in their study was the optimization of the coagulant dose. Once the coagulant dose was optimized, the effects of filtration rate changes or filter media type on the filtered water quality were minimal.

Inorganic coagulants such as alum (aluminum sulfate), ferric chloride, or ferric sulfate used to be the coagulants of choice. However, with the promulgation of new, more stringent, regulations on drinking water quality and on sludge disposal, cationic polymers began to gain popularity and started to substitute, partially or completely, for the inorganic coagulants.

Inorganic coagulants (aluminum or ferric salts), used as sole coagulants are capable of coagulating both turbidity and organics to a good extent. This coagulation, however, requires higher dosages of the inorganic coagulants, thus consuming alkalinity and producing large amounts of sludge. They are largely affected, especially alum, by low water temperature and they produce fragile weak flocs. On the other hand, cationic polymers as sole coagulants produce smaller volume of sludge which is easier to dewater (Beardsley 1973, Morrow and Rousch 1974, Carns and Parker 1985), produce larger and stronger flocs

(Shea et al. 1971) that can tolerate high shear forces encountered in the flocculation and/or in the filtration stage (Tanaka and Pirbazari 1986), and they function independent of some raw water characteristics such as alkalinity and pH. However, they are less effective in organics removal (Jacangelo et al. 1994, Crozes et al. 1994). Also, they are effective over a smaller dosage range.

These two coagulants seem to have a complementary role. The combined use of these coagulants is intended to utilize the benefits of both coagulants through the reduction of the inorganic coagulant dose and the production of a larger and stronger flocs.

Most of the early research on the use of cationic polymers concentrated on their use as sole coagulants, especially in direct filtration. The increased use of cationic polymers as coagulation aids, prompted the conduct of a few research studies on the use of dual coagulants. However, the studies were not conclusive and have some contradictory results. They were almost exclusively done with alum and cationic polymers. This research is intended to give a broader understanding to the combined use of ferric salts and cationic polymers and address the deficiencies in our understanding of this use.

The behavior of dual coagulants (in this dissertation, the phrase "dual coagulants" will refer to the combined use of cationic polymers and inorganic coagulants unless stated otherwise) would certainly depend on the behavior of the single coagulants each used alone. Therefore the use of these coagulants as sole coagulants is discussed first. The combined use of these coagulants is discussed afterwards.

2. PURPOSES OF THE STUDY

The purposes of the study can be summarized by the following points:

1- To understand the general behavior of the combined use of Iron (III) and cationic polymers at different temperatures and pH values. All previous work has been done using a combination of alum and cationic polymers. Essentially nothing has been done to study the use of Iron (III) in combination with cationic polymers.

2- To delineate the conditions under which the use of dual coagulants is the preferable alternative.

3- To study the effect of cold temperature on flocculation kinetics using dual coagulants. The effect of cold temperature on the effectiveness of dual coagulants has not been studied. Whether the combined use of Iron (III) and cationic polymers is better suited for the coagulation of particles at cold water temperatures than the sole use of only one of these coagulants is one of the main points investigated in this study. Iron (III) as a sole coagulant proved to be better than Al (III) in cold temperature waters (Hanson and Cleasby 1990, Morris and Knocke 1984). Cationic polymers are not as sensitive to water temperature as inorganic coagulants. In fact, at high mixing intensities, cationic polymers produced similar results at both 5 and 20 C (Hanson and Cleasby 1990).

4- To identify the optimum addition sequence for dual coagulants under different suspension characteristics (pH, clay concentration, sulfate concentration, and temperature).

Some researchers have recommended the addition of the inorganic coagulant before the cationic polymer (Duff and Barkley 1976, Swope 1977, Schlauch 1981, James and

O'Melia 1982). Other researchers have recommended the addition of cationic polymers before alum addition (Hanson and Cleasby 1990, Riffat 1991). Other researchers found that the addition of cationic polymers before alum addition to be successful (Beardsley 1973, Hubel and Edzwald 1987). However, no comparison with the reverse sequence of addition was reported in these two works. The addition sequence was reported by some researchers to have no effect on the coagulants efficiency (Edzwald et al. 1977, Letterman and Sricharoenchaikit 1982).

Cleasby et al. (1989) found five of six conventional plants added the dual coagulants at the same location, and only one added alum before the cationic polymer. In four direct and in-line filtration plants, two plants added the dual coagulants at the same location, and two added the alum before the cationic polymer.

5- To study the effect of rapid mixing on flocculation kinetics for the combined use of Iron (III) and cationic polymers both at room temperature and low water temperature.

In all the work found regarding the use of dual coagulants, only one (Riffat 1991) studied the rapid mixing effects on the coagulation process. Riffat (1991) studied the effect of rapid mixing on 25 mg/L Kaolin concentration at pH 7.0 and room temperature. No effect of rapid mixing intensity or duration was observed under these conditions.

6- To study the effect of sulfate concentration at different pH values on flocculation kinetics. Letterman and Sricharoenchaikit (1982) studied only the effect of sulfate at pH 6.0 using alum and a cationic polymer in combination.

3. FERRIC SALTS AS SOLE COAGULANTS

3.1 Introduction

The purpose of the coagulation process is to aggregate the suspended colloidal particles in water and grow them to a size necessary for their removal by sedimentation and/or filtration. This is first achieved by destabilizing the colloidal particulate matter suspended in water so that it becomes prone to aggregation. The flocculation step is the step through which the destabilized particles are brought together by means of slow mixing. Alum is the most commonly used destabilizing agent in water treatment followed by ferric salts. Ferric salts are becoming more common because of a number of problems associated with high aluminum concentration in finished water. Some of these problems are associated with the postprecipitation of aluminum hydroxide which results in a decrease in the carrying capacity and pressure drops in the distribution system, in addition to an increase in the delivered water turbidity (Rahman et al. 1992). Ferric chloride and ferric sulfate are the ferric salts that are usually used as coagulants. This chapter is intended to present some of the literature relevant to the use of ferric salts.

The chemistry of ferric salts is first discussed. Then rapid mixing, temperature and sulfate effects on the behavior and efficiency of ferric coagulants are discussed. When discussing these topics, the relevant literature on alum will also be presented. It is believed that these variables have similar effects (although the extent may be different) on aluminum and iron (III) coagulants.

3.2 Iron(III) Chemistry

The addition of Fe(III) coagulants to an aqueous media results in the production of a number of hydrolysis products, and (if the dosage is higher than the solubility limit) to the precipitation of ferric hydroxide, $Fe(OH)_3$. The following are the hydrolysis products that are formed along with their equilibrium constants at 25 °C (Snoeyink and Jenkins 1980, Flynn 1984):

$Fe^{+3} + H_2O \Leftrightarrow FeOH^{+2} + H^+$ $\log K = -2.16$ (3-1)

$Fe^{+3} + 2\,H_2O \Leftrightarrow Fe(OH)_2^+ + 2H^+$ $\log K = -6.74$ (3-2)

$Fe(OH)_{3(S)} \Leftrightarrow Fe^{+3} + 3OH^-$ $\log K_S = -38$ (3-3)

$Fe^{+3} + 4\,H_2O \Leftrightarrow Fe(OH)_4^- + 4H^+$ $\log K = -23$ (3-4)

$2\,Fe^{+3} + 2\,H_2O \Leftrightarrow Fe_2(OH)_2^{+4} + 2H^+$ $\log K = -2.85$ (3-5)

$3\,Fe^{+3} + 4\,H_2O \Leftrightarrow Fe_3(OH)_4^{+5} + 4H^+$ $\log K = -6.3$ (3-6)

The trimeric $Fe_3(OH)_4^{+5}$ has been identified by only one study. Therefore, this species has been neglected when the pC-pH diagram for Fe(III) has been drawn (Snoeyink and Jenkins 1980, Johnson and Amirtharajah 1983, Amirtharajah and O'Melia 1990). The pC-pH diagram, which shows the concentration of the various iron hydrolysis species (not including $Fe_3(OH)_4^{+5}$) as a function of pH, is shown in **Figure 3-1** (Snoeyink and Jenkins 1980).

As can be seen from this figure, the predominant hydrolysis species at high pH values (> 8) is $Fe(OH)_4^-$ whereas the cationic species $Fe(OH)_2^+$ predominates over the pH values usually encountered in natural waters (5 to 8).

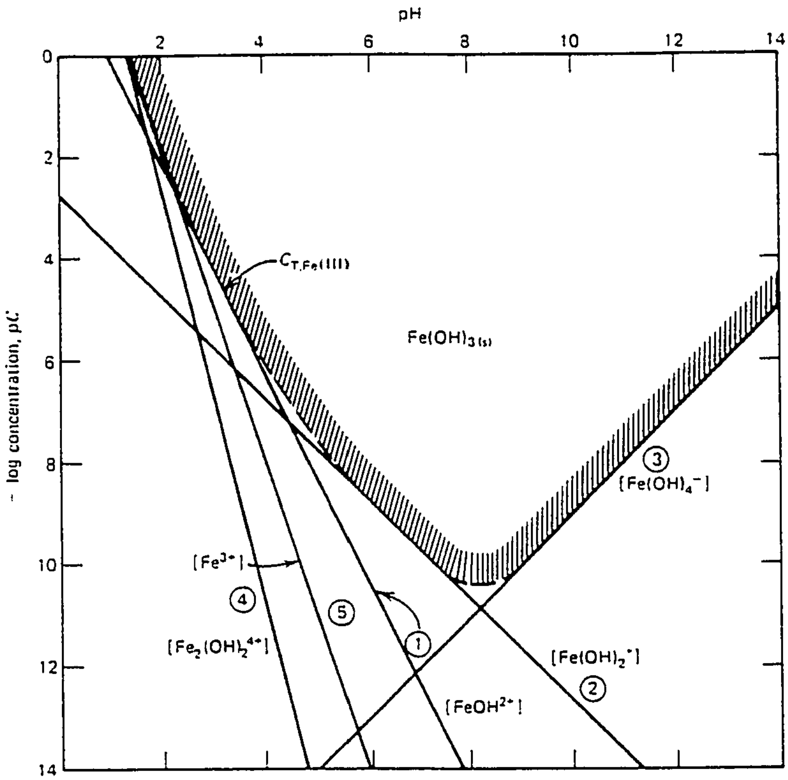


Figure 3-1: Equilibrium Fe(III) hydroxo complexes as a function of pH in a pure water solution in contact with freshly precipitated $Fe(OH)_{3(S)}$ at 25 °C (Snoeyink and Jenkins 1980).

When a dosage of Fe(III) coagulant is added where the solubility limit of ferric hydroxide is not exceeded, the soluble monomeric, dimeric, and perhaps the trimeric ferric hydrolysis products of equations 3-1 to 3-6 are formed. Equilibrium for the monomeric species is established quickly. The establishment of equilibrium for the dimeric species is significantly slower but it is still quick (Flynn 1984).

When the solubility limit of ferric hydroxide is exceeded, polynuclear hydrolysis species (polymers) are formed as an intermediate step toward the production of ferric hydroxide precipitate (O'Melia and Stumm 1967). There are studies that suggest that part of the precipitate can occur directly from the monomeric species, i.e. without polymer formation (Knight and Sylva 1974, Tang and Stumm 1987). Amorphous $Fe(OH)_3$ is produced in the time scale of water treatment. Geotite, α-FeO(OH), is the stable form of precipitated ferric hydroxide, but it takes a very long time (years at 25 °C) to establish equilibrium (Baes and Mesmer 1976).

It should be noted that although the formation of the ferric polynuclear species and the formation of ferric hydroxide precipitate take longer than the formation of monomeric species, the time scale is still very short. The time of formation of aluminum hydrolysis species ranges between microseconds if Al monomers are formed to less than 1 second if polymers are formed (O'Melia 1972, Hahn and Stumm 1968). Aluminum hydroxide precipitation occurs in the range of 1-7 seconds (Letterman et al. 1973). Time scale values for Fe(III) coagulants should be somewhat similar to those of aluminum.

Johnson and Amirtharajah (1983) recognized that **Figure 3-1** is not really useful for predicting the coagulation behavior due to the complex nature of the coagulation process. Instead they used empirical data from the literature and combined it with their own jar test experiments to define zones of no coagulation, adsorption-destabilization (A/D), restabilization, and sweep floc coagulation (see **Figure 3-2**). The no coagulation zone occurs when the amount of hydrolyzed metal coagulant is small. At such dosage, the kinetics are slower than would be needed to induce coagulation and sedimentation in the time scale practiced in water treatment. Adsorption-destabilization occurs when the negative charge on the colloidal matter is reduced by the adsorption of the positively charged inorganic hydrolysis species. The charge should be reduced to a value necessary for the attractive forces between these colloids to overcome the repulsive energy barrier. If excess amounts of the positive hydrolysis species are adsorbed so that the charge on the colloidal particles becomes sufficiently positive to prevent coagulation, restabilization occurs. Sweep floc coagulation occurs when the colloidal particles are enmeshed by the metal hydroxide precipitate as they are formed or by colliding with them afterwards. To cause sweep floc coagulation, a larger amount of the inorganic coagulant is required.

It should be noted that **Figure 3-2** is by no means complete. One should use this figure with caution and as a vague approximation. First, the coagulation process is complex and in most cases system specific. Concentrations of anions, cations, organics, and suspended matter all affect the coagulation process. An example taken from the present work will show the deficiency of **Figure 3-2**. As will be shown in the results chapter, a

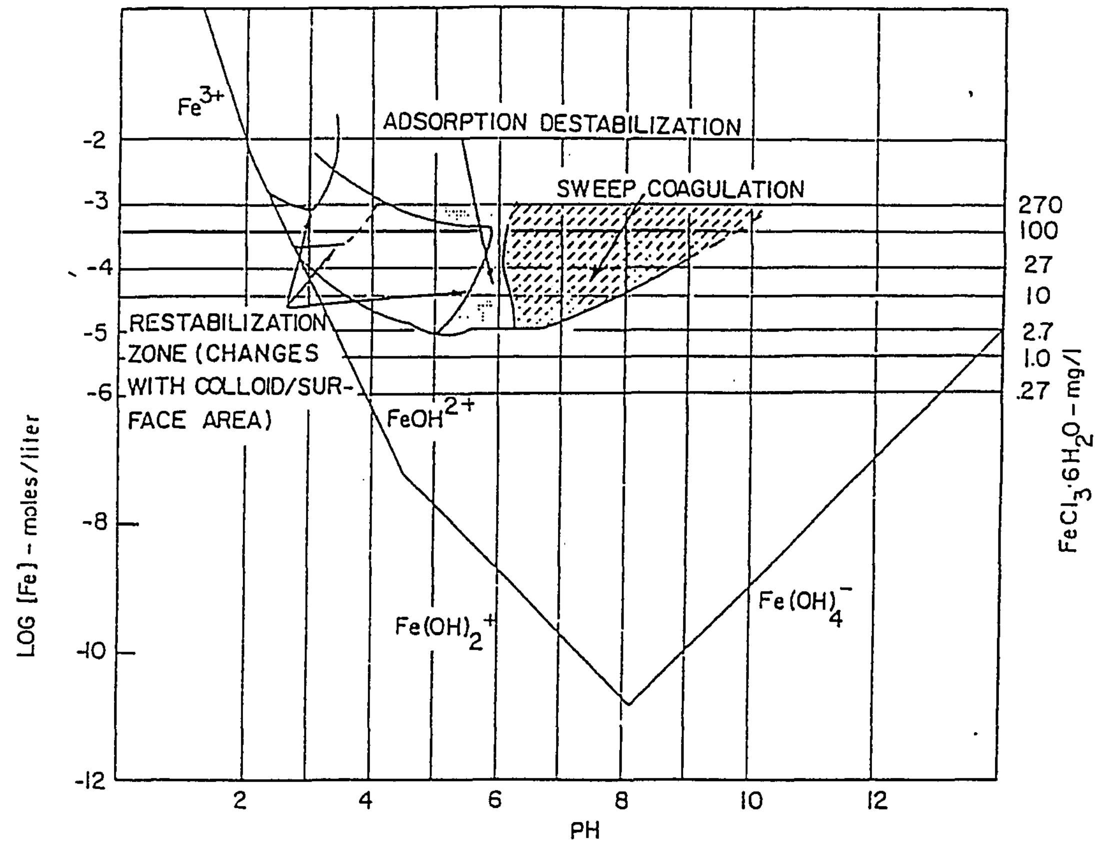


Figure 3-2: Design and operation diagram for Fe(III) coagulation showing the various zones of coagulation (Johnson and Amirtharajah 1983)

dosage of 2.5 mg/L $Fe(NO_3)_3.9H_2O$ was used to coagulate 25, 50, and 100 mg/L kaolin clay suspensions at pH 7.8. **Figure 3-2** tells us that no coagulation should occur. However, results show that the turbidity values were reduced from 24, 45, and 90 NTU to values as little as 2.5 NTU after flocculation followed by 30 minutes of settling. Second, **Figure 3-2** does not give any indication on the kinetics of flocculation. Flocculation kinetics are largely dependent on the suspended matter concentration which is not a variable in this figure. In fact, the flocculation kinetics is a function of both the combined concentration of the suspended matter concentration and the metal hydroxide precipitate concentration resulting from the coagulant addition.

3.3 Rapid Mixing Effects

Rapid mixing of inorganic coagulants is primarily intended to insure homogeneous coagulation through the uniform and rapid dispersion of the coagulant and its hydrolysis products. This would prevent the underdosing of parts and the overdosing of the remaining parts of the suspended solids by the hydrolysis products of the inorganic coagulant. Although the need for vigorous rapid mixing is realized, there are still no well defined values for the intensity of mixing or the detention time required for optimum performance. Monk and Trussell (1991) acknowledged that a wide range of G values (300 - 1000 s^{-1}) and detention times (<1sec - 1+ min) are recommended for use. G values even greater than 6000 s^{-1} for static mixers are also used. The recommended Gt value ranges from 10,000 to 40,000. *Water Treatment Plant Design* (1990) recommends a G value between 600 to 1000 s^{-1} for 1 to 3 seconds (Gt value of 1000 to 2000) for alum and polymer mixing.

Hudson and Wolfner (1967) stated that "The function of a rapid-mix chamber is to insure completely homogeneous coagulation. To accomplish this requires intense mixing to distribute the coagulating agent uniformly throughout the water, so that it makes contact with suspended particles before the reaction is completed. In the absence of intense mixing, part of the water is over-treated with coagulant, while other parts are undetreated or not treated at all." (Hudson and Wolfner 1967, pg. 1257). They recommended a rapid mixing time of less than a second.

O'Melia (1972) stated that "Virtually instantaneous mixing ("flash mixing") is desirable when Fe(III) or Al(III) salts are used as coagulants because (1) rates of formation of polymers are very fast, (2) the production of uniform coagulant species requires a uniform pH and coagulant dosage in the system, and (3) rates of adsorption of these small polymers are also fast. Long detention times are unnecessary, since these reactions are complete in a second or less." (O'Melia 1972, pg. 91).

Hudson (1981) stated that "while it has been traditional for designers to size rapid-mix chambers for residence times in the range of 30 sec-5 min, practice in respect to rapid mixing is changing in the direction of substantially shorter times of dispersion." (Hudson 1981, pg. 106). The traditional design values of G and time of mixing in rapid and slow mixing have been summarized by Amirtharajah and Trusler (1986) (see **Table 3-1**).

Kawamura (1991) states that a G value of 300 s-1 and a mixing time of 10-30 seconds are common design parameters for mechanical flash mixers. He acknowledged that recent studies showed that this rapid mixing period is long for metal salt coagulants. He

Table 3-1: Traditional mixing intensities and times (Amirtharajah and Trusler 1986).

Process (1)	Mean Velocity gradient G (sec^{-1}) (2)	Contact time t (sec) (3)	Comments (4)
Rapid mixing	700 - 1,000	40 - 20	for backmix reactors
	3,000 - 5,000	0.5	for in-line blenders
Flocculation	10 - 100	1,200 - 3,600	$Gt = 10^4 - 10^5$

suggested the use of a Gt value between 300-1600 as the most effective. For in-line static mixers a Gt value between 350-1700 (1000 average) and a mixing time between 1-5 seconds was recommended.

Amirtharajah (1978) and Amirtharajah and Mills (1982) distinguished between rapid mixing requirements for the different coagulation mechanisms, namely charge neutralization and sweep floc. The soluble hydrolysis products of the inorganic coagulants (Al(III) or Fe(III) monomers and polymers) play the major role in the coagulation by charge neutralization. These soluble hydrolysis products are formed within microseconds for monomers to about 1 second for polymers (Hahn and Stumm 1968, O'Melia 1972). Accordingly, Amirtharajah and Mills (1982) recommended extremely short dispersion time (less than 0.1 sec.) and high intensity of mixing. Amirtharajah and Tambo (1991) recommended G values of 3000-4000 s^{-1} for less than 1 second for the charge neutralization mechanism of coagulation. On the other hand, the inorganic hydroxide precipitate plays the major role in sweep floc mode. These precipitates need about 1-7 seconds to form (Letterman et al. 1973). Therefore, Amirtharajah and Mills (1982) suggested that short detention times and high G values are not crucial in the sweep floc mechanism of coagulation.

Amirtharajah and Mills (1982) presented experimental evidence to support their suggestions. A 500 mL silica suspension (Min-U-Sil) with turbidity values between 17 and 27 was coagulated with alum in a jar test study. Three rapid mixing modes were compared: G of 300 s^{-1} for 60 seconds; G of 1000 s^{-1} for 20 seconds; and G of about 16,000 s^{-1} for about 1 second. The Gt value of all these modes ranges from 16,000 to 20,000. From their results, samples of which are shown in **Figures 3-3 and 3-4**, the following were concluded: (1) The different G values used, (300, 1000, and 16,000 s^{-1}) did not have any different effects on the coagulation results for the optimum sweep floc conditions. (2) The high rapid mixing intensity blender (G = 16,000 s^{-1}) was superior to the back mix reactors with G values of 300 and 1000 s^{-1} in the charge neutralization region.

In contrast to the above, a number of studies suggest that the role of rapid mixing is more than chemical dispersion. A substantial growth of particles occurs during rapid mixing, particularly extended rapid mixing, that is necessary and has an effect on the efficiency of the flocculation and sedimentation processes (Mhaisalkar et al. 1991, Srivastava 1988, Francois and Van Haute 1984, Letterman et al. 1973, TeKippe and Ham 1971).

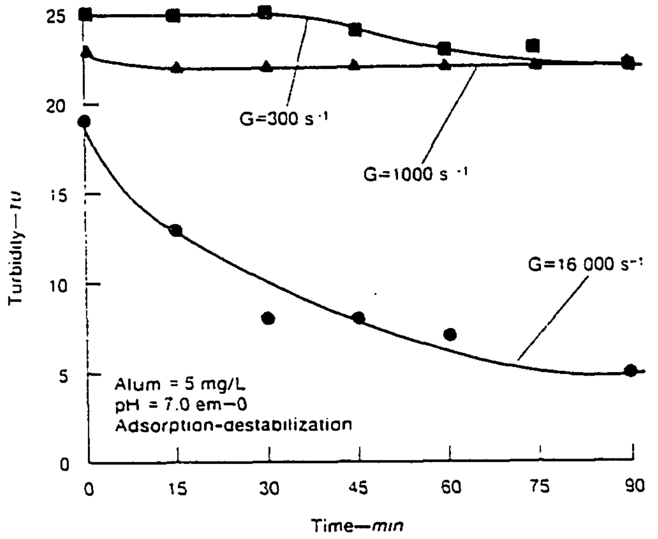


Figure 3-3: Settled water turbidity at different G values in the adsorption-destabilization region (Amirtharajah and Mills 1982)

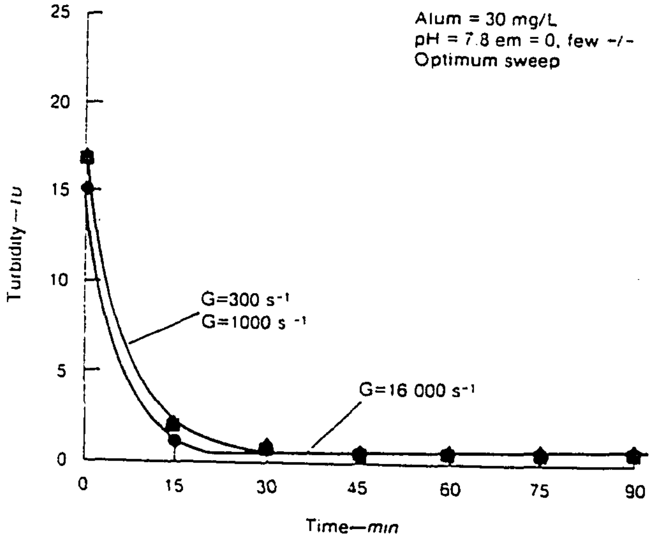


Figure 3-4: Settled water turbidity at different G values in the sweep floc region (Amirtharajah and Mills 1982)

TeKippe and Ham (1971) used 10 mg/L of alum to coagulate a suspension of 5 to 100 mg/L of silica (Min-U-Sil) at pH 7.0 in a jar test study and in a continuous bench-scale pilot plant. The time needed to see visible flocs and the turbidity of the settled suspension after flocculation and sedimentation were used to evaluate the results. Rapid mixing at G values of 50, 80, 140, or 200 s^{-1} for durations of 16, 10, 5.7, or 4 minutes, respectively, were used. The rapid mixing duration was followed by a 15 minutes slow mixing at 50 s^{-1}, which was followed by a 30 minutes settling period. They concluded that optimum sedimentation occurs when rapid mixing continues until floc particles reach near equilibrium sizes in the rapid mixing tank. They also recommended that rapid mixing should be followed by tapered flocculation.

Although the G values used for rapid mixing in the above work are rather low, the G value of 200 s^{-1} could still give a good insight on the effects of rapid mixing time, and their conclusions would still be valid.

Letterman et al. (1973) used alum in a conventional jar test procedure to coagulate a powdered activated carbon suspension at pH 8.1 (before coagulant addition). Concentration of the powdered activated carbon ranged from 20 to 1000 mg/L (3 JTU to ∞). Rapid mixing time and intensity were changed while slow mixing (30 min. at 10 s^{-1}) and sedimentation (30 min.) were kept constant. The residual turbidity after rapid mixing, slow mixing and sedimentation was used to evaluate the process. **Table 3-2** shows the results of the experiments performed. They found that for each combination of rapid mixing intensity and alum dose, an optimum rapid mixing time existed. The following equation was developed for

Table 3-2: Minimum residual turbidity and optimum rapid mixing time for different combinations of suspended matter concentration, alum dose, and velocity gradient (Letterman et al. 1973).

Minimum Residual Turbidity Jtu	Optimum Rapid-Mix Period min	Powdered Carbon Concentration mg/L	rms Velocity Gradient, G s^{-1}	Alum Dose mg/L
1.30	2.5	50	1,000	10
0.55	1.6	50	1,000	15
0.37	1.5	50	1,000	25
0.13	0.60	50	1,000	35
0.13	0.23	50	1,000	50
0.50	7.0	50	500	10
0.13	3.0	50	500	25
0.21	28	50	100	10
0.06	16	50	100	25
0.54	2.5	20	1,000	10
0.98	2.5	100	1,000	10
1.60	2.5	200	1,000	10
3.40	2.5	500	1,000	10
3.30	2.5	1,000	1,000	10
0.07	13.3	50	200	25
0.25	7.7	50	200	10
0.07	0.35	50	500	70
0.07	0.27	50	500	125
0.15	1.3	200	100	100
0.22	1.6	500	100	100
0.57	1.4	1,000	100	100
0.10	0.14	50	1,000	100
0.08	1.3	50	100	100

the optimum rapid mixing duration, t_{opt}:

$$Gt_{opt}C^{1.46} = 5.9 \times 10^{6} \quad (3\text{-}7)$$

Where C = alum dose, mg/L.

They found that there was no significant effect of suspended solids concentration on the optimum rapid mixing duration. The fact that an optimum rapid mixing period exists and that the initial flocculation rate was greatest when the optimum rapid mixing period was used, made the researchers conclude that the slow mix and the sedimentation operations are greatly influenced by the initial stage of floc formation during rapid mixing. Since the optimum rapid mixing durations were longer than the time of alum precipitation by a factor of 1.5 to 200, flocculation during rapid mixing is necessary for the growth and settling characteristics of the flocs in the slow mix and sedimentation tanks, respectively.

Mhaisalkar et al. (1991) investigated the effects of initial water turbidity on the rapid mixing intensity and duration. The effect of reactor geometry was also investigated. Samples of bentonite clay suspended in distilled water (2 L volume) with turbidities of 30, 120, and 480 NTU at pH 7.0 were used. Alum was used in these experiments. The slow mixing (30 min. at 56 s^{-1}) and sedimentation (30 min.) were held constant throughout the experiments regardless of variation in rapid mixing parameters. The residual turbidity after flocculation and sedimentation was used for comparison. Based on jar test results, the optimum alum dose to achieve residual turbidity values of 2.5 NTU were 16, 40 and 80 mg/L alum for initial turbidity values of 30, 120 and 480 NTU, respectively. The optimum velocity gradient and time of rapid mixing and the corresponding Gt values for the different initial turbidity values used are shown in **Table 3-3**.

They realized that even though the Gt values in **Table 3-3** are somewhat independent of raw water turbidity, every raw water turbidity value has its own unique optimum rapid mixing time and mixing intensity. Therefore they concluded that the Gt product is of limited significance in rapid mixing design. They suggested that an optimum combination of both rapid mixing velocity gradient and rapid mixing time exists for a given suspension turbidity and container geometry. This combination enables the flocs formed after rapid mixing to have a structural equilibrium which is necessary for effective flocculation and sedimentation.

Table 3-3: Optimum rapid mixing times and intensities for different initial turbidity values (Mhaisalkar et al. 1991).

Raw water turbidity N_o (NTU)	Velocity gradient G_r (s^{-1})	Time T_r (s)	G_rT_r
30	750	40	30,000
120	550	60	33,000
480	450	90	40,500

Camp (1968) studied the effect of rapid mixing on the floc volume concentration of turbidity free water. Ferric sulfate was used at pH of 6.0 in tap water. It was found that the floc volume concentration decreases as the value of G increases, within the range studied (80 - 1000 s^{-1}). With 2 minutes of rapid mixing, the floc volume concentration was 285 ppm by volume when G was 80 $^{-1}$ compared to 60 ppm by volume at G value of 1000 s^{1}. This was ascribed to the fact that less water was trapped between the coalescing hydroxide floc particles at high mixing intensity than at low mixing intensity. Water constituted the largest portion (89-98%) of this turbidity free floc volume.

The influence of the floc size formed by the end of rapid mixing on the flocculation process has also been stressed by Francois and Van Haute (1984, 1985). Francois and Van Haute (1985) referenced the work of Van de Ven and Hunter (1977) who defined a four level floc structure. "A floc aggregate is composed of flocs. These densely packed flocs consist of a number of flocculi which are formed at the highest rate of shear to which the system was ever subjected. The bonds between the different parts are elastic." (Francois and Van Haute 1985, pg. 1250).

Francois and Van Haute (1985) used a four liter suspension of 75 mg/L kaolin clay dispersed in distilled water to verify the existence of such a four level structure. Alum was used at pH 7.0 and 25 °C. A cylindrical five liter jar without baffles was used to reduce the spread of velocity gradient in the suspension. Breakup experiments of fully grown particles were conducted. It was observed that during breakup experiments, primary particles and some very small fragments were formed only if the breakup mixing intensity was higher than the mixing intensity applied during rapid mixing. This was an indication of the presence of such flocculi. Assuming that at breakup mixing intensities smaller than the originally applied rapid mixing intensity, the small fragments are multiples of the flocculi, they verified and calculated the diameter of such flocculi.

Francois and Van Haute (1984) studied the effect of rapid mixing time on the flocculation process. Similar experimental variables (kaolin clay concentration = 75 mg/L, pH = 7.0) to those used by Francois and Van Haute (1985) were used. Rapid and slow mixing velocity gradients were 389 s^{-1} and 34 s^{-1}, respectively. The equivalent diameter of flocs and their distribution were measured either by sedimentation studies or by a particle sizer. **Figure 3-5** shows the average floc diameter, measured after the flocs have reached an equilibrium diameter, as a function of rapid mixing time along with the optimum aluminum dosage. It can be seen from this figure that the average floc diameters were different for the different measurement procedures. A 120 seconds optimum rapid mixing time was obtained using the sedimentation procedure while a 30 seconds was optimum using the particle sizer.

The particle sizer was also used to compare the floc build-up curves for rapid mixing times of 30 and 300 seconds (see **Figure 3-6**). Particle size distribution was measured every 15 seconds. As can be seen from the figure the 300 seconds rapid mixing was detrimental, despite the fact that the initial build-up rate was higher than that at 30 seconds of rapid mix time.

The flocculi equivalent diameter at the end of rapid mixing was measured as a function of rapid mixing time (rapid mixing intensity was constant). Breakup experiments of

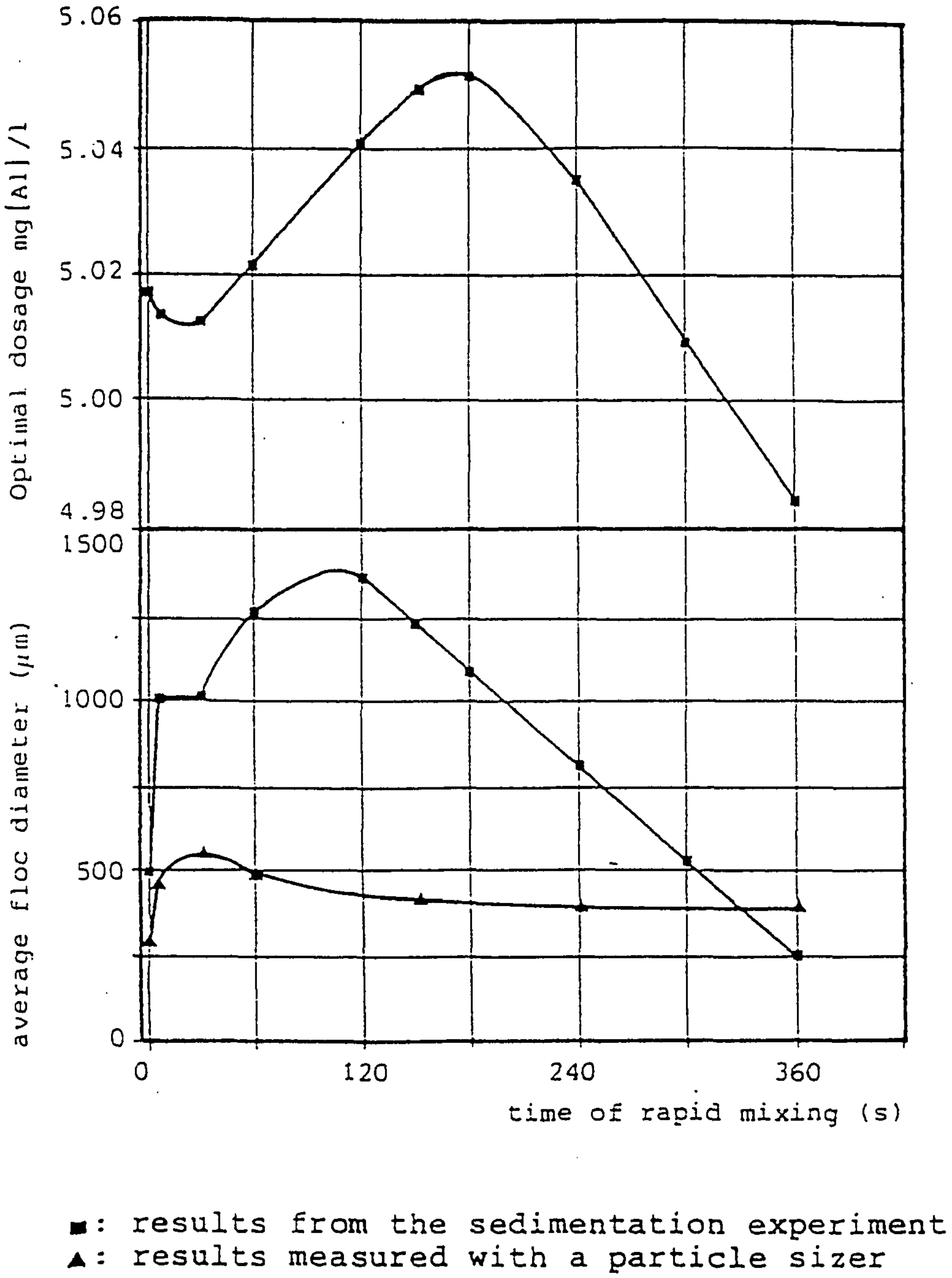


Figure 3-5: Rapid mixing time effect on floc size (Francois and Van Haute 1984).

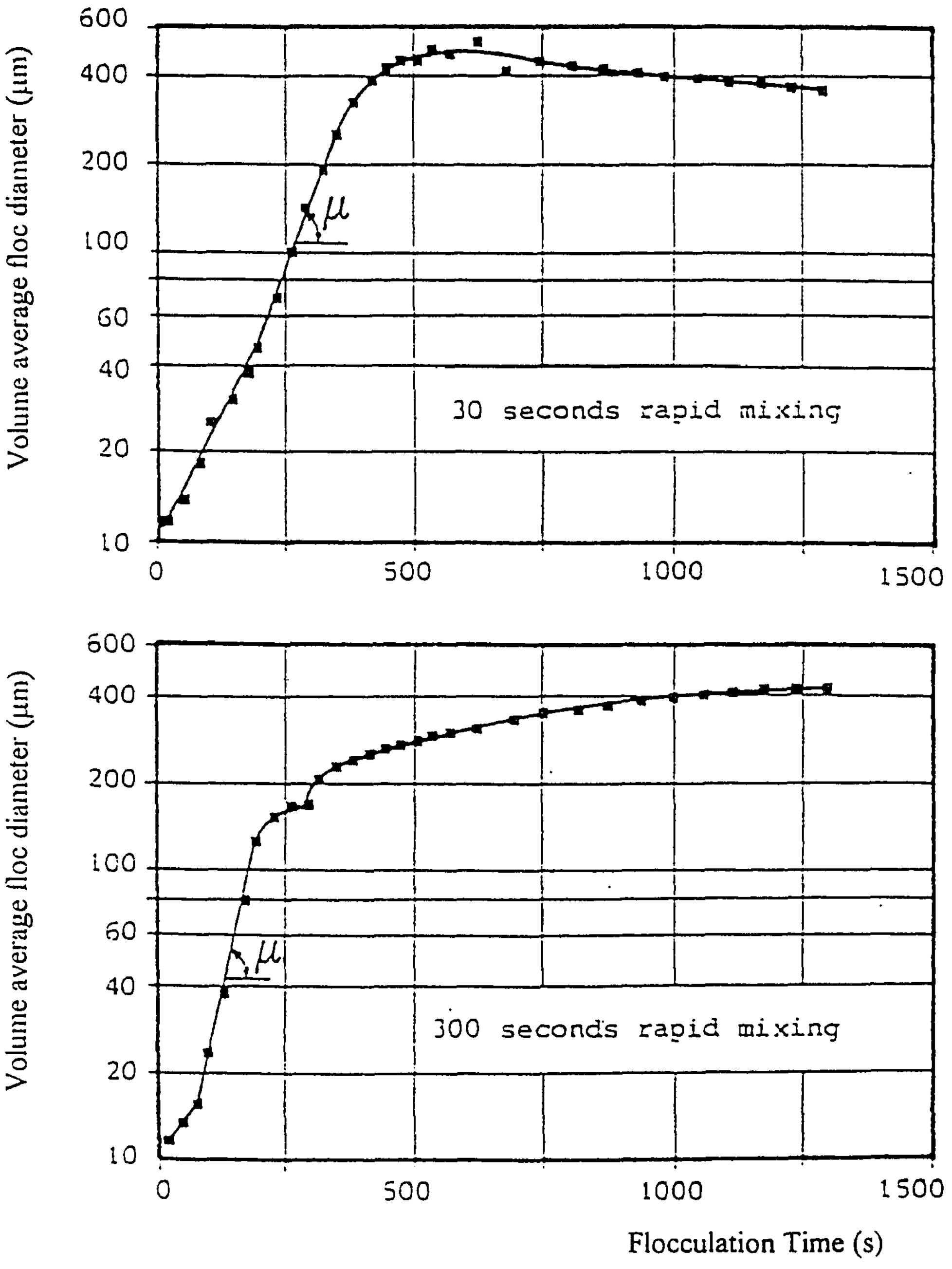


Figure 3-6: Comparison of floc build-up curves for two rapid mixing times (Francois and Van Haute 1984)

fully grown flocs was conducted by discontinuous increase in the mixing intensity. Assuming that the flocs formed after breakup at different mixing intensities are multiples of the flocculus, they calculated the limits between which the flocculus diameter lies. This is shown in **Figure 3-7**. As can be seen, the largest calculated flocculus diameter occurred when 30 seconds of rapid mixing is applied. Longer times resulted in smaller flocculi probably due to flocculi erosion.

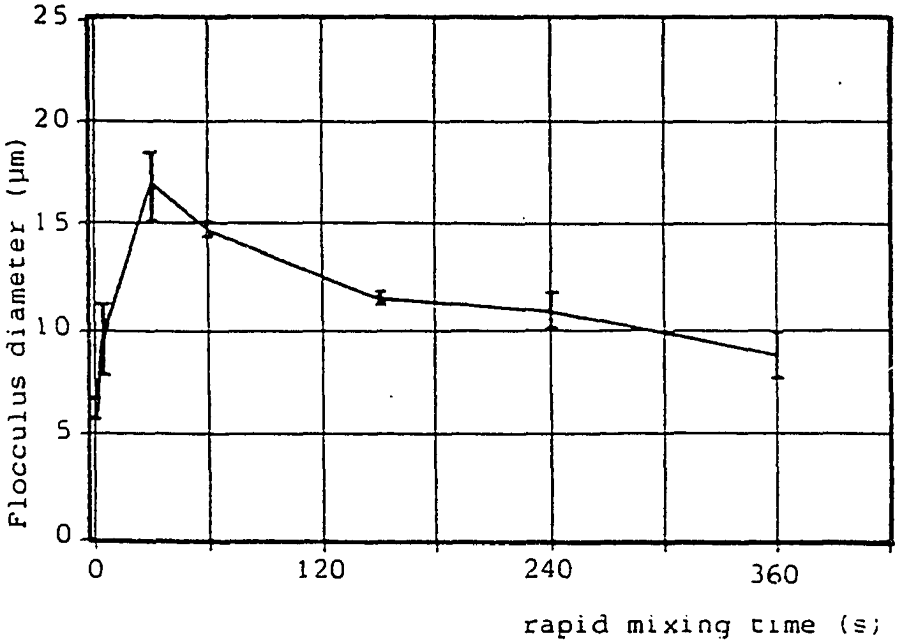


Figure 3-7: Flocculus diameter as a function of rapid mixing time (Francois and van Haute 1984).

Due to the similarities in **Figures 3-5 and 3-7** when the particle sizer was used (30 seconds of rapid mixing gave the largest flocculi diameter and the largest equivalent floc diameter), they concluded that the flocculi are the building stones of the floc structure. They also stated that "The largest and most resistant flocs are constructed with the largest flocculi which are the building stones of the structure. A rapid mixing time seems to be optimal." (Francois and Van Haute 1984, pg. 1100). They acknowledged, however, that the numerical values presented for rapid mixing time in their study are most probably not applicable for other raw water parameters.

3.4 Temperature Effects

The early studies (Velz 1934, Leipold 1934, Camp et al. 1940) of the effects of temperature on the coagulation-flocculation processes using inorganic coagulants had contradictory findings. Leipold (1934), by observing the appearance of the flocs during settling, found that low water temperature had no preventive or retarding effect on alum floc formation. Velz (1934), however, found that low temperature had a beneficial effect on color removal. Camp et al. (1940) suggested that the detrimental effect of cold temperature is only due to its effect on the sedimentation process, if the coagulation process is conducted at the unique optimum pH for each temperature.

However, most later studies conclude that turbidity removal by inorganic coagulants is impaired by low temperatures (Morris and Knocke 1984, Hanson and Cleasby 1990, Kang and Cleasby 1994, Mohtadi and Rao 1973, Leprince et al. 1984). Cold temperature still affected turbidity removal of filtered water in direct, in-line, filtration (in Haarhoff and

Cleasby 1988) as well as in conventional treatment (Hannah et al. 1967). The detrimental effects of cold temperatures on turbidity removal were also observed in full scale water treatment plants (Morris and Knocke 1984, Knocke et al. 1986, Hutchison and Foley 1974). Hutchison and Foley (1974) reported that water treatment plants in Ontario experience problems with slow forming flocs for three months a year when the temperature falls below 3 °C. Morris and Knocke (1984) documented a case study in a major city in Virginia where finished water turbidity increased when water temperature fell below 4 °C. Knocke et al. (1986) also documented a failure in a water treatment plant where finished turbidity values reached 5-7 NTU when water temperature reached 0-1 °C.

No single cause for the detrimental effects of low water temperatures on turbidity removal has been widely accepted. The following, however, are the changes that cold water has on the physical and chemical behavior of the water and the inorganic coagulants:

1- An increase in the viscosity and density of water

2- A decrease in the rate of metal hydrolysis and rate of precipitation

3- A decrease in the solubility product of the metal hydroxide precipitate

4- A decrease in the water ion product

These changes do not necessarily contribute to the cold water induced decreased turbidity removal efficiency. The relevant literature will now be reviewed with the following question in mind: which change or combination of changes discussed above contribute to the hindrance of turbidity removal? If this is known, then it would be possible to have a more rational correctional measures to reduce the effects of low temperature.

A number of researchers have found that the optimum pH values for coagulation change as temperature changes (Velz 1934, Camp et al. 1940, Mohtadi and Rao 1973). Hanson and Cleasby (1990) and Van Benschoten and Edzwald (1990a,b) recommended a change in the pH value to maintain a constant pOH value to correct for temperature changes. The earlier works did not explain or specify the amount, or even the direction, of the pH change necessary to accommodate for temperature changes. Camp et al. (1940) states that "There is insufficient information available at the present time to indicate the direction and amount of shift of the optimum pH for a particular water and coagulant." (Camp et al. 1940, pg. 1926). Velz (1934) found that cold temperature has a beneficial role in removing color from water. He recommended the adjustment of the pH value to the optimum value at each temperature to get rid of the detrimental effect of high temperature (room temperature). The results of Mohtadi and Rao (1973) show an increase in the optimum pH as temperature decreases. They however did not explicitly state the direction of the pH shift. Instead they stated that "the optimum pH for flocculation varies with temperature when alum is used as flocculant. This may be explained on the basis of the dependence of the concentration of the hydrolysis products of alum on pH and temperature." (Mohtadi and Rao 1973, pg. 766).

The direction and amount of shift of pH was first evaluated by Hanson and Cleasby (1989, 1990) who introduced the concept of constant pOH to correct for temperature changes. The concept was also stressed by Van Benschoten and Edzwald (1990a,b). Recently, however, Kang and Cleasby (1994) found that this concept is only valid at acidic pH values. In fact at pH 8.0, the use of a constant pOH at 5 °C (pH=8.7) instead of constant pH was deleterious to the flocculation process.

Mohtadi and Rao (1973) used either 200 mg/L Bentonite or 450 mg/L Kaolinite suspended in distilled water exposed to the atmosphere for 24 hours. The state of flocculation was observed by measuring the light absorption index of samples taken at regular time intervals during flocculation. Once stirring was stopped, a small drop of the suspension was photographed using a photomicroscope which provided a permanent evidence of the floc sizes. They found that at a certain pH value, higher alum dosage was required at low temperature than at higher temperatures to achieve similar degree of flocculation. They also found that the optimum pH value increased as temperature decreased (see **Table 3-4**). Furthermore, if coagulation was performed at the optimum pH values for each temperature, temperature did not have any influence on flocculation. It should be noted that these experiments were done at acidic pH values as **Table 3-4** shows.

Mohtadi and Rao (1973) reported the results obtained by Chojnacki (1968) regarding the influence of low temperature on the flocculation of river water using aluminum sulfate. They mentioned that Chojnacki (1968) found that the size of the flocs formed decreased as the water temperature decreased.

Morris and Knocke (1984) studied the effects of low temperature on turbidity removal using both alum and ferric chloride. Jar test studies using kaolin clay suspended in tap water with initial turbidity values ranging from 1 to 25 NTU at temperatures of 1 °C, 5 °C, and room temperature were conducted. Initial suspension pH values were 7.0 when alum

Table 3-4: Optimum pH at different temperature values when alum is used (Mohtadi and Rao 1973).

	Optimum pH corresponding to minimum residual turbidity			
	Bentonite dispersion			Kaolinite dispersion
	Flocculant dosage (ppm)			Flocculant dosage (ppm)
Temperature (°C)	20	30	40	15
20	5.6	5.3	5.1	5.4
15	6.0	5.6	5.4	5.6
10	6.3	6.0	5.8	5.8
5	6.5	6.4	6.2	6.2
1	6.6	6.8	6.8	6.3

was used and 8.0 when ferric chloride was used. Initial pH values were the same for both cold and room temperature experiments. Alkalinity was augmented to a minimum of 50 mg/L as $CaCO_3$ to limit the drop in pH to a maximum of 0.6 units for the highest dosage used. A one liter suspension was rapid mixed for 1 minute, flocculated for 20 minutes at 45 rpm and settled for 60 minutes. Residual turbidity and, in some experiments, residual alkalinity, particle size distribution, and coagulant metal concentration in the supernatant (soluble plus particulate species) were determined.

Regarding turbidity removal, the residual turbidity increased as the water temperature decreased. Almost no turbidity removal was observed at low temperatures when the initial turbidity was about 5 NTU or less. Another difference between low and room temperatures when alum was used was that restabilization occurred at low water temperature when high alum dosages were used, but did not occur at room temperature. When ferric chloride was used, no such restabilization occurred whether at room or cold temperatures. It should be noted that zeta potential values were not measured; the restabilization was based on residual turbidity values.

It should be noted that Kang and Cleasby (1994) found that the ferric nitrate coagulant used produced a more positive hydrolysis products at low temperature than at room temperature. This could explain the restabilization behavior at cold temperatures, when alum was used, noticed in Morris and Knocke (1984) study. The occurrence of restabilization with alum but not with ferric chloride could be due to the fact that they conducted their experiments at pH 7.0 with alum, but at pH 8.0 with ferric chloride. More positive hydrolysis products are produced at lower pH values. Furthermore, the isoelectric point for alum precipitates occurs at higher pH values than for precipitates resulting from ferric salts, which means that even at the same pH values, alum produces more positive precipitates.

Regarding residual inorganic coagulant concentration, Morris and Knocke (1984) found that residual aluminum concentration (soluble + suspended) was much higher than residual total ferric iron concentration at low temperature. Typical soluble aluminum and ferric iron concentrations were, respectively, < 0.5 mg/L and < 0.1 mg/L indicating that precipitation did occur. They attributed the high residual total aluminum concentration to the fact that the aluminum hydroxide precipitates were not large or dense enough to promote settling.

Regarding particle size distribution at low temperature, alum produced relatively large flocs in the adsorption destabilization (A/D) region (1 mg/L Al^{+3}), and markedly smaller flocs in the sweep floc region (5 and 10 mg/L Al^{+3}). Ferric chloride, however, produced relatively large flocs in both the A/D and the sweep floc regions.

It should be noted that the dosages used in the above study were very high dosages for the low turbidity waters tested (10 mg/L Al^{+3} is equivalent to about 110 mg/L alum, as $Al_2(SO_4)_3.14.3\ H_2O$). Even dosages that were claimed to produce coagulation by the A/D mechanism are high. It is possible that the high dosage of alum produced a large number of small and light aluminum hydroxide flocs that caused the reduction in the floc diameters at high alum dosages (in the sweep floc region, as they claimed).

Temperature effects on the rate of precipitation of iron and aluminum salts were also investigated by adding 3 mg/L of either Fe^{+3} or Al^{+3} to both turbidity free and turbid waters at low temperatures (1 °C and 5 °C). The samples were rapid mixed for 1 minute followed by the regular flocculation step. Samples were taken 1 minute after the coagulant addition (after rapid mixing) and continued at time intervals for about 4 hours. Results showed that a significant amount of precipitation occurred during the rapid mixing time, even at low temperatures. The following were the main conclusions of Morris and Knocke (1984) work:

"1. Temperature had a significant effect on turbidity removal by means of metal-ion coagulants, with extreme-low-temperature conditions reducing turbidity removal efficiency.

2. Temperature had a greater impact on coagulation systems that used alum as a coagulant. Effects were less severe, although still significant, for ferric chloride coagulation.

3. Low-temperature conditions did not inhibit the rate of aluminum or ferric hydroxide precipitation.

4. Decreased turbidity removal efficiency under low-temperature conditions could be related to fundamental changes in floc characteristics. Flocs formed under low-temperature conditions were often smaller than those formed during coagulation under room-temperature conditions." (Morris and Knocke 1984, pg. 79).

The fourth conclusion was true when the same dosages of the inorganic coagulants were compared at room and cold temperatures. Cold temperature experiments using 1 mg/L Al^{+3} produced larger flocs than 10 mg/L Al^{+3} at room temperature. Again, this could be the result of the extremely high alum dosage that left the small and light aluminum hydroxide precipitate in suspension.

Hanson and Cleasby (1990) used a reactor identical to the one used in the present work to study the influence of temperature on the flocculation kinetics. Particle size distribution of samples taken before coagulant addition, directly after rapid mixing and at several times during the flocculation period were determined using an Automatic Image Analysis system coupled to a light microscope. A 25 mg/L Kaolinite clay suspended in Ames, Iowa tap water and buffered with a 100 mg/L $NaHCO_3$ was used as the primary particle system. The pH (6.8 for alum and 5.5 for ferric sulfate at 20 °C) and the coagulants' dosages (5.0 mg/L alum or 4.0 mg/L ferric chloride) were chosen so that the coagulation would take place in the A/D region. The following are the main conclusions resulted from their study:

1. The use of different mixing intensity parameters (average root mean square velocity gradient G, Kolmogorov microscale η, or energy input per unit mass $\in$) can not eliminate the effect of temperature on the flocculation process using inorganic coagulants.
2. The use of constant pOH instead of constant pH can reduce (with alum) and almost eliminate (with ferric sulfate) the detrimental effects of cold temperature on flocculation.
3. The difference between the flocculation kinetics at low and room temperatures is mainly due to the floc strength. Flocs formed at low temperatures were smaller than those formed at room temperature.
4. Iron flocs are stronger than alum flocs. Ferric salts are therefore better suited for low water temperatures than alum.

Kang and Cleasby (1994) also used an identical system to the one used in the present work. They found that the deleterious effects of low temperature can be decreased, but not eliminated, by using a constant pOH in the acidic pH range (pH < 6.8) (see **Figure 3-8**). The constant pOH concept is not appropriate at high pH values. In fact it was detrimental at pH 8.0 (see **Figure 3-9**).

As was shown above, there is a controversy whether conducting the coagulation at the optimum pH value for different temperatures would eliminate the effects of low

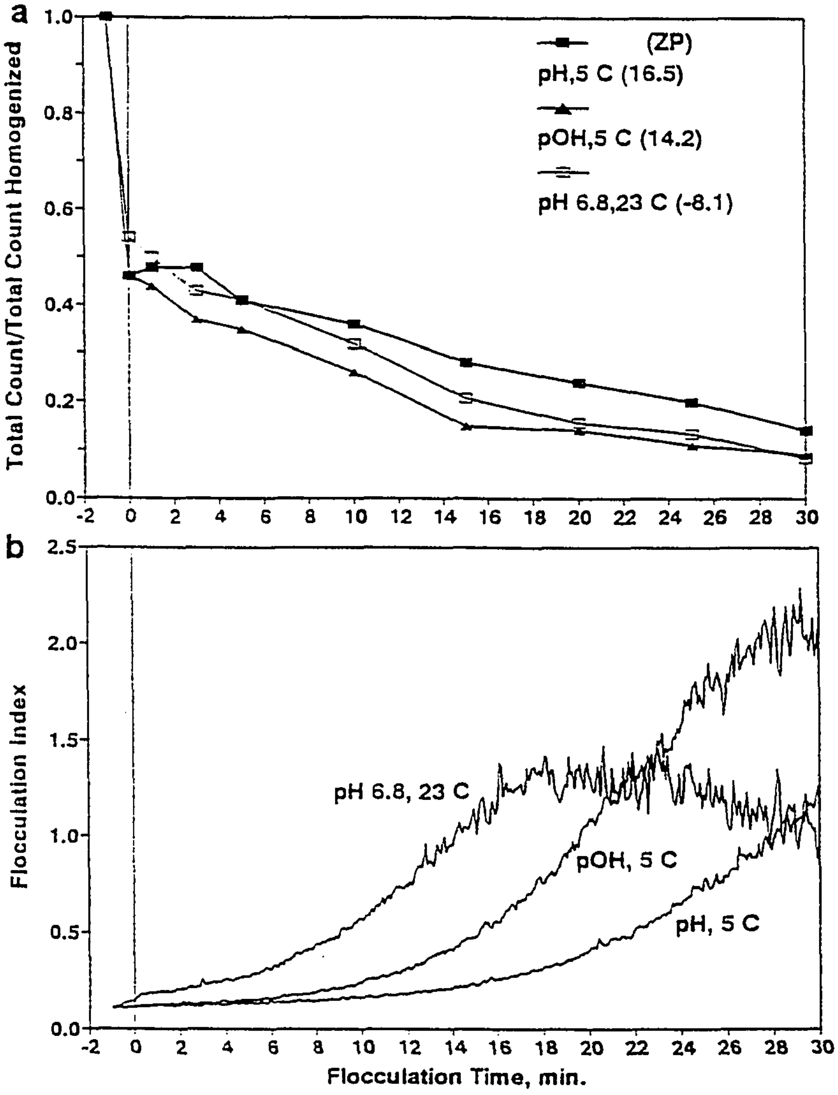


Figure 3-8: The improved flocculation kinetics using constant pOH at low temperature at acidic pH values (constant pH requires a pH of 7.5 at 5 °C). Kaolin clay concentration = 25 mg/L (Kang and Cleasby 1994).

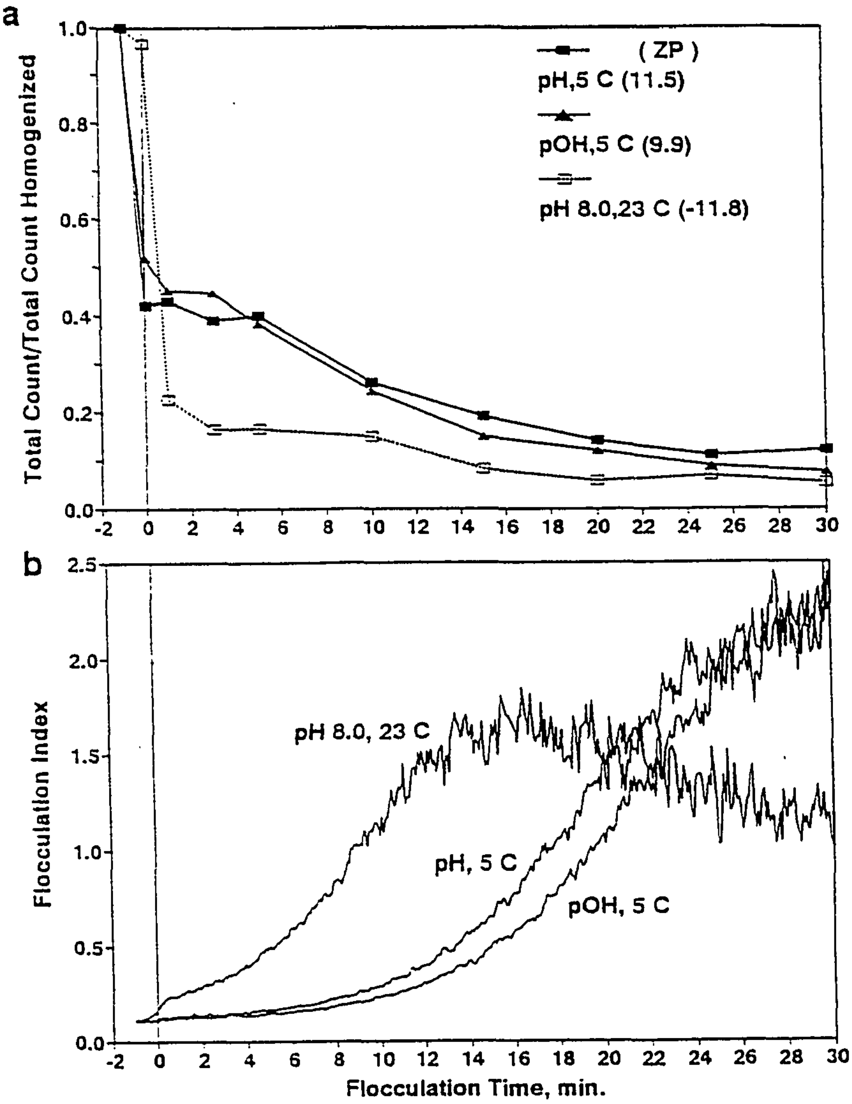


Figure 3-9: The deleterious effect of using constant pOH at low temperature at high pH values (constant pOH requires a pH of 8.7 at 5 °C). Kaolin clay concentration = 25 mg/L (Kang and Cleasby 1994).

temperature. Camp et al. (1940) and Mohtadi and Rao (1973) found that temperature effects can be eliminated by using optimum pH values. Hanson and Cleasby (1990) found that constant pOH improves but does not eliminate the detrimental cold temperature effects when alum is used and eliminates the detrimental cold temperature effects when using ferric chloride. Kang and Cleasby (1994) found that constant pOH only improves but does not eliminate the detrimental effects of cold temperature with ferric nitrate and only in acidic pH range.

It can also be seen from the above literature that flocs formed at cold temperatures are smaller than those formed at room temperatures (Hutchison and Foley 1974, Morris and Knocke 1984, Chojnacki 1968 in Mohtadi and Rao 1973, Kang 1994). Morris and Knocke (1984) related that to fundamental changes in floc characteristics at cold temperatures leading to smaller flocs. Hanson and Cleasby (1990) ascribed that to a decrease in floc strength at cold temperatures.

4. CATIONIC POLYMERS AS SOLE COAGULANTS

4.1 Introduction

Polymer use in water treatment began in the late fifties. Although their use in potable water treatment was rare at that time, only one polymer was approved by the USPHS for use in potable water treatment until 1967 (Pressman 1967), their use in wastewater treatment and sludge conditioning was rapidly growing. In 1982, a survey on polyelectrolyte coagulant use in the United States indicated that about 50% of water treatment plants were using polymers in their treatment (AWWA Coagulation and Filtration Committee, 1982). Recently a study showed that among the 23 water treatment plants studied, 20 were using polymers either as primary coagulants or as coagulant or filter aids (Cleasby et al. 1989).

During the last 25 years a large number of products have been approved for use in water treatment. In 1985, the list of accepted products promulgated by the USEPA contained more than 1300 products from 134 manufacturers. It is believed that these products do not contain more than 11 to 12 chemical compounds, and many products are simply dilutions of a single formulation or differ only by molecular weight or charge density (Letterman and Pero 1990). This list expired in 1990 when a second list of a consortium led by the National Sanitation Foundation (NSF) was to become effective. The consortium includes the American Water Works Association (AWWA), the AWWA Research Foundation, and the Association of Safe Drinking Water Administrators (ASDWA). The NSF is responsible for testing and certifying polymer products on the basis of a case by case program (NSF Standard 60, 1992). This voluntary program examines each product from a specific production plant and gives approval only to that product from that plant after passing specific tests. The same product from other plants, and even from the same plant at other locations has to be tested before approval.

A number of researchers have studied the use of cationic polymers as sole coagulants to explore the benefits that they can provide for water treatment and the restrictions associated with their use.

Cationic polymers have shown an advantage over inorganic salts in direct, in-line, filtration (Shea et al. 1971, Adin and Rebhun 1974, Carns and Parker 1985). They also have been proved to be effective in direct filtration, if appropriate pretreatment is practiced (Letterman et al. 1979, Stump and Novak 1979).

Using four in-line pilot plant filter beds to filter 6 and 24 mg/L suspended solids using alum or a cationic polymer, Shea et al. (1971), found that the use of cationic polymers and coarse dual media filters achieved acceptable filtrate turbidity and the longest filter runs.

Adin and Rebhun (1974) compared alum and a cationic polymer performance in direct, in-line, filtration process. They used a two pilot filtration columns to filter a 20 mg/L kaolinite suspension. Compared to the use of alum alone, the filter run was longer and the turbidity removal efficiency was better when the cationic polymer alone was used. However, the ripening period (the initial water quality degradation) was longer and the head loss development was higher when the cationic polymer was used. They recommended the use of coarse media to reduce this higher head loss development. The cationic polymer was efficient even at hydraulic loads as high as 20 m/hr.

The long filter runs in direct, in-line, filtration with cationic polymers was also observed by Cleasby et al. (1984). The filter runs were substantially longer when the cationic polymer was used than those when alum was used. The filtrate quality was slightly inferior with the cationic polymer, however.

Carns and Parker (1985) have reported on a direct, in-line plant scale testing at East Bay Municipal Utility District, Oakland, California, that using cationic polymer alone when the water turbidity was over 3.5 NTU, or cationic polymer with clay when water turbidity was less than 3.5 NTU has resulted in effluent turbidity values comparable to those obtained with alum alone. However, with cationic polymers the plant capacity could be increased by about 50 % above the capacity obtained when using alum. This was possible, primarily, through increasing the filtration rate and partially through extending the filter run. The sludge production and the quantity of backwash water were reduced by about 55 % and 50 %, respectively compared with those of alum. They also found that the cost of using clay-polymer coagulant or alum plus lime, which was used for pH adjustment following filtration when alum was used, were almost the same. Nonetheless, the overall cost of coagulants, sludge handling, and backwash water was in favor of using cationic polymer coagulants.

Letterman et al.(1979) used three different dual media filters to filter a suspension that consisted of a combination of 44 mg/L bentonite clay and 22 mg/L kaolin clay in tap water resulting in a turbidity of 32 FTU. The following conclusions were drawn from their study: "Direct filtration using cationic polyelectrolytes and dual media filters can be used effectively to treat high turbidity water, and effective operation can be achieved by pretreatment control. The operation of a dual media filter with a cationic polyelectrolyte as the sole coagulant is characterized by the formation of a distinct clogging front or filtration zone moving down through the bed at a rate that is a function of the filter media size distribution and the pretreatment and filter operating conditions. The rate of clogging front advancement can be increased by (1) increasing or decreasing the polyelectrolyte concentration above or below a concentration which results in a particle zeta potential of approximately zero; (2) increasing the filtration rate; (3) increasing the pretreatment mixing intensity; and, to a certain extent, (4) increasing the effective size of the anthracite media." (Letterman et al. 1979, pg. 337). They recommended the use of a period of flocculation between 2 to 10 minutes to control the rate of the clogging front advancement.

The need for appropriate pretreatment in direct filtration with cationic polymers has also been emphasized by Stump and Novak (1979). A 100 mg/L kaolin clay suspension in distilled water, and a number of cationic polymers having different molecular weights were used. A rapid mixing intensity (the duration was fixed to 2 minutes) specific to each molecular weight cationic polymer was necessary in order for the terminal head loss and turbidity breakthrough to occur simultaneously. In general a G value between 600-1000 s-1 was best for molecular weight cationic polymers in excess of 100,000, while a G value in the 300 s-1 was best for molecular weights in the range 10,000 to 50,000. Cationic polymers with molecular weights less than 10,000 performed poorly with regard to turbidity removal, while cationic polymers with molecular weights in excess of 1 million caused excessive head losses. Accordingly, they recommended the use of cationic polymers in the molecular weight range 10,000 to 200,000 for direct filtration. A 20 minutes flocculation period increased the filter runs for these polymers.

4.2 Chemistry of Cationic Polymers

Polymers are defined as a series of repeating chemical units called monomers held together by covalent bonds. Polyelectrolytes are polymers with ionizable groups. According to Mandel (1981), polyelectrolytes are defined as "macromolecules which, in a suitable polar solvent, usually water, carry a large number of ionized or ionizable groups, often one per monomer unit. Under well defined conditions the macromolecules will bear a considerable charge distributed along the chain (the 'fixed charges') accompanied by an equivalent number of small ions of opposite sign (the 'counterions') in solution." (Mandel, 1981 pg. 179). Cationic polymers are polymers with a positive ionizable group. Polymers produced by linking a single repeating unit are known as homopolymers whereas those containing a random arrangement of two repeating units are known as copolymers (Rosen 1982).

Synthesis of polymers, whether homopolymers or copolymers, is made by two types of chemical reactions: condensation and addition reactions (Rosen 1982). Condensation is called so because a small molecule, often water, is split out as a result of the reaction. The addition polymerization is a process in which no molecule is split out and, therefore, the repeating unit has the same chemical formula as the monomer. Instead, the opening of a double bond is required to form the addition polymerization reaction. Monomers of the type $C=C$ undergo addition polymerization. Polyacrylamide is produced by this method.

High molecular weight coagulant aid polymers (nonionic and anionic polymers) used in water treatment are based on the homopolymerization or copolymerization of acrylamide monomer. The homopolymerization of acrylamide by the addition type polymerization produces the nonionic polyacrylamide. If high molecular weight anionic polymers are required, then the comopolymerization of acrylamide with acrylic acid or sodium acrylate, or the homopolymerization of acrylamide is used with subsequent hydrolysis of some of the acrylamide groups to sodium acrylate (Mangravite 1983).

The anionic nature of the acrylamide/acrylic acid polymers (ACM/ AAP) or the hydrolyzed polyacrylamide come from the dissociation of the acrylic acid groups and the ionization of the sodium acrylate respectively. The degree of ionization of these polymers depends on the solution pH. In fact, the pk_a of ACM/AAP is not constant and changes due to the influence of the acrylate groups upon each other. Moreover, the pk_a varies slightly for each molecule depending upon the distribution of acrylic acid among acrylamide units even for the same acrylamide/ acrylic acid ratio (copolymerization ratio). In general, the acrylic acid group is in the nonionic form below pH 3.5 and in the anionic acrylate form above pH 6.0 (Mangravite 1983). It should be noted that even nonionic polymers become cationic at low pH values (by adding a Hydrogen ion to their structure) and anionic at high pH values. They are only nonionic at intermediate pH values.

The primary coagulants (cationic polymers) acquire their positive charge due to the presence of amine or quaternary amine (quaternary ammonium) sites. The quaternary amine is produced when the hydrogen atoms in the amine group are exchanged by three alkyl groups (Morrison and Boyd 1973).

$$\underset{\text{primary}}{RNH_2} \text{ -----> } \underset{\text{secondary}}{R_2NH} \text{ -----> } \underset{\text{tertiary}}{R_3N} \text{ -----> } \underset{\text{quaternary}}{R_4N^+X^-} \qquad (4\text{-}1)$$

It is important to know if a polymer contains amines or quaternary amines groups. The degree of ionization of a polymer containing quaternary amine groups does not change with the pH, whereas that of other polymers containing either primary, secondary, or tertiary amines changes with the pH value. In simple amines (amines that are not part of a polymer), the primary amines lose their cationic charge above pH 5.5, whereas tertiary amines lose their charge above pH 8.0. However when these groups are present in a polymer, they do not lose their charge until pH 10 in some cases (Mangravite 1983). Polyamines are a mixture of primary, secondary, and tertiary amines. Polyethyleneamine (PEI), for example, has about 25% primary amine, 50% secondary amine, and 25% tertiary amines (Lindquist and Stratton 1976).

Chlorine can react with unquaternized amines, reducing their charge, and even making them ineffective. So, it is recommended to use quaternized amine polymers if prechlorination is practiced. Sometimes, even quaternized amine polymers are affected by chlorine. The efficiency of the polymer may increase or decrease (Mangravite 1983). The most common cationic coagulants used in water treatment are discussed below.

4.2.1 Poly(DADMAC)

Poly (diallyldimethyl ammonium chloride) or Poly(DADMAC), and sometimes abbreviated also as Poly(DMDAAC), polymers are manufactured by addition polymerization (Mangravite 1983). The manufacturing process requires two steps: the formation of the monomer and then its polymerization. The monomer is produced by the reaction of dimethylamine and allyl chloride in the presence of a metal hydroxide, usually sodium hydroxide NaOH. The production of the monomer and the polymerization processes are shown in **Figure 4-1** (Mangravite 1983, Letterman and Pero 1990).

As mentioned above, typically the hydrogen ion produced as a result of the reaction of dimethylamine and allyl chloride (the hydrogen ion on the nitrogen atom in dimethylamine) is neutralized with sodium hydroxide. As a result of that, an appreciable amount of sodium chloride is formed. From the above chemical equation, it can be seen that only one chloride ion from the two chloride ions present in the two molecules of allyl chloride participates in the formation of DADMAC monomer. Therefore, it is unavoidable to form a salt such as NaCl or any other chloride salt when poly(DADMAC) is being formed. It can be easily shown that the percentage by weight of NaCl to DADMAC produced whether in monomer or polymer form is equal to 36.2%. In certain cases, the crystallized inorganic salt is removed by filtration to minimize its effects on the polymerization (Letterman and Pero 1988). Hunter and Siedar stated that salt removal is not necessary under certain conditions (In Letterman and Pero 1988).

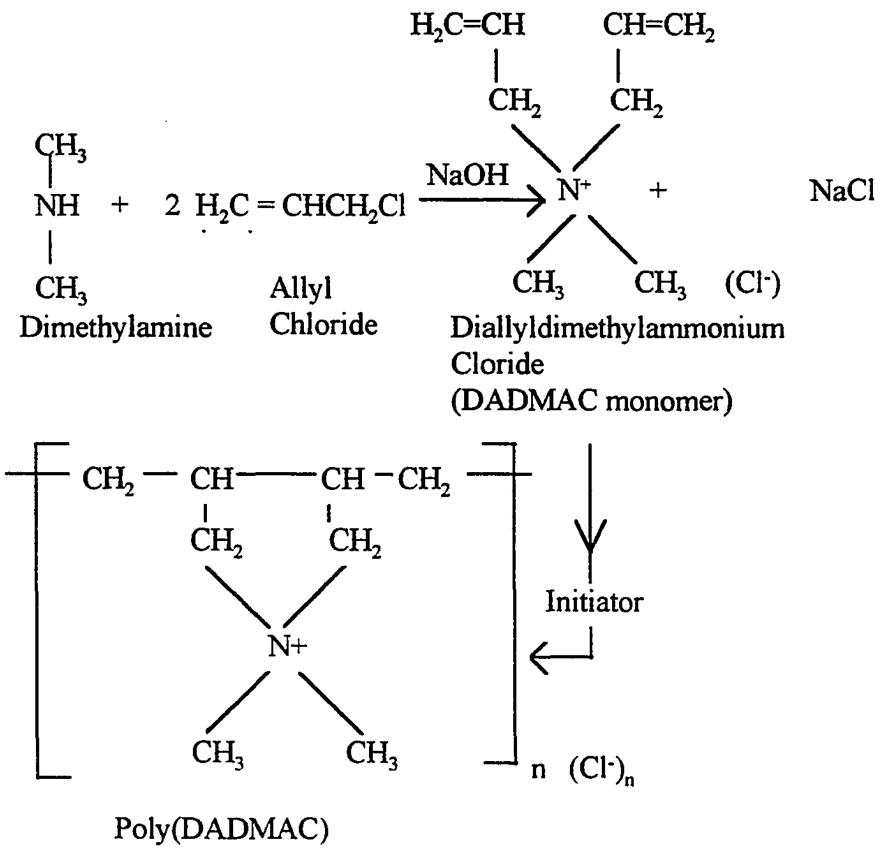


Figure 4-1: Synthesis of poly(DADMAC) by the reaction of allyl chloride and dimethyl amine (Mangravite 1983).

From what is known about the manufacturing of poly(DADMAC), one can expect the following chemicals to be present in the final polymer product: DADMAC monomer due to incomplete polymerization, sodium chloride or another chloride salt, dimethylamine or allyl chloride and their by-products. However, in the monomer manufacturing process, usually allyl chloride is added in excess amounts than its stoichiometrically need, and therefore the limiting chemical (dimethylamine) is essentially consumed. Also, at the end of the monomer formation, the unreacted allyl chloride and some by products such as allyl alcohol and diallyl ether are purged using either nitrogen or steam and vacuum (Letterman and Pero 1988). Consequently, it is reasonable to say that the only contaminants that can be found in a poly(DADMAC) polymer solution are NaCl and DADMAC monomer.

The amount of residual monomer was probably in the range of 4% to 5% by weight of the polymer in the past. However, due to the introduction of new initiators and the application of new procedures, it is likely that the percent by weight of the residual monomer to polymer is less than 1% (Letterman and Pero 1988). The AWWA standard for the poly(DADMAC) polymer solution (AWWA Standard B451-87; AWWA, 1987), requires that the DADMAC monomer percent by weight of the polymer to be less than 5%. It should be noted that the above percentages are with respect to the active polymer weight, not to the polymer product weight.

Poly(DADMAC) is a linear cationic polyquaternary amine, and, as was mentioned earlier, its charge is pH independent. Poly(DADMAC) is probably the most widely used primary polymer in water treatment (Mangravite 1983).

4.2.2 Poly Epichlorohydrin-Dimethylamine (EPI-DMA)

Poly(EPI-DMA) is the common name applied to the polymer produced by the polymerization of the monomer 2-hydroxy-3-dimethylaminopropyl chloride. The name EPI-DMA polymer refers to the primary raw material from which the monomer is synthesized (Mangravite 1983, Letterman and Pero 1988,1990). The polymer produced is a linear poly quaternary amine of low to moderate molecular weight (10^4-10^5 g/mole) (Mangravite 1983).

Synthesis of EPI-DMA polymers (Letterman and Pero 1990) starts by adding epichlorohydrin (EPI) to a dimethylamine (DMA) solution in a pressurized reactor. The initial amount of EPI added is slightly less than the stoichiometric amount necessary to react with the whole DMA. After the start of the polymerization reaction, which is induced by increasing the temperature to 40-70 ^oC, the remainder of EPI is added slowly to maximize polymerization. A small quantity of dimethylamine is added to terminate the reaction by reacting with the terminal chloride group. The terminal amines could then be quaternized by adding methyl chloride. The monomer formation, polymerization, termination, and quaternization reactions are shown in **Figure 4-2**. EPI-DMA polymer is one of the two (EPI-DMA, poly(DADMAC)) most widely used cationic polymers in drinking water treatment (Letterman and Pero 1990). It is the most frequently used cationic polymer for colored waters (Mangravite 1983).

The molecular weight of EPI-DMA polymer can be increased by adding a branching and/or crosslinking agent, such as ethylenediamine (EDA). The amount of EDA added is

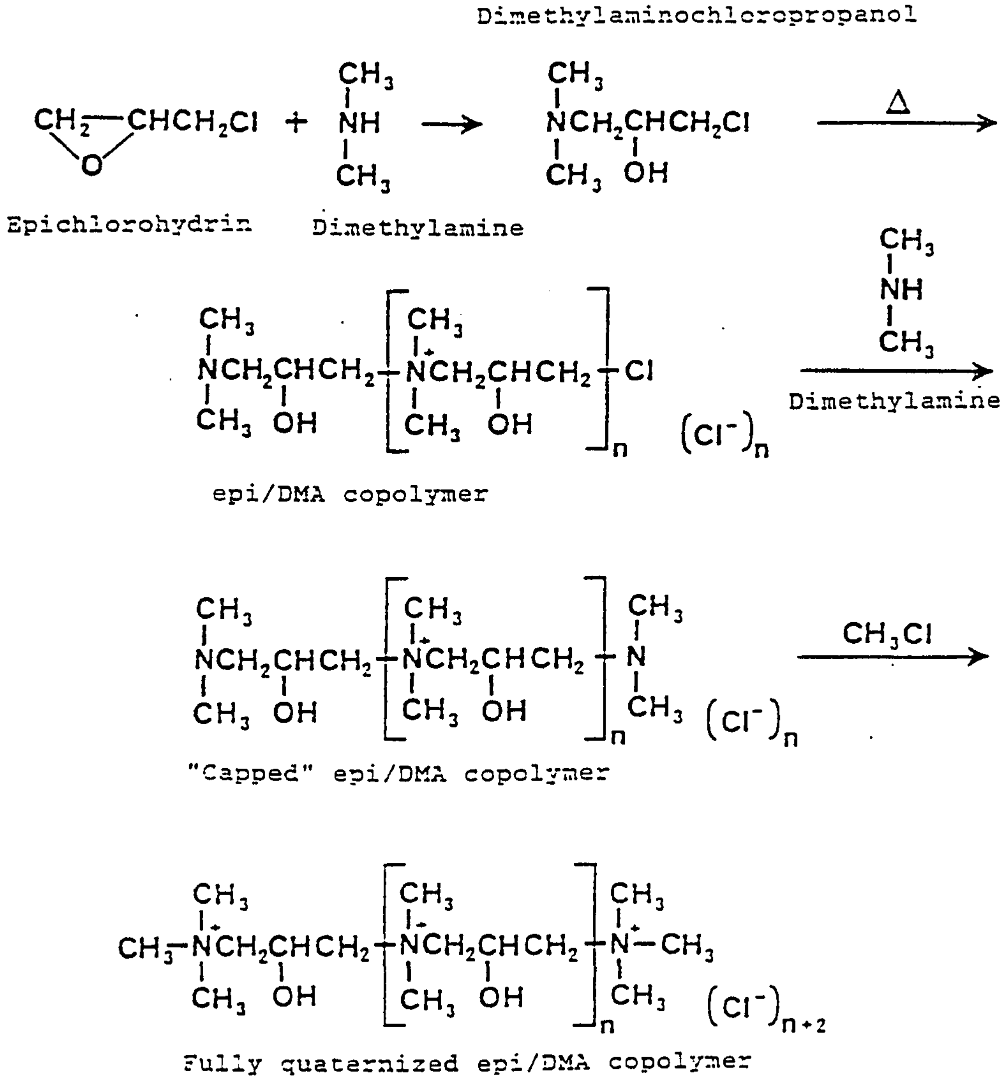


Figure 4-2: Synthesis and Quaternization of EPI-DMA (from Letterman and Pero 1988).

usually less than 5 mol % of total amines (Letterman and Pero 1990, Mangravite 1983). The polymer formed by the addition of EDA (EPI-DMA-EDA) has been termed as EPI-DMA copolymer (Letterman and Pero 1988). The addition of EDA can reduce the chlorine resistance of the polymer (Mangravite 1983). The linear type (EPI-DMA) is more common than EPI-DMA-EDA in water treatment (Mangravite 1983).

4.3 Mode of Action

Cationic polymers are the only type of polymers that can be used as primary coagulants. Anionic and nonionic types are not effective in this regard, but can be used effectively as coagulant aids. Bridging is the mechanism by which anionic and nonionic polymers act. However, the mode of action of cationic polymers has been a controversial issue of whether charge neutralization alone or charge neutralization and bridging result in flocculation.

The mode of action of cationic polymers was believed to be charge neutralization and bridging (Pressman 1967, Black et al. 1965). This belief was based on the fact that higher molecular weight polymers improve the coagulation process. Gregory in 1973 introduced the concept of "electrostatic patch" model, which explained the reason for the improvement in the coagulation process with high molecular weight cationic polymers (Gregory 1973). This model attributes the improvement of coagulation with higher molecular weight polymers to the uneven charge distribution of polymers on the particles' surfaces. The concept can be explained with reference to **Figure 4-3**.

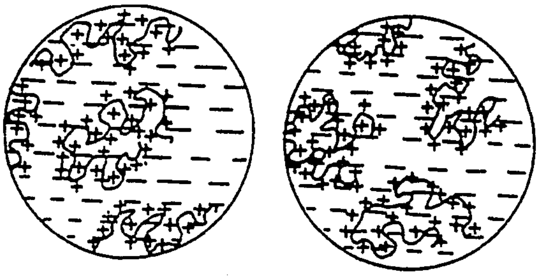


Figure 4-3: The "Patch theory" concept (Gregory 1978).

When high molecular weight cationic polymer molecules adsorb on the particle surface, there occur some areas on the particle surface that have a high positive charge density caused by the adsorbed high molecular weight cationic polymer. These are surrounded by low negative charge density areas, which are the original particle surface. This uneven distribution causes increased attractive forces between the positive patches on one particle and the negative surfaces on other particles, and therefore improves the coagulation process. If the same amount of charge has to adsorb on a particle in order to destabilize it, then low molecular weight cationic polymer having the same charge density will adsorb more evenly on the particle surface. Hence, the attractive interaction between the positive patches and the negative surfaces is reduced. This concept was supported by the fact that the optimum dosage of polymers having the same charge density and different molecular weight was the same (but with different turbidity removal efficiencies), and this dosage corresponds approximately to the point where particles' charge reversal occurred (electrophoretic mobility = 0). This concept has been backed up by several studies (Gregory 1976, Mabire et al. 1984, Tiravanti et al. 1985)

The concepts of charge neutralization and the patch model are particularly appropriate with moderate to low molecular weight, high charge density cationic polymers. The bridging model may play a minor role, at least, in the coagulation process when the molecular weight is large and the charge density is low (Mishra 1989a, Ghosh et al. 1985). In contrast Nakris et al. (1991) attributed the mode of action of cationic polyelectrolytes to bridging only, not to charge neutralization. The authors, coagulating a suspension of 150 ppm montmorillonite with a linear polyquaternary amine, having a molecular weight of 350,000 g/mole, based their opinion on the fact that at optimum dosage of about 0.6 mg/l of the polymer, the electrophoretic mobility of the particles had not changed from that of the untreated suspension. The zero electrophoretic mobility occurred at the beginning of the overdose range.

4.4 Effects of Charge Density

Charge density of cationic polymers is a measure of the number of positive charges associated with the polymer molecule per unit mass of the polymer. It is usually expressed as melliequivalents per gram of active polymer (meq/g) or columb per milligram of the acive polymer. One equivalent is equal to 96, 484 Coulomb.

The dependence of optimum dose of cationic polymers on the charge density is known. It was found that as the charge density of a certain polymer increases its optimal dosage decreases(Gregory 1973, Lindquist and Stratton 1976, Gregory 1976, Yeh and Ghosh 1981, Mabire et al. 1984, Ghosh et al. 1985, Leu and Ghosh 1988, Gregory and Lee 1990). In some studies, the same amount of the cationic polymer charge was necessary to have optimum coagulation. This cationic charge gave almost zero electrophoretic mobility of the coagulated suspension. (Lindquist and Stratton 1976, Gregory 1976, Ghosh et al. 1985, Hubel and Edzwald 1987, Gregory and Lee 1990). In other studies, however, different amounts of the cationic polymer charge were applied for the same suspension to get optimum performance (Yeh and Ghosh 1981, Leu and Ghosh 1988) and this dosage did not produce suspended solids with zero electrophoretic mobility (Mohtadi and Rao 1973, Nakris et al. 1991, Black and Vilaret 1969).

Gregory and Lee (1990), who used a single polymer type with different charge densities and different molecular weights, noticed a strong inverse correlation between the optimum dosage and the charge density; i.e, less polymer was required for optimal coagulation at higher charge density. This dose was close to (usually slightly less than) the dose required to have a zero electrophoretic mobility. In general, the results indicated that roughly the same amount of charge was necessary for optimal coagulation dose. A similar observation was obtained by Gregory (1976). The same amount of positive charge of a cationic surfactant, and a low molecular weight cationic polymer were essential to produce maximum rate of coagulation which occurred at zero electropheritic mobility.

A linear relationship between the log molar optimum polymer dosage, and the log cationic charge per molecule has been reported (Lindquist and Stratton 1976, Ghosh et al. 1985). The relationships of Ghosh et al. and Lindquist and Stratton for the case when no salt is present have slopes of 1 and 0.94 respectively. This suggest that the same amount of charge must be added at optimum efficiency regardless of the polymer type. In the case of the presence of 0.1 M NaCl, the slope is 0.71. Ghosh et al. (1985) attributed that to the possibility of increased role of polymer bridging.

Hubel and Edzwald (1987) found that the optimum cationic polymer positive charge added to coagulate a 10 mg/L humic acid with negative charge of 34 μ eq/L was always between 32 and 38 μ eq/L. This was observed despite variations in polymer type, structure, charge density or product strength.

On the other hand, Leu and Ghosh (1988) used ten different cationic polymers, namely 7 poly diallyl dimethyl ammonum (PDADMA) with different charge density and molecular weights from Calgon corporation (Catfloc) and 3 poly quaternary amine from American Cynamid (Magnifloc) with different molecular weights but with single charge density. A stoichiometry was found between the concentration of the colloidal particles and the optimum dosage of the polymer. This optimum dosage was inversely proportional to the charge density. In addition, they concluded that charge density rather than molecular weight is the predominant factor that affects the optimal polymer dosage. However the applied polymer charge at optimal coagulation was found to differ for some polymers according to the molecular weight and charge density of the polymers. A particular suspension needed a cationic polymer charge of 0.46 coul/L of a small molecular weight (4.8 x 10^4 g/mole) cationic polymer relative to a 0.25 coul/L for a polymer with a 3.3 x 10^6 g/ mole molecular weight, both having approximately the same charge density. Similarly, for two PDADMA polymer having approximately the same molecular weights (1.3 x 10^5 g/mole, 2.1 x 10^5 g/mole), and different charge densities (1.05 coul/mg, 0.54 coul/mg), the charges applied at optimum dosages were 1.37 and 0.27 coul/L, respectively.

This situation of having different amounts of added charge at optimum coagulant dosage has also been observed (Yeh and Ghosh 1981). They noticed different colloid to polymer charge ratios at optimum doses of different polymers. The same was noticed even for the same polymer types differing in charge density and molecular weight. There was no one to one charge neutralization observed at optimum dosage. They speculated that this may be a result of bridging.

Mohtadi and Rao (1973) found that optimum turbidity removal occurred at cationic polymer dosages well below the dosage required for zero zeta potential. Similar results have been reported by Nakris et al.(1991).

Black and Vilaret (1969) found that the optimum dose for a fairly low molecular weight cationic polymer occured when the zeta potential of the particles was highly negative. This was observed for polystyrene suspensions as well as for clay suspensions.

The charge density also affects the lag time between the addition of polymer and the beginning of the flocculation (Gregory 1990). This lag time is due to the time necessary for the polymer to adsorb and reconform on the particles' surfaces. His results are shown in

Figure (4-4) where three polymers with approximately the same molecular weight and different charge densities are used to coagulate a salt free suspension. It is clear that the polymer having the lowest charge density gave almost no coagulation. As the charge density increased, the coagulation was more pronounced and the lag time decreased. The reason for that, as stated by Gregory is that at higher charge densities, especially in salt free suspensions, the repulsive interaction between polymer segments increases resulting in a more expanded polymer chain. This expanded chain has a higher collision radius and. therefore will adsorb more rapidly

4.5 Effects of Molecular Weight

The role of molecular weight of polymers should be understood if effective usage of polymers is desired. High molecular weight polymers are more expensive than low molecular weight polymers. If the use of high molecular weight cationic polymers does not improve the flocculation process by an amount that exceeds the difference in cost, then their use is not economically justified.

It was generally noticed that the optimum dose of a cationic polymer does not depend on its molecular weight (Habibian and O'Melia 1975, Gregory 1976, Yeh and Ghosh 1981, Mabire et al. 1984, Ghosh et al. 1985, Leu and Ghosh 1988, Gregory and Lee 1990). This means that if we have two polymers of the same type having the same characteristics, and different only in molecular weight, then they would have the same optimum dosage. However, some benefits of higher molecular weight polymers have been noted.

Higher molecular weight cationic polymers broaden the range of optimum

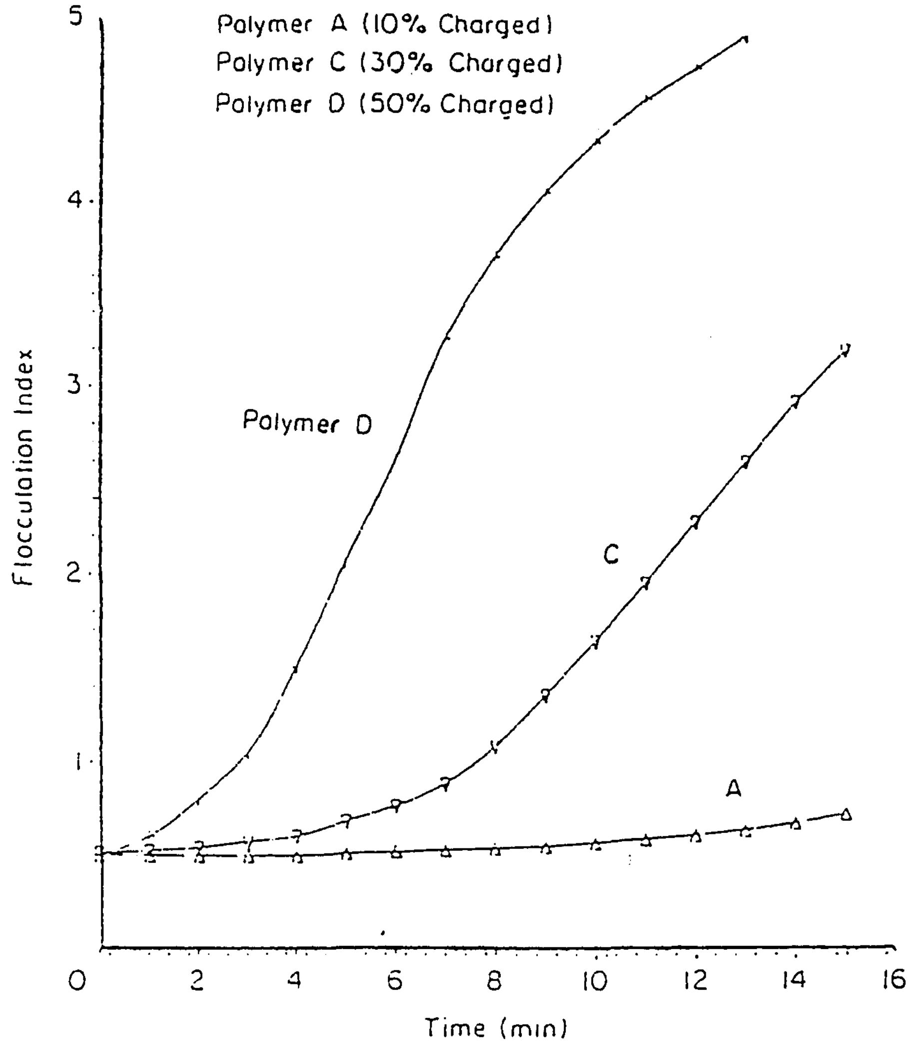


Figure 4-4: Effect of charge density on the lag time between polymer addition and the begining of flocculation (Gregory 1990).

flocculation (Gregory 1973, Gregory 1976, Ghosh et al. 1985, Gregory and Lee 1990). This phenomenon was observed in salt free suspensions (Gregory 1973, Gregory and Lee 1990), and in suspensions with different ionic strengths (Gregory 1973, Gregory 1976). However, above a specific molecular weight (in this case 1.5 $x10^5$ g/mole), any increase in the molecular weight had no further effect regarding the broadening phenomenon (Gregory 1976). The broadening phenomenon was explained by the increase in bridging with high molecular weight polymers (Ho and Howard 1982). Another explanation suggests that polymers would kinetically prefer to adsorb onto smaller particles which experience charge reversal. These positive particles act as bridges between the larger particles which still have the negative charge (Ditter et al. 1982).

The effectiveness of the polymer also changes with its molecular weight. Results with two polymers of the same type and with the same charge density, but with different molecular weights showed that , at the same dosages, the higher molecular weight polymer was more effective; giving a shorter lag time between the application of the polymer and the onset of flocculation, and a more rapid flocculation (Gregory and Lee 1990). They attributed this to faster adsorption to the larger size of the polymer molecule which has a higher collision probability with the particles. The rapid flocculation was attributed to a greater bridging effect or to a more 'patchy' configuration which lead to more attractive forces between the patches and other particles' negative surfaces. The improved effectiveness with higher molecular weight polymers was also noted by Tanaka and Pirbazari (1986). Nonetheless, they found that the highest molecular weight polymer (> 1,000,000 g/mole) was less effective than the lower two. This trend was duplicated for different suspension types and different cationic polymers.

Other benefits of higher molecular weights include larger and stronger flocs (Ghosh et al. 1985, Leu and Ghosh 1988). Molecular weight of the polymers is the dominant parameter that determines the floc strength and the particle size distribution (for a given shear level). If high shear levels are expected to be encountered, then the use of high molecular weight polymers should be taken into account. On the other hand, they could be detrimental if used in non appropriate situations. Excellent filtrate quality was achieved when high molecular weight cationic polymers were used in direct filtration, but excessive headlosses were produced (Yeh and Ghosh 1981, Tanaka and Pirbazari 1986). Coarse filter media has been recommended for high molecular weight cationic polymers (Adin and Rebhun 1974).

4.6 Effects of Rapid Mixing

Rapid mixing is necessary to disperse cationic, polymeric, coagulants throughout the water, so that every suspended particle in the water will get the right amount of the cationic polymer necessary to destabilize it. If inadequate mixing is provided, then some particles will experience charge reversal and restabilization due to overdosing, while the other particles will still be stable since insufficient cationic charge necessary for destabilization has been adsorbed. There are, however, some studies that proved that rapid mixing of cationic polymers, especially extended rapid mixing, can be considered as an intensive flocculation period through which a considerable floc growth can occur (Ghosh et al. 1985, Leu and

Ghosh 1988). Both rapid mixing time and intensity are important parameters in the design of rapid mixing units. The product Gt is the dimensionless parameter sometimes used to designate the rapid mixing conditions, as discussed previously.

Generally, rapid mixing at high velocity gradient (300-1000 s^{-1}) proved to be the optimum for cationic polymers (Morrow and Rausch 1974, Ghosh et al. 1985, Yeh and Ghosh 1981, Keys and Hogg 1979). Stump and Novak (1979) found that high molecular weight cationic polymers performed better at mixing intensities between 600-1000 s^{-1}, and lower molecular weight cationic polymers performed better at 300 s^{-1}.

Morrow and Rausch (1974), using cationic polymers as primary coagulants, found in a pilot plant study that a rapid mixing intensity of 300 s^{-1} was not effective in producing particle destabilization. This was attributed to the nonuniform distribution of the polymer at this velocity gradient. Velocity gradients of 400 s^{-1} or greater proved capable of coagulating both low turbidity water (1-15 JTU) and high turbidity water (50-2000 JTU). The mixing time necessary to provide complete dispersion of the polymers decreased as the velocity gradient increased. They recommended a mixing time from several seconds to less than two minutes. Shearing of the particles began when rapid mixing was prolonged for more than 2 minutes when the G value was equal to 400-450 s^{-1}. The resulting flocs were small, and did not reform during subsequent flocculation. For a G value of 1000 s^{-1}, only few seconds of rapid mixing were necessary to achieve optimum destabilization. At G values of more than 1000 s^{-1}, the flocs formed during flocculation became smaller and less settleable. In comparing the effectiveness of cationic polymers to alum, each used alone, in one of the pilot plant studies, comparable treatments were obtained when rapid mixing velocity gradient greater than 400 s^{-1} was applied for the cationic polymer. The optimum G for the cationic polymer was 730 s^{-1}. The rapid mixing time was not reported for these studies.

Yeh and Ghosh (1981) studied the effect of rapid mixing intensity and duration on cationic polymer performance in a pilot direct, in-line, filtration plant study. The suspension was a 75 mg/L bentonite clay with a turbidity value of 20 NTU. Nine cationic polymers were used, with molecular weights ranging from 1200 g/mole to more than 5 million g/mole. For most of these polymers, a rapid mixing intensity of 650 s^{-1} and a duration of 3 to 8 minutes was sufficient (No flocculation period was provided). Beyond 8 minutes of rapid mixing, floc breakup started. For low to medium molecular weight cationic polymers (10,000-100,000), a rapid mixing intensity of 300 to 650 s^{-1} for 3 to 8 minute was necessary. Taking G as 650 s^{-1} and 3 minutes rapid mixing duration as the optimum, the optimum Gt value becomes equal to 1.2×10^5.

Ghosh et al. (1985) found the optimum rapid mixing Gt value to be 9.6×10^4 with optimum G equal to 800 s^{-1} in good agreement with the value obtained by Yeh and Ghosh (1981) above. They used 12 commercially available cationic polymers (with molecular weights ranging from 2.2×10^4 to 1.1×10^7 g/mole and charge density at pH 8.0 of 0.46 to 1.11 Coulomb per mg of polymer) to flocculate a 120 mg/L bentonite suspension and a 40 mg/L silica suspension both having 25 NTU turbidity values. The rapid mixing time (2 min.) and the flocculation time and intensity were kept constant. During the rapid mixing time, as shown in **Figure 4-5**, a significant amount of floc aggregation occurred as evidenced by the

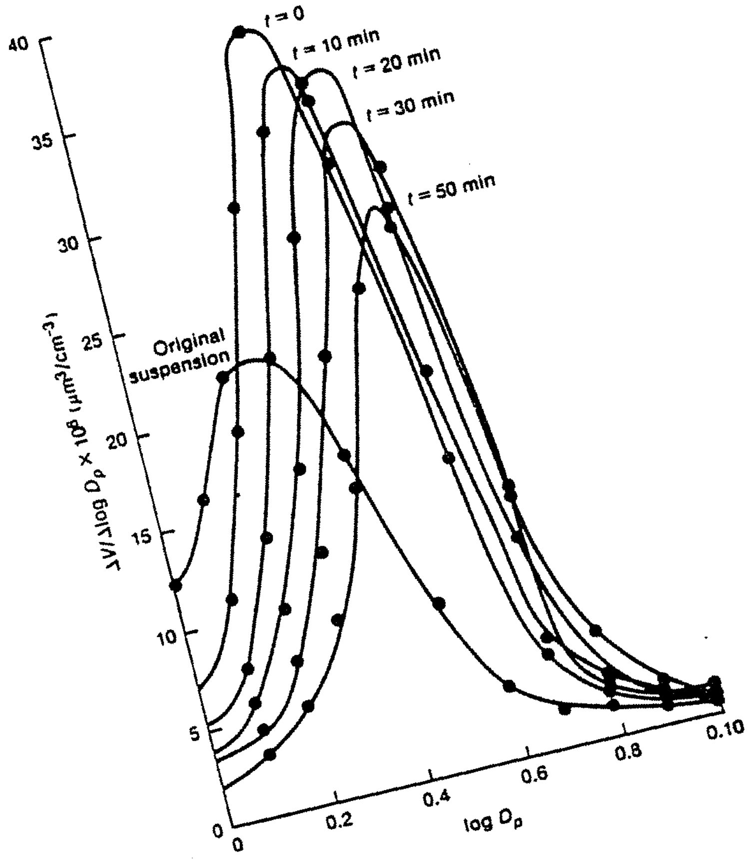


Figure 4-5: Floc growth during rapid mixing (Ghosh et al.1985).

curve labelled t = 0 minutes (i.e. just after 2 minutes rapid mixing). This is in agreement with the results of Letterman et al. (1973) for inorganic coagulants.

The growth of particles during rapid mixing with cationic polymers has also been reported by Leu and Ghosh (1988). The particles' diameters increased from about 1 μm to about 12 μm within a few seconds of rapid mixing at 840 s^{-1}. The suspension used was a 120 mg/L bentonite clay suspended in tap water with a turbidity value of 25 NTU. Floc breakup during rapid mixing started at Gt values between 2.8×10^5 to 4.5×10^5 for the cationic polymers tested (molecular weight from 4.8×10^4 to 1.1×10^7 g/mole) with higher values of Gt associated with higher molecular weight polymers.

In contrast to these high values, Keys and Hogg (1979) found the optimum rapid mixing Gt value to be in the range 15,000 - 28,000. Although these values were reported for nonionic polymers (polyacrylamide), they said that "Experiments have been conducted on clay and quartz using a cationic polymer, an anionic polymer and a second nonionic polymer (of lower molecular weight). While the actual performance of these polymers was of course different, the effects of the mixing variables (mixing time, agitator speed, etc.) were found to follow the same general trends" (Keys and Hogg, 1979, pg. 70-71).

Based on literature evidence and theoretical concepts, Amirtharajah and Kawamura (1983) recommended the following design values for rapid mixing for cationic polymers: "Cationic polymers as primary coagulants. Velocity gradients of 400 sec^{-1} to 800 sec^{-1}. Mixing times of 60 secs - 30 secs with GT values of 15,000 to 30,000. The speed of the impellers in the range of 500 to 1000 rpm and the tip speed of the impellers from 2.0-5.0

ft/sec. Mixing times greater than 2 minutes may cause floc degradation. A tapering of rapid mixing from the high velocity gradients is found to be advantageous. For direct filtration, use low to medium weight polymers (mol. wt. = 10,000 to 100,000)and initial mixing at 300 s^{-1} to 650 s^{-1} for a period of 8 - 3 minutes. Use longer mixing periods for the smaller velocity gradients." (Amirtharajah and Kawamura 1983, pg. 62).

The role of rapid mixing is not just to disperse the coagulant to the particles' surfaces. As shown previously, a considerable amount of flocculation occurs during rapid mixing (Ghosh et al. 1985, Leu and Ghosh 1988). Rapid mixing also reduces the lag time between polymer addition and the onset of flocculation. Rapid polymer adsorption on particles' surfaces is a plausible explanation (Gregory 1988).

4.7 Effects of Temperature

The effects of temperature on flocculation kinetics using inorganic coagulants have been discussed earlier. In this section, the literature related to the effects of cold temperature on flocculation kinetics using cationic polymers is presented.

The study by Mohtadi and Rao (1973), was the earliest that could be found concerning cold water effects on flocculation using cationic polymers. Either a suspension of 200 mg/L bentonite or a suspension of 450 mg/L kaolinite clay suspended in distilled water was used for this study. The cationic polymer was added to the suspension in a beaker being stirred by a paddle stirrer at a peripheral velocity of 29 cm/sec. Mixing continued at this speed for the entire experiment. A spectrophotometer was used to measure the state of flocculation of the particles by measuring the absorption of light (light absorption index) by the test samples. The test samples (about 3 mL) were withdrawn 1 cm below the water surface at regular time intervals during flocculation. The particle concentration was almost directly proportional to the light absorption.

After comparing light absorption and residual turbidity results (see **Figure 4-6 and Figure 4-7**), they concluded that "temperature has no significant effect on the optimum pH, the flocculant dosage or the rate of flocculation when a cationic polyelectrolyte is used as the flocculant." (Mohtadi and Rao, 1973, pg. 766).

Recently, Hanson and Cleasby (1990) and Srivastava (1988) studied the effect of cold temperature on flocculation kinetics using cationic polymers (an EPI/DMA polymer, Magnifloc 573 C was used). In both studies, an automatic image analysis system was used to determine the particle size distribution (in the size range between 0.87 μm to about 100 μm) of a 25 mg/L kaolin clay suspended in tap water, and coagulated with the cationic polymer. With reference to **Figures 4-8, 4-9,** (which show the ratio of total number of particles at a specific flocculation time during the experiment compared to the initial number of particles prior to the addition of the coagulant (total count fraction) and its variation with flocculation time), the following conclusion was drawn: cold water temperature has a deleterious effect on the flocculation kinetics using cationic polymer coagulants. This detrimental effect can be somewhat lessened or even nearly eliminated by rapid mixing at high intensity (about 1250 s^{-1}) and for an extended period (2+ min), as evident in **Figure 4-9**.

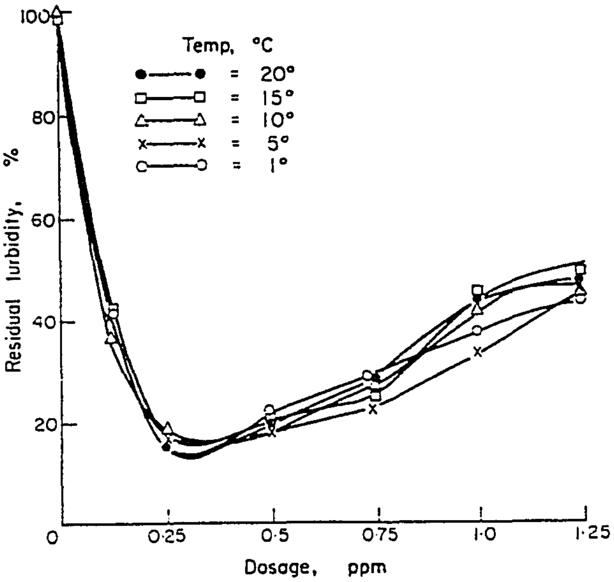


Figure 4-6: Effect of temperature on residual turbidity of a 450 mg/L kaolinite dispersion at pH 5.0 (Mohtadi and Rao 1973)

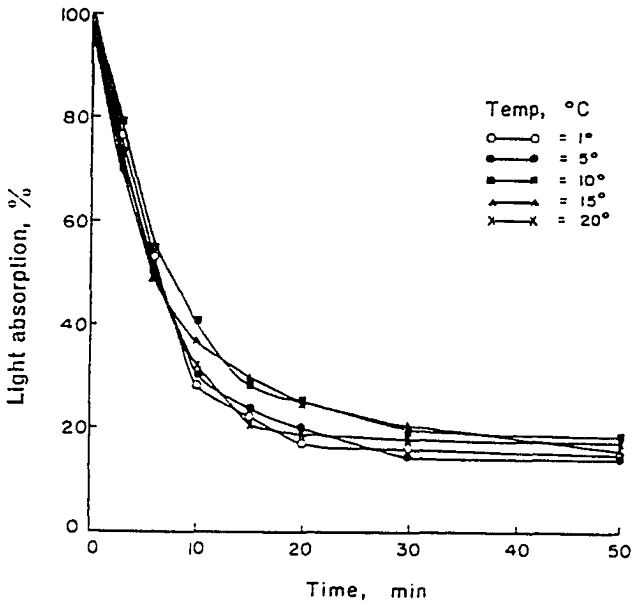


Figure 4-7: Temperature effects on flocculation efficiency measured as the percentage light absorption with time. Kaolin concentration=450 mg/L, pH=5.0 (Mohtadi and Rao 1973)

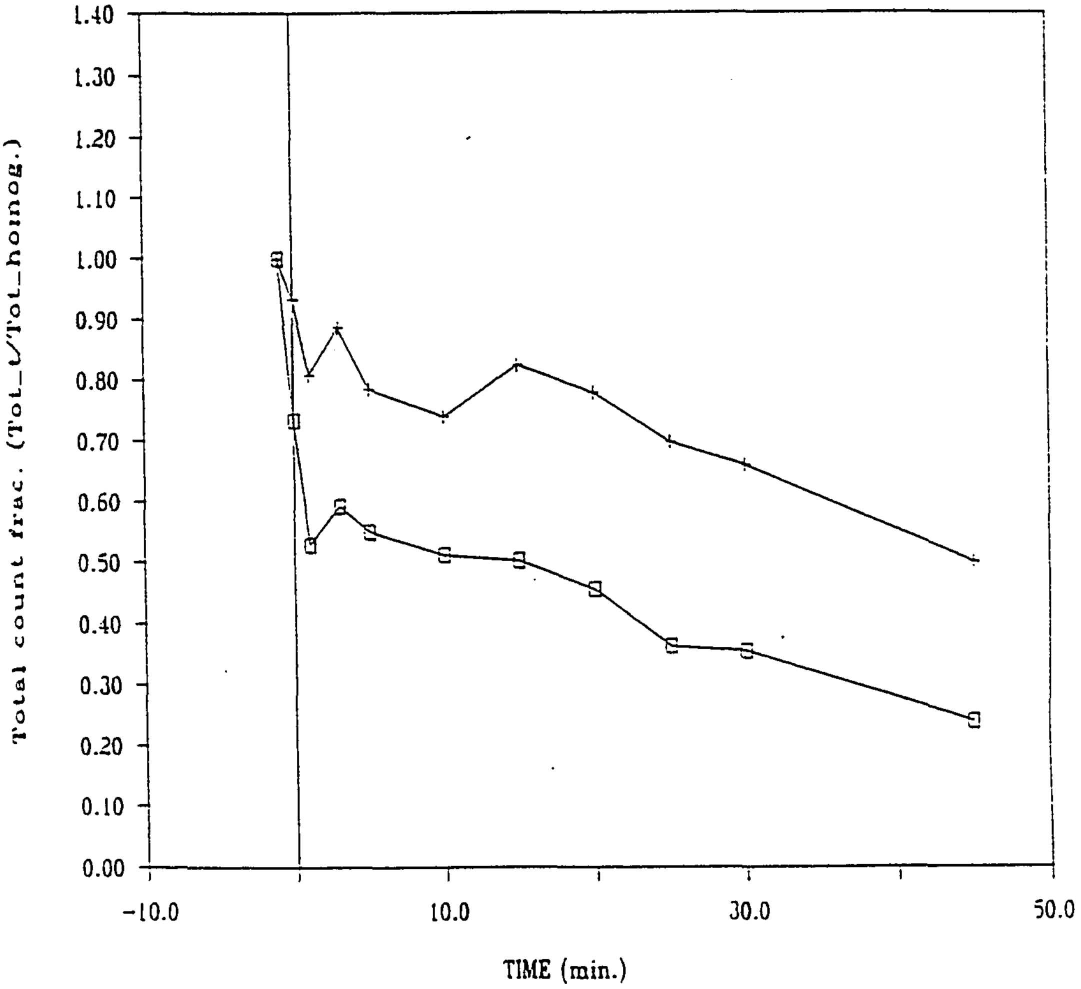


Figure 4-8: Temperature effects on flocculation kinetics in a 25 mg/L kaolin suspension. Rapid mixing at 250 rpm (about 500 s^{-1} at 20 °C) for 1 minute. + represent 5 °C while □ represent 20 °C (Srivastava 1988)

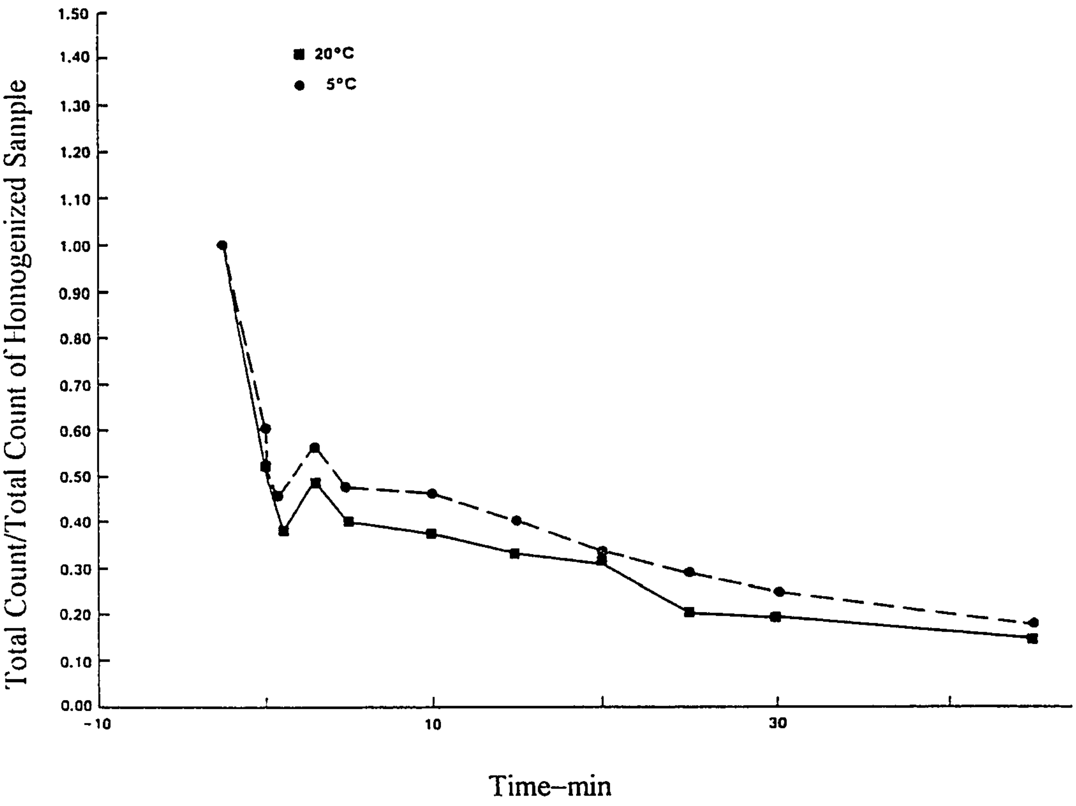


Figure 4-9: Temperature effects on flocculation kinetics in a 25 mg/L kaolin clay suspension. Rapid mixing at 500 rpm (about 1250 s^{-1} at 20 °C) for 2.25 minutes (Hanson and Cleasby 1990).

5. USE OF CATIONIC POLYMERS IN COMBINATION WITH INORGANIC COAGULANTS

The use of cationic polymers as coagulant aids is becoming common. This is due to the benefits that dual coagulants (cationic polymers + inorganic coagulants) have over the sole use of inorganic coagulants or cationic polymers. These benefits are primarily connected to the reduction of the inorganic coagulant dose and to the production of larger and stronger flocs. Less inorganic coagulant use means less production of sludge, less alkalinity consumption, and longer filter runs of direct filtration plants. Stronger and larger flocs are necessary for the flocs to withstand high shear forces and to settle more quickly.

The combined use of cationic polymers and inorganic coagulants has been found to be effective in both direct filtration (Monscvitz et al. 1978, McBride et al. 1977, Tate et al. 1977) and conventional (McBride et al. 1977) water treatment plants.

Due to the small amount of literature concerning the use of dual coagulants, they will be treated here in two steps. First a detailed review of each reference is presented. Then inferences from these reviews regarding rapid mixing effects, addition sequence,...etc. are presented.

McBride et al. (1977) compared four different coagulant schemes in a pilot plant study of the Owens river in Los Angeles. The water studied had an average 200 mg/L total dissolved solids, 80 mg/L total hardness, and 110 mg/L total alkalinity. The purpose of the study was to select a process train that would meet the EPA and state of California standards, especially for turbidity. In all the process trains tested (direct, in-line, filtration, direct filtration, and conventional treatment), a combination of 2 mg/L of alum and 2 mg/L of a cationic polymer (Catfloc T) (Calgon Corporation) was the most effective alternative. It consistently produced filtered water turbidity that met the requirements and eliminated any performance problems when direct or conventional treatment trains. In-line filtration did not always meet the water quality requirements.

Monscvitz et al. (1978) also found that the combined use of alum and a cationic polymer produced the best overall performance of a direct filtration pilot plant study. A flocculation step was necessary for reliable treatment of the low turbidity water (< 1 NTU on average) of Lake Mead, Nevada, at filtration rate of 5 gpm/sq ft. Tate et al. (1977) also reported that the use of a cationic polymer in combination with alum in a direct filtration pilot plant study was able to produce finished turbidity values of 0.04 to 0.18 turbidity units. The turbidity of the raw water averaged 2.6 but fluctuates between 0.1 and 60 turbidity units.

Some of the parameters that affect the coagulation with dual coagulants were studied by a number of researchers. The following is a summary of these works.

Letterman and Sricharoenchaikit (1982) used a cationic polymer and alum in combination to coagulate 500 mg/L commercial crystalline silica suspension (quartz powder) with a turbidity value of about 70 NTU in a jar test study. They conducted their experiment using water containing 0.01 molarity $NaNO_3$ (Ionic Strength = 0.01) and a pH of 6.0. The mixing steps consisted of 2 minutes on a magnetic stirrer followed by 15 minutes flocculation period with the rotational speed of the impeller being 40 rpm. Quiescent settling of 15 minutes was provided before turbidity measurement. The time between the alum and cationic polymer addition was 1.0 minute. They used a poly(DADMAC) polymer (Cat-Floc T) as the cationic polymer. They mentioned, however, that they tested two other cationic polymers, Nalco 8103 and Magnifloc 575 C and found that they produced the same general results during the preliminary studies.

When the suspension had no anionic species such as sulfate (they mentioned that the nitrate had no effect at 0.01 M concentration as far as the anion effects were concerned), a trade off relationship was found between aluminum and Cat-Floc T dosages required to give an electopheritic mobility (EM) of zero resulting in minimum turbidity (**Figure 5-1**). Figure 5-1 shows two sequences of additions: aluminum first then the cationic polymer, and cationic polymer first then aluminum. The figure shows that the sequence of addition had essentially no effect on the amounts of each coagulant necessary to reach zero EM or minimum residual turbidity. In this case, if the amount of aluminum was increased above that necessary to produce EM = 0, restabilization occurred (**Figure 5-2**). The minimum residual turbidity for the case of combined alum and Cat-Floc T, when no anions were present, was intermediate (15-20 NTU) between the case of using cationic polymer alone (10-15 NTU) and the case of using alum alone (20-25 NTU) under the same conditions. The use of the cationic polymer alone produced the best minimum residual turbidity in this case.

When 10^{-3} M sulfate was present in the suspension, the residual turbidity and electrophoretic mobility curves for different cationic polymer dosages (10^{-3}, 10^{-5}, 10^{-6} g/L

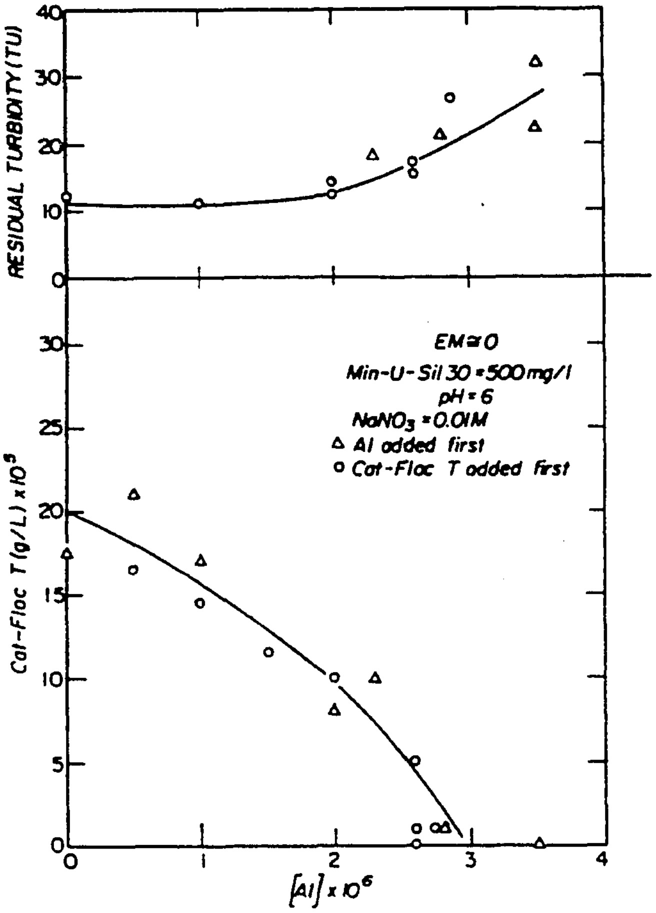


Figure 5-1: The trade off relationship between a cationic polymer and Aluminum to yield a zero Electrophoretic mobility when $[SO_4]$ =0.0. The corresponding residual turbidity are also shown. Al added first; cationic polymer added first, pH=6.0, $[NaNO_3]$=0.01M, silica suspension concentration= 500 mg/L. (from Letterman and Sricharoenchaikit 1982).

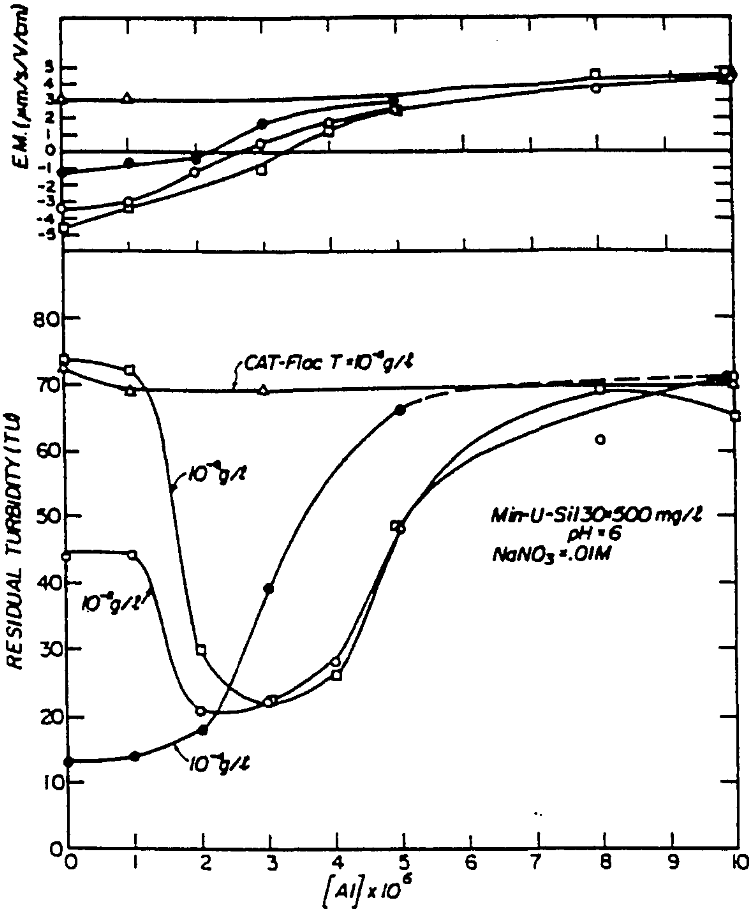


Figure 5-2: Electrophoretic Mobility and residual turbidity versus aluminum concentration for several cationic polymer concentrations when sulfate concentration = 0.0; pH = 6.0, susp. conc. = 500 mg/L silica, [$NaNO_3$]=0.01.(from Letterman and Sricharoenchaikit 1982).

of the polymer product) coincided at aluminum concentrations of 10^{-5} M or above whether the polymer was added before or after alum (**Figure 5-3**, for the case when polymer was added before alum). At higher aluminum dosages, the electropheritic mobility of the particles coincided with that of aluminum hydroxide precipitate (+2 mm/s/v/cm). This was also observed even when the particles had originally higher positive electrophoretic mobility that resulted from a high cationic polymer dosage (Figure 5-3, Cat-Floc concentration 10^{-3} g/L). It was suggested that the aluminum hydroxide precipitate neutralizes both the cationic polymer charge and the anionic charge on the surface of the particles. In this case no restabilization was observed and the residual turbidity (after sedimentation) decreased as long as the aluminum dosage increased. The combined use of alum and the cationic polymer produced the best turbidity removal values when 10^{-3} M sulfate anions were present. Again, the authors reported that the sequence of addition of the polymer and alum did not have any effect on the residual turbidity or electrophoretic mobility.

James and O'Melia (1982) compared the performance of three different coagulants (alum, a cationic polymer with a low molecular weight and high charge density (polymer A), and a cationic polymer with a high molecular weight and low charge density (polymer B)) when each was used alone versus the performance of a combination of alum and the cationic polymer with the high molecular weight and low charge density (polymer B). Jar test experiments were conducted on a natural lake water that had a turbidity of 26-27 NTU, a TOC of 8-9 mg/L and a pH of 6.5-6.6. When alum was used, the pH was prevented from

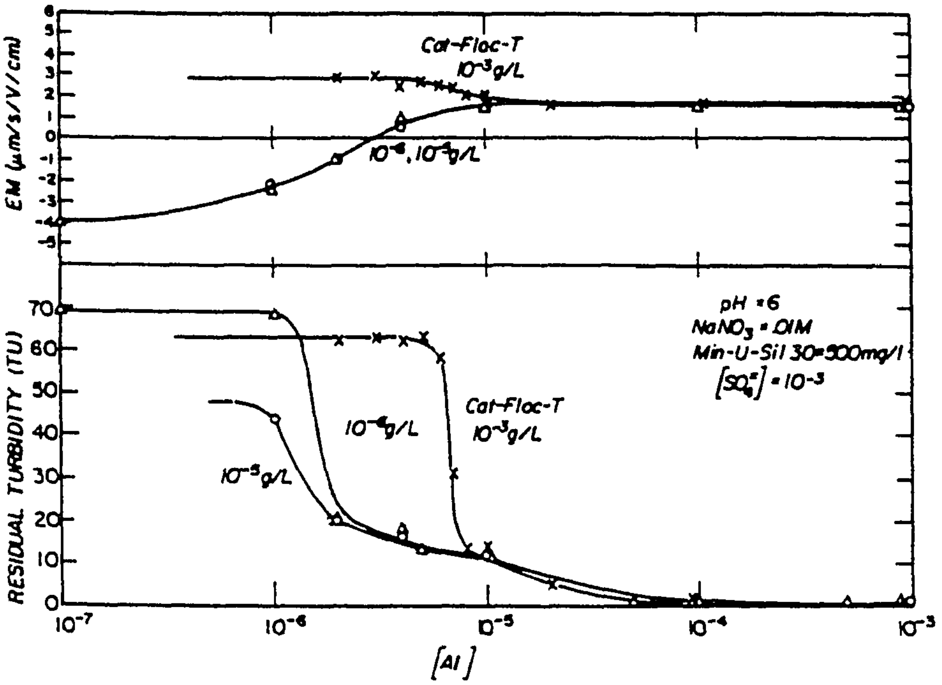


Figure 5-3: Electrophoretic Mobility and residual turbidity versus aluminum concentration for several cationic polymer concentrations; Sulfate conc. = 10^{-3} mole/L, pH = 6.0, susp. conc. = 500 mg/L silica, [$NaNO_3$] = 0.01, the polymer was added before alum addition. (from Letterman and Sricharoenchaikit 1982).

falling below 6.2 by adding NaOH. The experimental conditions of rapid mixing (in a variable speed rapid mix unit), flocculation (in a jar test apparatus), settling (in an Imhoff cone) are shown in **Table 5-1**. These conditions were established from preliminary tests. When alum and the high molecular weight low charge density cationic polymer were used in combination, the rapid mixing intensity suitable for alum was used (70 s^{-1}).

Table 5-1: Test conditions for the different coagulants used; polymer A = high charge density low MW, polymer B = low charge density high MW. (James and O'Melia 1982).

	Coagulant			
Parameter	Polymer A	Polymer B	Alum	Alum + Polymer B
Velocity gradient in rapid mix—s^{-1}	100	400	70	70
Reaction time in rapid mix—*min*	1	1	1	1 + 1*
Velocity gradient in flocculation—s^{-1}	30	50	20	20
Reaction time in flocculation—*min*	30	30	30	30
Reaction time in settling—*min*	60	60	60	60

*Chemicals added in series, with 1 min of stirring provided after the first addition and another minute provided after the second addition

When alum alone was used, the maximum removal of both TOC and turbidity occurred at the same alum dosage (60 mg/L). Sludge production at this dosage was about 20 mL/L (20 mL of sludge per liter of suspension). In the case of using the high charge density low molecular weight polymer alone, two optimum dosages for the removal of TOC or turbidity were observed. The optimum dosage for turbidity removal occurred at 12 mg/L of polymer as supplied by the manufacturer, while that for TOC removal occurred at 4 mg/L. The sludge volume was on the order of 1.5 mL/L at the 12 mg/L dosage. When the low charge density high molecular weight polymer was used, no significant removal of TOC was observed. The optimal dosage for turbidity removal was 8 mg/L as supplied with higher dosages restabilizing the particles. Sludge production was as low as 0.2 mL/L. Both polymers were worse than alum in removing TOC and turbidity, but with substantial sludge reduction. Their optimum dosages were also very high.

The authors (James and O'Melia, 1982) hypothesized that the use of alum (to interact with TOC and destabilize turbidity) in combination with the high molecular weight low charge density cationic polymer, polymer B (to adsorb on the solid products of these reactions) could produce improved results. Alum and the high charge density low molecular weight cationic polymer combination was not tried. The results are shown in **Figure 5-4**. with optimum dosages in **Table 5-2**. Table 5-2 shows the improved turbidity and TOC removal and the reduction of sludge volume and chemical coagulants cost of the combined alum and polymer (B) over the use of alum alone. Table 5-2 was produced when alum was added 1.0 minute before polymer (B) addition. This sequence of addition proved to give the

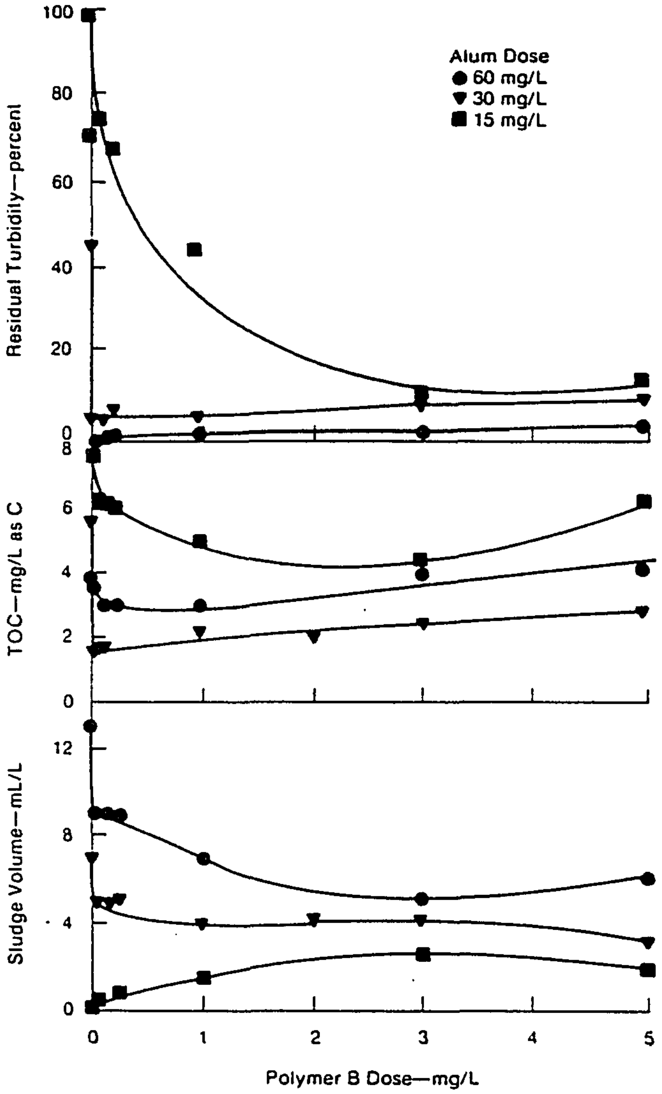


Figure 5-4: Effect of the use of alum and a high MW low charge density cationic polymer in combination on TOC removal, Turbidity removal, and sludge production; Turbidity = 26-27 NTU, TOC = 8-9 mg/L, pH = 6.2-6.6. (from James and O'Melia 1982).

Table 5-2: Comparison between the use of dual coagulants (alum + polymer B) and alum alone; Turbidity = 27 NTU, TOC = 8 mg/L, pH = 6.2-6.6. (from James and O'Melia 1982).

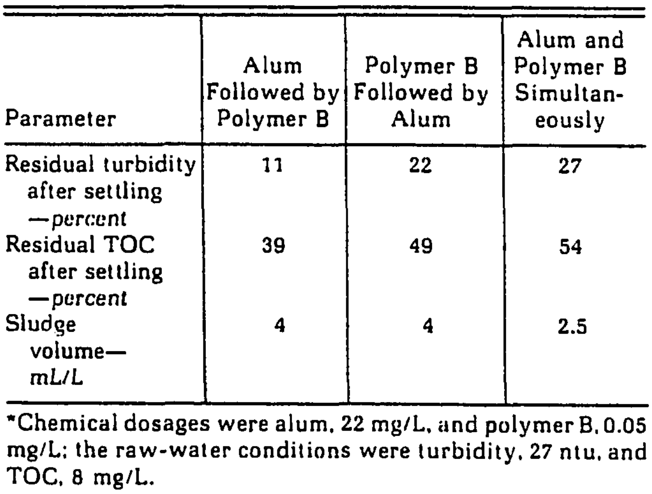
	Chemical Application *	
Parameter	**Alum (60 mg/L)**	**Alum (30 mg/L) Polymer B (0.05 mg/L)**
Residual turbidity after settling—percent	**24**	**4**
Residual TOC after settling—percent	**68**	**21**
Sludge volume—mL/L	**14**	**5**
Chemical costs†—$/d	**140**	**80**

***For the raw water, turbidity was 27 ntu and TOC 8 mg/L.**
†Based on a plant flow of 0.24 m^3/s, alum cost was $0.11/kg and Polymer B cost $6.56/kg.

best results (**Table 5-3**), followed by the reverse addition sequence of polymer (B) and alum, and finally the simultaneous addition. The authors suggested that simultaneous addition produced the minimum sludge production by leaving the turbidity and TOC in the water.

It should be noted that James and O'Melia did not measure or report the charge density or the molecular weight of the high molecular weight low charge density cationic polymer (1160 Betz) used in their experiments. Hubel and Edzwald (1987) reported the charge density and the molecular weight of the same polymer to be 0.07 meq/g solid of the polymer and a MW of > 10^6 g/mole. If the same low charge density was present in James and O'Melia's (1982) work, this could shift the interpretation of their results regarding the

Table 5-3: Effect of addition sequence on coagulation efficiency. (from James and O'Melia 1982).



Parameter	Alum Followed by Polymer B	Polymer B Followed by Alum	Alum and Polymer B Simultaneously
Residual turbidity after settling —percent	11	22	27
Residual TOC after settling —percent	39	49	54
Sludge volume— mL/L	4	4	2.5

*Chemical dosages were alum, 22 mg/L, and polymer B, 0.05 mg/L; the raw-water conditions were turbidity, 27 ntu, and TOC, 8 mg/L.

combined use of alum and a cationic polymer to be more indicative of the use of alum and a nonionic polymer. High cationic charge density polymers, such as Magnifloc 573, have a charge density of the order of 8.5 meq/g solid of the polymer (Edzwald et al. 1987, Hubel and Edzwald 1987) and a molecular weight of about 10^5.

Hubel and Edzwald (1987) used dual coagulants, in which the cationic polymers was added before alum addition. They used this combination to coagulate a low turbidity (2.3 NTU), low alkalinity (20-40 mg/L as $CaCO_3$) waters containing high levels of humic matter (9.4 mg/L TOC, 746 mg/L TTHMFP) in a jar test machine. The mixing intensities consisted of rapid mixing of the cationic polymer at 100 rpm for 5 minutes followed by alum addition with another 2 minutes of rapid mixing. The flocculation and settling periods are shown in **Table 5-4**. When alum or a cationic polymer alone were used, the suspension was rapid mixed for 2 minutes at 100 rpm. A chemically equivalent amount of sodium bicarbonate was added to prevent pH changes when alum was used. Two pH values (5.5 and 7.2) were used in these experiments.

This sequence of addition (cationic polymer first then alum) was used because the authors hypothesized that the cationic polymers would remove part of the humic materials as well as to decrease the solubility of $Al(OH)_3$, thus decreasing the alum dosage. The results are shown in **Table 5-5** and **Figure 5-5** for pH 7.2.

Table 5-4: Flocculation and settling periods used in jar tests. (from Hubel and Edzwald 1987).

Coagulant	Flocculation at 20 rpm min	Settling min
Alum alone and alum-polymer combinations at pH 7.2	20	30
Alum alone and alum-polymer combinations at pH 5.5	60	45
Polymers alone	60	30

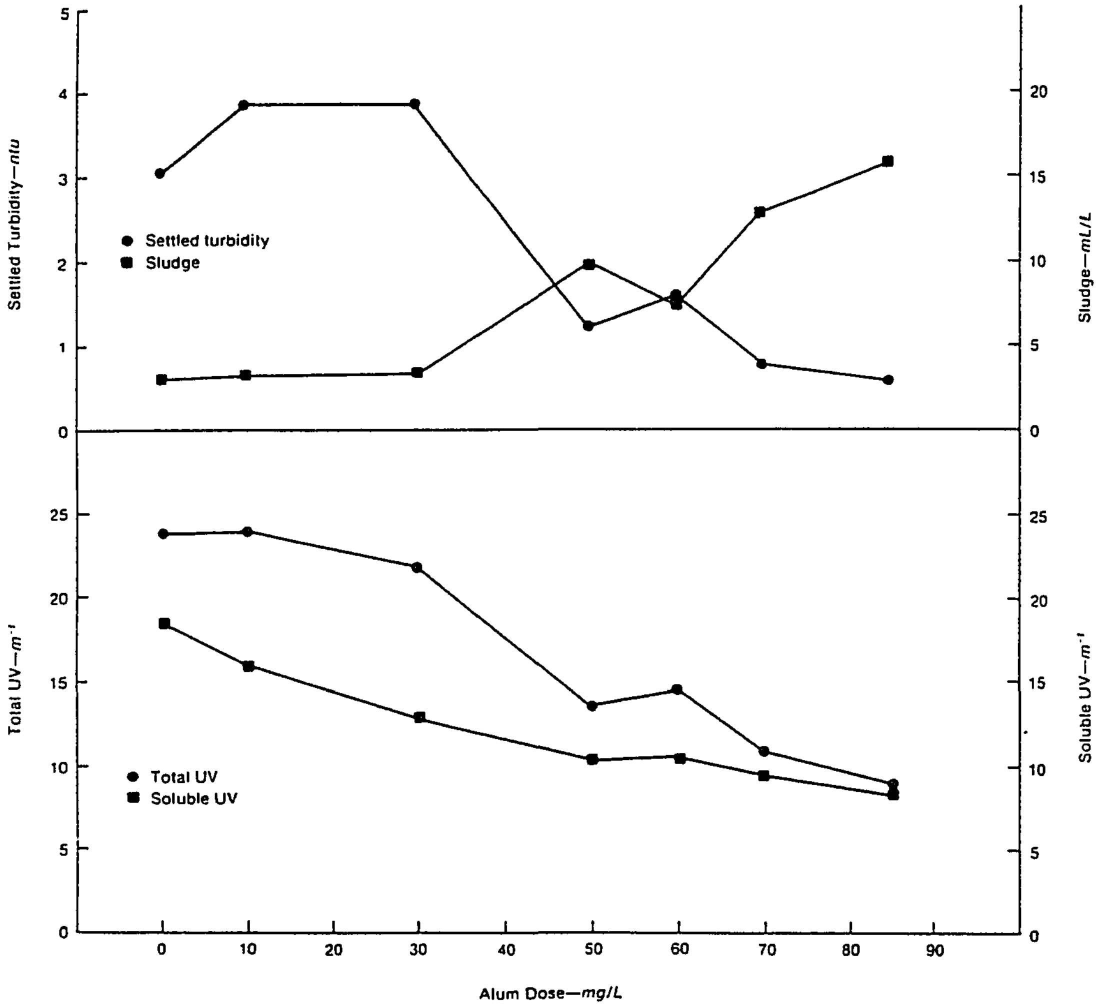


Figure 5-5. Results of coagulation with 9.0 mg/L Magnifloc 573 C (EPI-DMA) and alum at pH 7.2. (from Hubel and Edzwald 1987).

Table 5-5: Results of tests with high charge density cationic polymers and alum as coagulant aid; Turbidity = 2.3 NTU, TOC = 9.4, polymer G = Magnifloc 573 C, polymer D = an experimental polymer from Allied Chemical Company. (from Hubel and Edzwald 1987).

		Optimum	Percent Removal				Sludge
Experiment	Coagulant	Dose (mg/L)	Turbidity	Total/Soluble UV	TOC	TTHMFP	mL/L
7/6/82 Grasse River water at pH 7.2							
29	Alum	125	13	63/68	55	46	19
30	Polymer D/alum	28/70	48	73/74	55	55	10
31	Polymer G/alum	9/70	65	74/75	58	52	13
7/6/82 Grasse River water at pH 5.5							
32	Alum	50	74	87/87	78	70	14
33	Polymer D/alum	28/30	61	85/85	59	67	8
34	Polymer G/alum	9/30	59	84/87	73	71	9

In obtaining Table 5-5 and Figure 5-5, the optimum cationic polymer dosage for TOC removal when used alone was used. The aluminum dosage was then varied to obtain the optimum dosage for the combination. It can be seen from Table 5-5 that the turbidity and organics removal were improved by the combination over the use of alum alone at pH 7.2 but not at pH 5.5. It seems that the pH effect of alum coagulation mechanisms on the removal of THM precursor was much more significant than the benefit of cationic polymer. It can also be seen that turbidity and organics removal were better at pH 5.5 than at pH 7.2 with alum alone or with cationic polymer and alum combination. They stated that " The better removals at pH 5.5 versus pH 7.2 might be explained by the formation of aluminum-humate precipitate at pH 5.5 or by greater adsorption of organics by $Al(OH)_3$ solids at the lower pH." (Hubel and Edzwald 1987, pg. 105).

The combination of alum plus cationic polymer produced much less sludge than the sludge produced by alum alone due to the reduction of alum dose. This was true at both pH 5.5 and pH 7.2.

They concluded that alum-cationic polymer combination could be useful in direct filtration systems if the organic matter concentration is low (5 mg/L or less TOC). Higher TOC values require high alum doses thus shortening filter runs.

Narkis et al. (1991) used jar test experiments to coagulate a 150 mg/L montmorillonite clay suspended in distilled water containing 0.5 meq/L $NaHCO_3$ at pH 6.0. Cationic polymers with high molecular weights (3.5×10^5 and 2.27×10^6) in combination with aluminum nitrate were investigated to determine the optimum dose for their combined use. Aluminum nitrate was added first and rapid mixed for 2 minutes followed by the cationic polymer and rapid mixing continued for another 3 minutes both at 100 rpm. They found that the cationic polymer improved the turbidity removal only if the suspension was underdosed by aluminum nitrate (i.e., when the particles were still negatively charged).

When half of the optimum aluminum nitrate dosage was applied the cationic polymer improved the flocculation efficiency and gave similar turbidity removal results to the cases where nonionic or anionic polymers were used along with aluminum nitrate. They, therefore, concluded that the major mechanism of action of all polymers used in their case, including the cationic polymers, was bridging.

Duff and Barkley (1976) tried to optimize the time interval between alum and cationic polymer addition, using a latex suspension and a pH of 6.0. The cationic polymer

(Nalco 607) was added before, with, and after alum addition. The amount of alum added (1-5 mL) was less than that necessary to give a zero zeta potential (about 10 mL) (the alum dosages were given in mL in this study, and the dosing solution concentration was not given). The same was done to the cationic polymer dosage (0.7-1.0 mL of polymer alone was not enough to give zero zeta potential). The experimental procedure consisted of adding the first coagulant while rapid mixing at 50 rpm in a jar test apparatus. This mixing continued until the second coagulant was added. After that, 1.0 minute of rapid mixing at 100 rpm followed by 20 minutes of slow mixing at 30 rpm were conducted. After allowing a settling period of two minutes, a sample from one inch below the surface was taken to measure zeta potential, turbidity, total solids, and Al^{+3} concentration. Their results are shown in **Table 5-6**. In Table 5-6, a relative time of (-5) or (+2) minutes means that the cationic polymer was added 5 minutes before or 2 minutes after alum addition, respectively (i.e. relative to alum addition time). From Table 5-6, the writer observes the following :

1- For a given alum dose and a given relative time, increasing the cationic polymer dosage did not have a specific trend on the residual turbidity.

2- It is hard to correlate the zeta potential values to the turbidity values. Small negative zeta potential values produced better turbidity than even smaller positive zeta potential values in some experiments. In other experiments both small negative and positive zeta potential values gave good turbidity values, with the positive zeta potential values producing lower turbidity..

Table 5-6: Turbidity, total solids, and zp of the latex suspension. A relative time of -4.0 minute, for example, means that the cationic polymer was added 4.0 minutes before alum addition; pH = 6.0, settling period = 2.0 minutes, PE = polyelectrolyte dosage. (from Duff and Barkley 1976).

	Relative Time (min)																				
	-5			-4			-2			0			+2			+4			+5		
	Alum (ml)			Alum (ml)			Alum (ml)			Alum (ml)			Alum (ml)			Alum (ml)			Alum (ml)		
PE	1	3	5	1	3	5	1	3	5	1	3	5	1	3	5	1	3	5	1	3	5
(ml)	Turbidity (FTU)																				
.7	280	48	290	200	275	275	300	50	215	250	125	185	260	83	170	215	56	20	260	100	24
.85	300	88	98	285	43	165	280	40	320	265	38	315	330	69	100	230	70	33	250	58	9.5
1.0	275	97	295	240	90	270	320	51	320	400	55	125	155	280	120	215	53	39	290	63	10
	Total Solids (ppm)																				
.7	72	16	40	96	98	74	66	4	66	112	50	28	112	36	48	108	10	10	110	36	12
.85	84	10	78	78	16	56	96	26	76	116	14	78	108	28	8	120	28	32	98	8	18
1.0	78	14	84	50	30	76	88	20	88	78	20	52	124	112	34	110	14	8	98	18	8
	ZP (mv)																				
.7	-23	0	+13	-37	-27	+11	-22	+11	-3	-34	-23	+14	-37	-11	+11	-43	-18	+16	-36	-19	+21
.85	-24	0	-10	-28	- 8	+10	-22	-13	+7	-44	-13	+ 5	-25	- 8	+20	-40	-17	+20	-45	- 9	+18
1.0	-18	+14	+13	-17	+ 6	+ 6	-15	+ 9	+8	-15	- 9	+ 4	-44	+14	+16	-35	- 5	+13	-33	- 7	+19

3- The best turbidity values and total solids were obtained when 5 minutes interval separated the alum and cationic polymer addition (alum added first), with higher alum doses producing better removals.

Wu and Barkley (1976) used similar experimental conditions as Duff and Barkley (1976) to compare alum, a cationic polymer (Nalco 607), and a combination of them (alum added first) to coagulate a latex suspension at pH 6.0. The suspension was mixed for one minute at 100 rpm when alum or the cationic polymer alone were used followed by 30 minutes of slow mixing at 30 rpm, and 20 minutes of settling. In the case of dual coagulants, the cationic polymer was added one minute after alum addition. Rapid mixing continued for one additional minute (2 minutes total rapid mixing time) at 100 rpm in this case. The combination of alum and the cationic polymer gave the best overall performance.

Recently Riffat (1991) studied the effects of addition sequence and rapid mixing intensity and duration on the flocculation kinetics using dual coagulants (a cationic polymer + alum). Ames, IA tap water buffered with 100 mg/L $NaHCO_3$ having 25 mg/L kaolin clay concentration was coagulated at pH 7.0 with 1.0 mg/L alum in combination with a cationic polymer (Magnifloc 573 C from American Cynamid Company). The dose of the cationic polymer was that producing near zero zeta potential (0.15 mg/L). An Automatic Image Analysis (AIA) was used to evaluate the flocculation kinetics.

For experiments used to evaluate the addition sequence effects, the total rapid mixing time was 60 seconds (60 seconds were applied when the cationic polymer and alum were added simultaneously; 30 seconds were applied for each coagulant when one was added before the other, totaling a 60 second period) at 500 s^{-1}. This was followed by tapered flocculation (15 minutes at 60 s^{-1} followed by an hour at 22 s^{-1}). She found that the addition of the cationic polymer before alum addition to be the best addition sequence in these experiments.

To evaluate the effects of rapid mixing intensity and duration on flocculation kinetics, Riffat (1991) conducted two sets of experiments. In the first set, the cationic polymer was added first, rapid mixed at either 500 s^{-1} (for either 30 or 60 seconds) or 1000 s^{-1} (for 30 seconds) followed by the addition of 1.0 mg/L alum, and rapid mixing continued for an extra 30 seconds at 500 s^{-1}. In this set of experiments, no effect of rapid mixing time or intensity was found.

In the second set of experiments, 1.0 mg/L alum was added first, rapid mixed for 5 seconds at 1000 s^{-1} followed by the addition of the cationic polymer and rapid mixing continued for another 1.0 or 3.0 minutes at 290 s^{-1}. Again, she found no difference in the flocculation kinetics for these different rapid mixing regimes.

Comparing the first set of experiments (when the cationic polymer was added first) with the second set of experiments (when alum was added first), Riffat (1991) found that the former performed better than the latter.

The combined use of inorganic and cationic polymer coagulants seems to have the capability of reducing the ripening period in direct, in-line, filtration plants using cationic polymers and coarse dual media filters. Shea et al. (1971) compared the sole use of a cationic polymer and the sole use of alum and the combined use of these two coagulants.

They were using two coarse dual media filters to filter a 6 mg/L suspension of kaolinite and bentonite clays. Quoting them “When 20 mg/L of alum and no polyelectrolyte was used, floc breakthrough occurred very rapidly. The alum floc was not strong enough to be retained by the coarse media. With the addition of 1.0 mg/L of Cat-Floc, an acceptable effluent was obtained after a ripening period of about seven hours. The combination of 20 mg/L alum followed by 1.0 mg/L Cat-Floc added after 30 sec of alum addition produced an acceptable effluent immediately after the start of the run. The alum floc is strengthened by the polymer, thus eliminating the early breakthrough of alum floc. The large mass of alum floc provides the necessary coating to the media, which makes it effective in collecting the incoming flocs.” (Shea et al. 1971, pg. 45).

From the above studies and other studies that did not have an experimental verification of their recommendations, a number of observations can be made.

1- Regarding addition sequence:

Some researchers recommend the addition of the inorganic coagulant before the cationic polymer (Duff and Barkley 1976, Swope 1977, Schlauch 1981, James and O'Melia 1982). Swope (1977) states that " cationic polymers should be applied from one to three minutes after the application of alum, alum plus silica, or a ferric salt. The purpose of the time interval is to produce microflocs to which the polymer can become attached." (Swope 1977, pg. R-65 - R-66). Schlauch (1981) states that " when a cationic polymer does show a decided advantage, it normally should be added to the coagulation stage either in place of inorganic agents, with inorganic agents, or within a few minutes after." (Schlauch 1981, pg.

126). He also adds " There have been no cases found, either within personal experience or work cited, where it has been advisable to add the cationic polymer before the inorganic coagulant." (Schlauch 1981, pg. 126).

Although it is questionable to consider the polymer used by James and O'Melia (1982) as a representative of cationic polymers (due to its very small charge density and high molecular weight), they found that alum addition before the cationic polymer produced the best residual turbidity and TOC removal. The addition of alum after the cationic polymer ranked second while the simultaneous addition ranked the last. They hypothesized that alum interacts with TOC and destabilizes turbidity while the high molecular weight low charge density cationic polymer adsorbs on the solid products of these reactions providing additional destabilization.

Duff and Barkley (1976) found that the addition of cationic polymer after alum addition is preferable to the simultaneous addition, and also to the addition of the cationic polymer before alum.

Kasper and Reichenberger (1983) reported on a case study where alum was added first at 12 mg/L followed by 0.3 mg/L cationic polymer (Cat-Floc T, a poly(DADMAC)). This addition sequence produced equivalent water quality with a dose of alum of 28 mg/L used alone and with 2.3 mg/L cationic polymer used alone. The economic analysis was in favor of using the dual coagulants. In this study, no comparison with other sequences of addition was conducted.

Other researchers have recommended the addition of cationic polymers before alum addition (Hanson and Cleasby 1990, Riffat 1991). Hanson and Cleasby (1990) hypothesized (based on experiments conducted using each coagulant alone) the application of the cationic polymer first and alum second. The cationic polymer should be mixed hard ($G=1250\ s^{-1}$) and long (2+ minutes) followed by the addition of alum at a G value of 500 s^{-1} for 1 minute. They stated that "the polymer provides a strong base structure for the flocs, and the alum helps pick up the remaining primary particles. The rapid mix with the alum acts as an intense flocculation stage for the polymer."(Hanson and Cleasby 1990, pg. 72). Coagulating 25 mg/L Kaolin suspension at pH 7.0, Riffat (1991) found that polymer addition before alum was superior over both the reverse addition sequence and the simultaneous addition. Other researchers found that the addition of cationic polymers before alum addition to be a good alternative (Beardsley 1973, Hubel and Edzwald 1987). No comparison with the reverse sequence of addition was reported in these two works. Quoting Beardsley (1973) "a plant treating soft water containing color, iron, and manganese was using 35 ppm alum, 2 ppm sodium aluminate, and lime. Carryover of the light floc caused short filter runs of 24 hr. Use of a polycation at 1 ppm followed by 20 ppm alum resulted in lower cost, a better water, and filter runs in excess of 72 hr. An increase in the coagulated water pH from 5.7 to 6.3 also helped in the removal of manganese." (Beardsley 1973, pg. 88) Hubel and Edzwald (1987) used this sequence because they expected the cationic polymer to remove a fraction of the trihalomethane precursor material and to decrease the solubility limit of $Al(OH)_3$.

The addition sequence was reported by some researchers to have no effect on the coagulants efficiency (Edzwald et al. 1977, Letterman and Sricharoenchaikit 1982). Edzwald et al. (1977) observed no difference in humic acid removal when a cationic polymer (Cat-Floc B, Nalcolyte 607, or Nalcolyte 8101) was added before or after alum. Letterman and Sricharoenchaikit (1982) found also no sequence effect on turbidity removal of a silica suspension, whether a sulfate concentration of 0.0 or 10^{-3} M was present.

Cleasby et al. (1989) found five of six conventional plants added the dual coagulants at the same location, and only one added alum before the cationic polymer. In four direct and in-line filtration plants, two plants added the dual coagulants at the same location, and two added the alum before the cationic polymer.

2- Regarding rapid mixing effects:

Riffat (1991) studied the rapid mixing effects on the coagulation process using a 25 mg/L Kaolin clay concentration at pH 7.0 and room temperature. No effect of rapid mixing intensity or duration was observed at these conditions. McBride et al. (1977) recommended a rapid mixing intensity of 1000 s-1 for the combined use of alum and a cationic polymer. Two flash diffusion mixers were recommended in a direct filtration treatment plant. Amirtharajah and Tambo (1991) stated that "when polymers are used as coagulant aids in combination with an inorganic coagulant, it is useful to consider rapid mixing in two stages, the first with higher G values (700-1000 s^{-1} for a few seconds) to destabilize the colloids with the inorganic coagulants and the second to enhance bridging and floc formation with the polymers with lower G values (200-400 s^{-1} for a few minutes). Very often, when inorganics and polymers are added together for coagulation, engineering cost criteria would tend to give least cost designs based on the mixing requirements for polymers (G values of 200-400 s^{-1} for a few minutes).

3- Regarding cold water temperature effects:

The effect of cold temperature on the effectiveness of dual coagulants has not been studied.

4- Regarding sulfate concentration effects:

Letterman and Sricharoenchaikit (1982) studied only the effect of sulfate at pH 6.0 using alum and a cationic polymer in combination. They found that in the absence of sulfate, the use of cationic polymers alone outperformed the use of dual coagulants. In the presence of 0.001 M sulfate, dual coagulant use outperformed the use of either alum or the cationic polymer each used alone. They found no effect of addition sequence of dual coagulants on turbidity removal whether zero or 0.001 M sulfate was present.

5- Regarding the use of cationic polymers in combination with Fe (III) salts:

All previous work, reported herein, was done using a combination of alum and cationic polymers. Essentially nothing has been found on the dual use of Iron (III) in combination with cationic polymers.

6. MATERIALS, EQUIPMENT, AND METHODS

6.1 Introduction

The experimental work reported herein was designed to study the effects of different parameters on flocculation kinetics using a combination of cationic polymers and ferric salts. Kaolinite clay suspended in distilled water with added salinity was used to simulate natural water and to provide a suspension with consistent characteristics.

The effects of temperature, rapid mixing time and intensity, coagulant addition sequence, in addition to other variables were investigated using primarily a Photometric Dispersion Analyzer (PDA). The PDA is an on-line, flow-through instrument that gives a sensitive indication of the state of aggregation of the particles in suspension. Supernatant turbidity analysis after flocculation and settling was also used as another measure of the effects of the various variables studied. Zeta potential was measured before and after the addition of the coagulant or coagulants (after rapid mixing) as a quality control measure and as a means to explain some of the results.

In a limited number of experiments, an Automatic Image Analyzer (AIA) (Lemont OASYS) was used. The description of the AIA and the results obtained using the AIA are shown in the appendix.

The following is a detailed description of the methods used to prepare the various materials used in the experiments as well as the equipment and methods used in this experimental study.

6.2 Materials

6.2.1 Ferric Nitrate Coagulant

Ferric nitrate, $Fe(NO_3)_3.9H_2O$, was used as the inorganic coagulant. Ferric sulfate or ferric chloride were not used because sulfate was one of the variables studied and both sulfate and chloride have a higher tendency than nitrate to form complexes which affect the flocculation process. By using nitrate, the possible masking effects of chloride on complex formation with the inorganic coagulant hydrolysis species is almost eliminated.

A 0.25 molarity stock solution of $Fe(NO_3)_3.9H_2O$ was prepared using a reagent grade ferric nitrate salt in deionized water. The pH of this stock solution which was checked periodically was 1.30 ± 0.02. The stock solution was stored for at least three days before its first use. The dosing solution had a concentration of 10 mg/mL $Fe(NO_3)_3.9H_2O$. This was prepared the day before the experiments were done by diluting 19.8 mL of the 0.25 M stock solution with distilled water in a 200 mL volumetric flask. The pH of this dosing solution was checked before every experiment. The pH was always equal to 2.08 ± 0.03.

6.2.2 The Cationic Polymer Coagulant

Three cationic polymers were tried in this study. Almost all of the results hers are reported using Cat-Floc TL (a poly(DADMAC) polymer from Calgon Corporation). A similar cationic polymer from the same supplier but with higher molecular weight was also used (Cat-Floc L). The third cationic polymer was an EPI/DMA polymer from American Cyanamid (Magnifloc 573 C). Only preliminary studies were done using the latter two polymers and only a limited number of the experimental results using these two polymers are reported in the results section.

As mentioned above, the main cationic polymer used was Cat-Floc TL. This is a low molecular weight cationic polymer with relatively low charge density. The molecular weight and charge density were measured using the viscosity and colloid titration methods, respectively. These methods are detailed later in this section. The solid content of the polymer was measured by evaporating 1.000 g of the polymer at 103 °C for 24 hours. The inorganic content was also measured by exposing the already evaporated polymer to a 550 °C oven for 30 minutes. The solid content was equal to 51 % by weight, while the inorganic content was equal to 0.45 % by weight of the polymer as supplied. The solid content of Cat-Floc L was about 50 % by weight.

To prepare the stock solution, 1.000 g of the polymer as supplied was weighed in an aluminum weighing dish. The polymer was then added to the vortex of about 200 mL sample of deionized water in a beaker being mixed by magnetic stirrer. Water was added to the aluminum weighing dish to clean it and to be sure that all the polymer was added and nothing was still sticking to the dish. This was confirmed by comparing the original dish weight to that after drying for 24 hours. The remaining volume of water from a volumetric flask was then added to the beaker to give a final volume of 1.0 liter. The polymer stock solution was kept mixing for about 20 minutes. The polymer stock solution was prepared the day before the experiments were performed. The polymer dosing solution was prepared about half an hour before the experiment. The dosing solution concentrations were 0.02 and 0.1 mg/mL for experiments done with the 2 L and the 18 L reactors, respectively.

6.2.3 The Clay Suspension

Kaolinite clay (Kentucky Ball Clay) was used as the source of turbidity in the present study. An 800 mg/L stock suspension of kaolin clay with a mean diameter of 1.8 μm was prepared in 45 L of distilled water in a 60 L plastic tank. The tank was equipped with a stainless steel pump that provided the necessary mixing for the suspension **(Figure 6-1)**. Before each experiment, the pump was turned on for at least 30 minutes to insure the homogeneity of the stock suspension.

Kaolinite clay was dried overnight at 103 °C and desiccated for 30 minutes. Then, 36.00 g of the dried clay was weighed and added to distilled water in the tank and the volume was brought up to 45 L with distilled water. The mixing pump was turned on for at least one hour. The stock clay suspension was then kept for about 48 hours before it was used to insure that any changes that might occur to the clay have been completed. The suspension was discarded once its volume reached the 15 L mark.

During the course of this work, some changes in the coagulation tendency of the clay suspension was noticed. The cause of these changes was not identified, but the writer thinks that changes in the "distilled water" characteristics are probably the cause of such changes. The water that comes from the distilled water tap is not really distilled, because it is prepared from condensed steam from the university heating system that is passed through a deionizer and an activated carbon filter.To get over this problem, only experiments conducted using the same clay stock suspension batch and the same dilution water (which was stored in 400 L tank) were compared. Experiments conducted using different clay suspension batches and

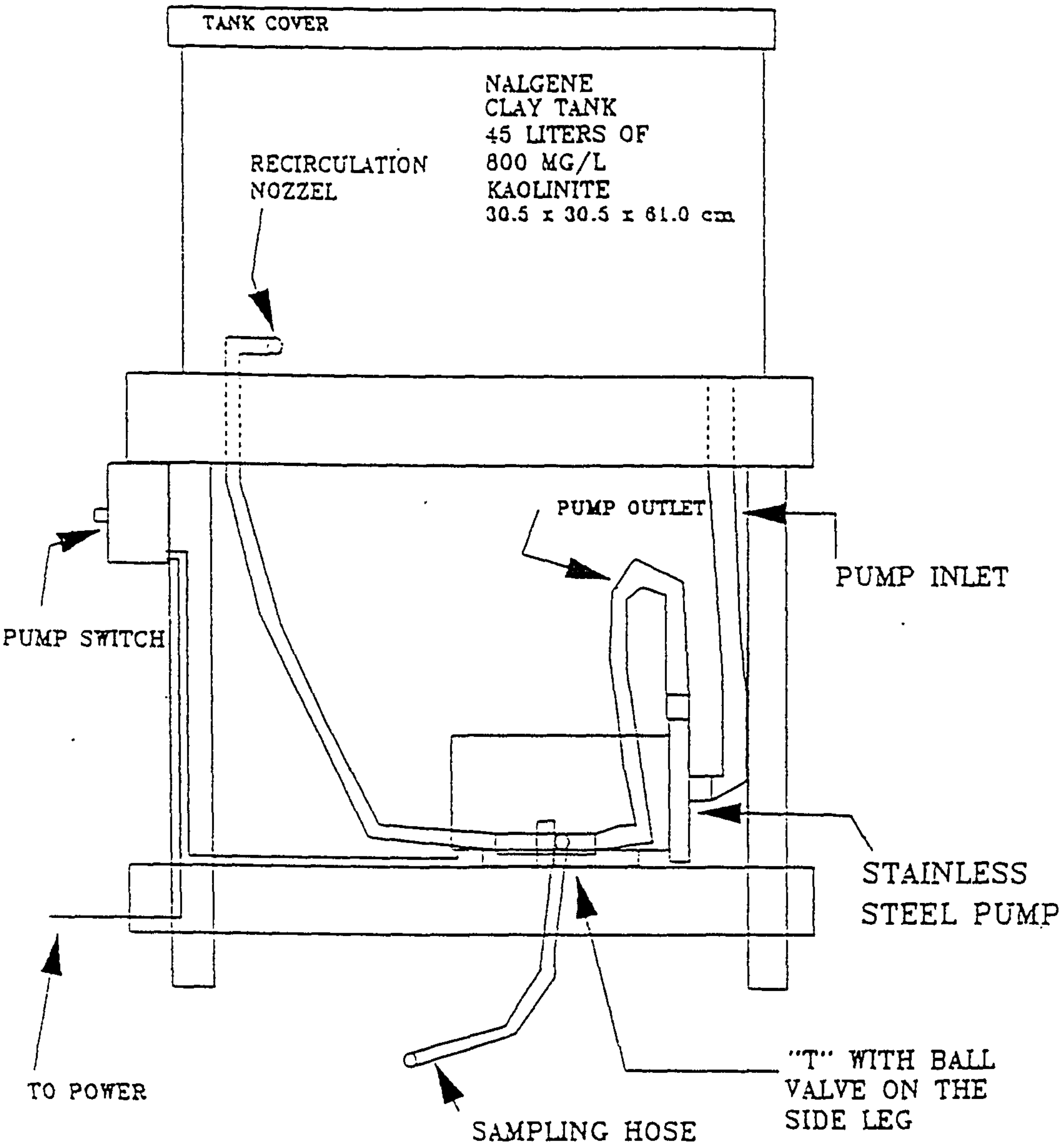


Figure 6-1: Schematic of clay mixing tank and associated equipment.

different dilution water were not compared in this study. The reader, also, should not try to compare results presented in one figure with other results presented in other figures, because they may have been conducted using different clay suspension characteristics.

6.2.4 Dilution Water

The dilution water was distilled water with added chemicals to provide the required ionic strength and pH. First, distilled water was stored in a large polyethylene tank (about 400 L) for at least two days to provide the necessary time for the carbonate system to come to an equilibrium with the atmosphere. The required volume of this water was transferred directly to the 18 L reactor (for room temperature experiments) or two days before the low temperature experiments to the controlled temperature room. Sodium nitrate, $NaNO_3$, was added at 0.425 g/L to achieve 0.005 ionic strength (when sulfate was used, the amount of sodium nitrate was reduced so that the total ionic strength would still be 0.005). This ionic strength value did not cause any coagulation by double layer compression, and provided a consistent and reproducible zeta potential values.

6.3 Equipment

6.3.1 Batch Reactor System

Two batch reactors with volumes of 2 L and 18 L were used. The 2 L reactor and the associated two blade turbine impeller were identical to those in Phipps and Bird jar test machine. The jar is an 11.5 × 11.5 cm cross section with water depth of 15 cm. The impeller had two opposing blades, each 3.0 cm by 2.0 cm. The sampling tap is located 10 cm below water level. The impeller was rotated using a variable speed electric motor and motor controller (Heller Corp., Floral Park, NY). The motor controller was also used to measure the rotation speed of the impeller.

The 18 L plexiglass reactor used in the present work was identical to that used by Argamam and Kaufman (1968, 1970) and Hanson and Cleasby (1990). A schematic of the reactor along with its dimensions and the dimensions of the 2 blade turbine impeller are shown in **Figure 6-2**. As can be seen in this figure, the sampling port through which the coagulants were injected are at the same level as the impeller. This enables the coagulants to be dispersed very quickly throughout the reactor.

The stainless steel turbine impeller blade was rotated by an electric motor and a speed controller (Master Servodyne motor and motor controller, Cole-Parmer Instrument Company, Chicago, IL). The impeller was connected to the electric motor through a plexiglass shaft and a plexiglass coupler in order to reduce the effects of the current associated with high rapid mixing intensity on pH measurements. The stirrer rotation speed was measured using an Ametek Model 1736 tachometer. The electric motor was mounted on a wooden support placed on the top of the reactor. The wooden support has two holes to support a pH probe and a thermocouple.

The power inputs and consequently the G values applied at various rapid mixing intensities were determined using a rotating torque meter (Bex-O-Meter, Model 38, The Bex Company, San Fransisco, CA). Because the torque meter was rotating at the same speed as the shaft, it was necessary to use a 35 mm camera with high shutter speed (1000/s) and high

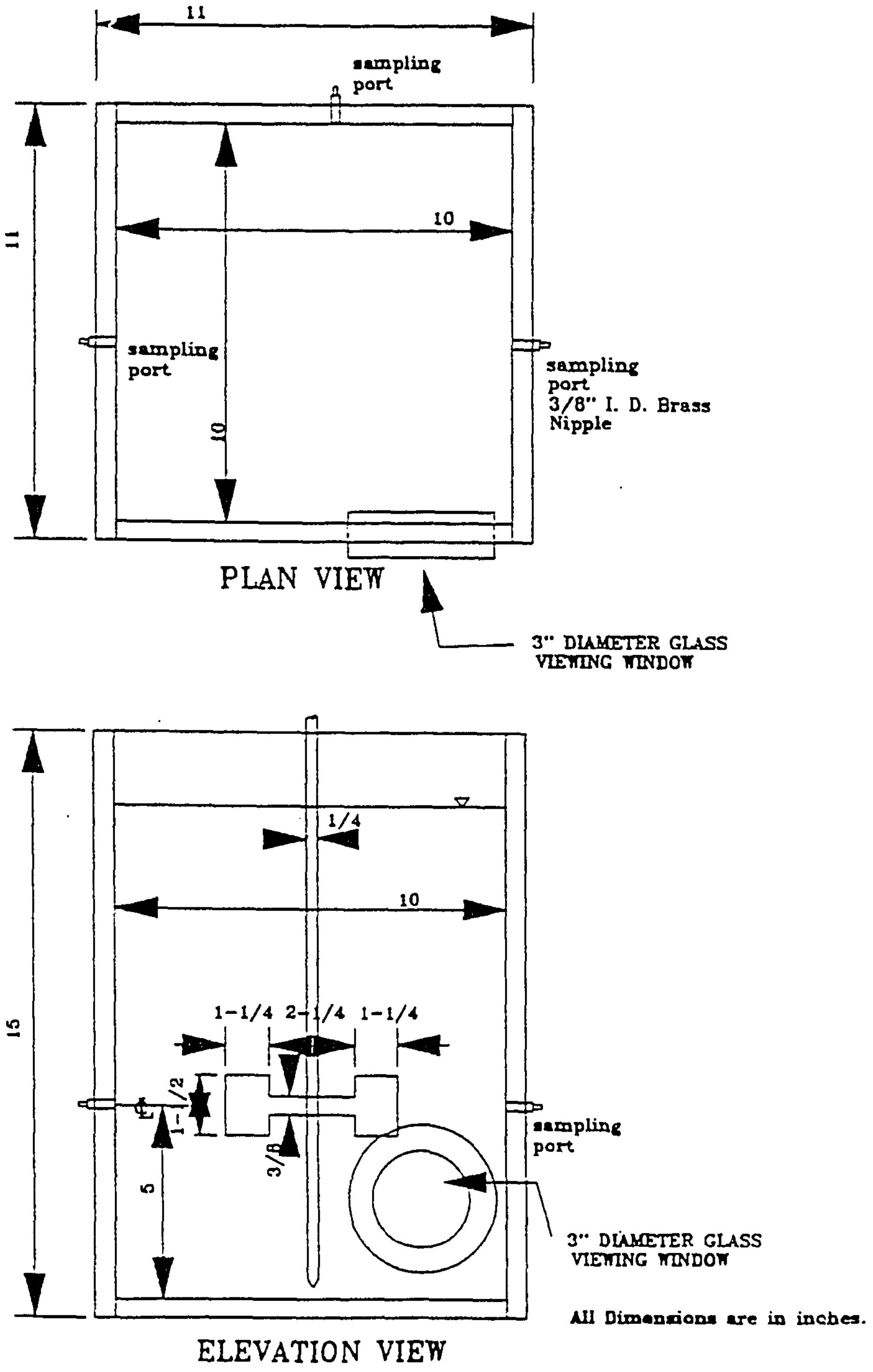


Figure 6-2 Schematic of the 18 L plexiglass reactor with the turbine impeller.

speed black and white film to record the torque values. Once the torque values are determined at different rotating speeds, the power input and consequently the G values can be calculated. **Figure 6-3** shows the results obtained using this method for the 2 blade impeller shown in Figure 6-2. From this figure, the G value was related to the rotational speed by:

$$G = 0.135\ N^{1.471} \qquad (N = \text{rev/min, at } 23\ ^{\circ}\text{C}) \qquad (6\text{-}1)$$

For experiments conducted at 5 °C, the same rpm values as those used at room temperature were used. This, however produces different G values but the same power input as was found by Hanson and Cleasby (1990), because full turbulance exists in all experiments.

6.3.2 pH Measurement and Control

The pH was measured using a Fisher Accumet number 610 pH meter connected to a 12 mm diameter pH probe. The pH meter was standardized according to the manufacturer's specifications, using pH 7.0 buffer and either a pH 10.0 buffer (for pH 7.8 experiments) or pH 4.0 buffer (for pH 6.0 experiments).

The pH of the dilution water with the added clay was in the range of 5.6 and 6.0. For pH 6.0 experiments, 0.02 M NaOH was used to achieve the required initial pH. For pH 7.8 experiments, both sodium bicarbonate, $NaHCO_3$, and sodium carbonate, Na_2CO_3, were used to achieve the required initial pH. Theoretically, the amounts of sodium carbonate and sodium bicarbonate required to achieve a suspension with a pH value of 7.8 that is in equilibrium with the atmospheric carbon dioxide can be calculated. In the present study, values around the theoretical values were experimentally tried. It was found that 43 mg/L of

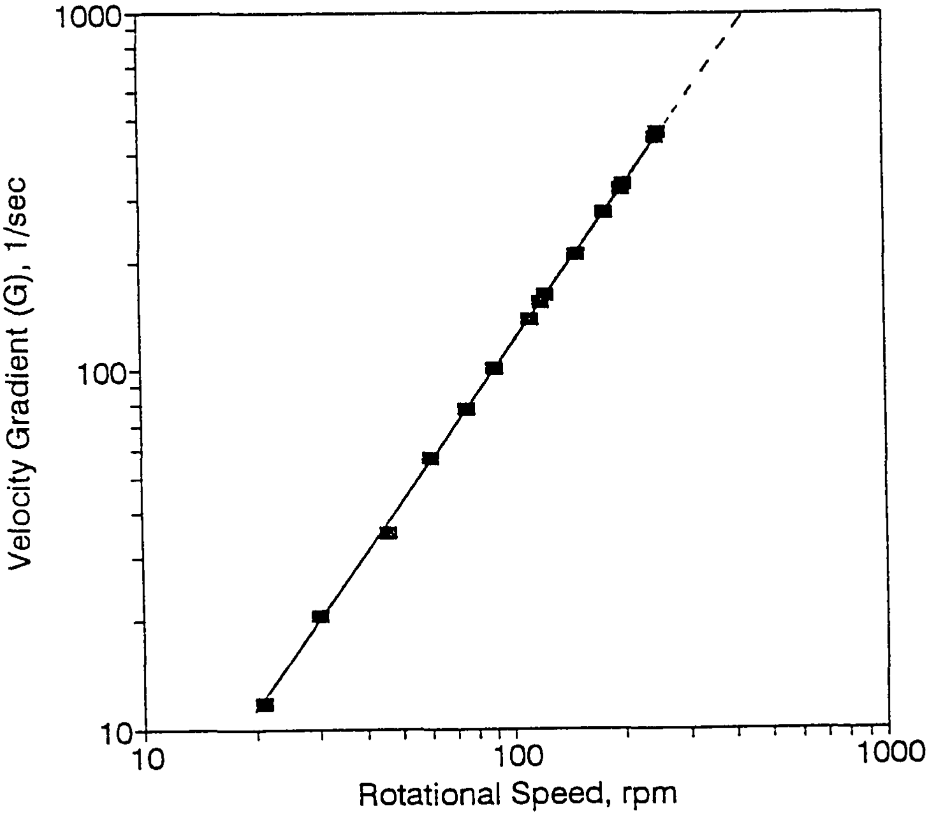


Figure 6-3: The relationship between root mean square velocity gradient, G and the rotational speed in the 18 L reactor at 23 °C.

$NaHCO_3$ plus 2.0 mg/L of Na_2CO_3 were necessary to give a pH value of 7.8. The pH was consistently equal to 7.8 ± 0.2. The pH was then brought to pH 7.8 by using either 0.02 M NaOH or HNO_3.

The use of a buffer system to bring the pH to 7.8 and the use of only NaOH to bring the pH to 6.0, is intended to simulate surface water conditions that are at or near equilibrium with the atmosphere. The pH in experiments done at pH 7.8 with the buffer system was less prone to fluctuations during the rapid and slow mixing periods.

At the time of the ferric nitrate coagulant addition, a chemically equivalent amount of NaOH to the ferric nitrate dose was added simultaneously to prevent the pH from dropping due to the ferric hydrolysis and precipitation. Fine tuning of the pH continued during the rapid mixing period. In all experiments done at both pH 7.8 (with the buffer) and at pH 6.0 (without buffer), adjustment of pH during flocculation was not necessary.

6.3.3 Turbidity Measurements

Hach Model 18900 Ratio Turbidimeter (Hach Chemical Company, Loveland, CO.) was used to measure both the initial and the supernatant turbidity values. The supernatant turbidity at a specific depth and time of settling is a measure of the flocculation efficiency, while the initial turbidity was used as a quality control measure for the clay concentration. The Turbidimeter was standardized periodically against Formazin Standards. It was checked before every experiment using Gelex secondary standards.

For the 2 L experiments the turbidity samples were withdrawn from the sampling tap which is located 10 cm below the 2 L mark which was the starting water level. Samples were taken before coagulant addition and after 10.0 minutes of settling at the end of the flocculation period. For the 18 L experiments, samples were taken before coagulant addition as well as 10, 20, and 30 minutes after settling. The samples were withdrawn from the sampling ports using a syringe with an attached # 13 gauge needle.

6.3.4 Zeta Potential Measurement

A model 102 Laser Zee Meter (Pen-Kem Inc., Croton-on-Hudson, NY) was used to measure the initial (before coagulant addition) zeta potential of the suspension as well as zeta potential of the suspension directly at the end of rapid mixing. The electronics in the Laser Zee Meter have been upgraded to model 104 electronics, but the optics were still original. The zeta potential measurements were conducted about half an hour after sample collection. The average of three measurements for each sample is reported as the "zeta potential" in the results section of this work.

The measurement and cleaning techniques reported in the manufacturer's manual were exactly followed, especially the determination of the stationary layer location in the zeta potential cell. This provided consistent and reproducible zeta potential measurements.

A standard colloid suspension purchased from Pen Kem Inc. with a zeta potential value of -62.2 ± 1.5 mV was used to check the calibration of the instrument. Throughout the course of this work, the zeta potential values of the standard suspension and the homogenized kaolin suspension were consistent (i.e. within ± 2 mV).

6.3.5 Temperature Measurement and Control

A type "T" thermocouple was used for temperature measurements. For room temperature experiments, no temperature control was performed. For low temperature experiments (5 °C), the temperature in the constant temperature room was controlled and monitored using a personal computer based data acquisition and control system (Strawberry Tree Computers, Sunnyvale, CA). To get the required low temperature for cold temperature experiments, distilled water in 18 L carboys was transferred 2 days before the experiments to the constant temperature room which was held at a temperature of 5 °C. Very cold water (about 1 °C) was also added to the reactor to compensate for the warm stock clay suspension dose which had a temperature of more than 25 °C after being mixed in the stock clay suspension tank.

In room temperature experiments, the water temperature was in the range 23 ± 1 °C. For low temperature experiments (5 °C), the water temperature was always kept between 4.5 and 5.5 °C throughout the flocculation period.

6.3.6 The Photometric Dispersion Analyzer (PDA)

The PDA 2000 (Rank Brothers Ltd., Cambridge, England) was the major device used in the present study to investigate the effects of the different variables on the flocculation kinetics. This device measures the fluctuations of light that occur when a light beam passes through a suspension that is flowing through an aperture. The fluctuations of transmitted light increase as particle aggregation occurs. The following is a summary of the theory of the PDA taken from Gregory and Nelson (1984, 1986) and Gregory (1985).

When a light beam passes through a flowing suspension, the transmitted light fluctuates around a mean value due to the inevitable change in particle concentration in the path of the light beam. The particle number concentration follows a Poisson distribution. In other words, the standard deviation of the number of particles around the mean in a certain volume of suspension is equal to the square root of the average value of the number of particles in that volume. For example, if the average number of particles in the light beam path is equal to 1,000,000 particles, the standard deviation will be equal to 1000. Therefore, 95 % of the time, the number of particles in the light beam path would be between 1000,000 ± 2000 (within two standard deviations). By dividing 2000 over 1,000,000 one obtains that the variation of the number of particles is equal to less than 0.2 % of the average value. By reducing the diameter of the light beam, the number of particles in the path of the light beam becomes smaller and the variation in the number of particles becomes relatively larger (if the average number of particles is equal to 900 particles, the number of particles would be 900 ± 60, 95 % of the times, or within 6.7 % of the average value). The latter variation is much easier to detect than the former. The PDA, therefore, utilizes a small diameter light beam (1.0 mm) along with a small diameter glass tube (2.5 mm internal diameter in the present study) through which the suspension flows.

When light passes through a suspension of particles, the average transmitted light intensity (which is usually converted to a dc voltage for monitoring purposes) (see Figure 6-4) is, according to Lambert-Beer law, equal to:

$$I / I_o = V / V_o = \exp(-NCL) = \exp(-n\ C / A) \qquad (6\text{-}2)$$

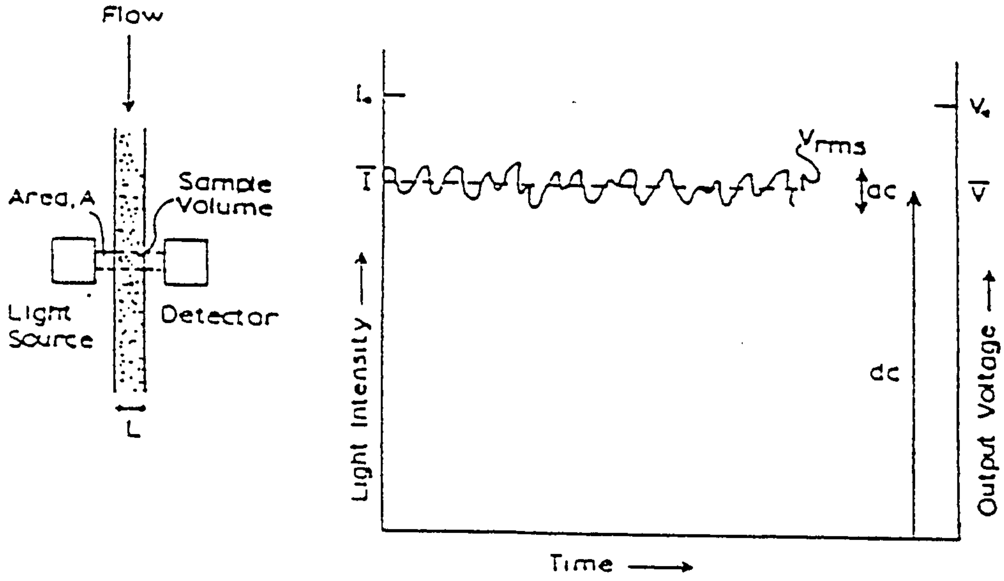


Figure 6-4: Light fluctuations as a result of changes of particles number in a suspension, which constitutes the theory behind the PDA (Gregory 1985).

where

I = The average transmitted light intensity, which is usually measured as voltage, V

I_o = The incident light intensity, which is also measured as voltage V_o

N = The average number of particles per unit volume

C = Average scattering cross section of the particles

L = The optical path length

n = The average number of particles in the light beam = NLA

A = The light beam cross sectional area

As mentioned earlier, the actual number of particles in the light beam path shows a random variation around the mean value, n. This results in fluctuations in the actual transmitted light intensity. The easiest measure of these fluctuations is their standard deviation (root mean square value) about the mean value. This is also measured as an ac voltage and is given the symbol V_{rms}. Due to the exponential term in **Equation 6-2** it is not easy to derive an exact expression for V_{rms}. However, an approximate expression was introduced by Gregory (1985) as:

$$V_{rms} = V \sinh (n^{1/2}\, C / A) \tag{6-3}$$

Gregory (1985) stated that the term $(n^{1/2}\, C / A)$ will usually be much less than 1.0 even for very turbid suspensions. Accordingly **Equation 6-3** simplifies to:

$$V_{rms} = V (n^{1/2}\, C / A) \tag{6-4}$$

As **Equation 6-4** shows, the value of V_{rms} increases as the number of particles increases and as the scattering cross section of the particles increases. When aggregation occurs, the number of particles decreases while the scattering cross section of the particles increases. These changes have opposite effects on the V_{rms} value. However, Gregory and Nelson (1986) showed that the value of V_{rms} always increases as aggregation occurs. They showed this fact theoretically for two kinds of model particles. The first model particles were spherical particles that coalesce to form larger spheres. The scattering cross sectional area of both the primary particles and the aggregate composed of these primary particles was assumed to be proportional to their cross sectional area. The second model particles were spherical particles that form extended aggregates for which the scattering cross sectional area is equal to the sum of the individual scattering cross sectional areas. They mentioned that real particles behave differently during aggregation, and the above two models can define the extremes for real particles.

It should be noted that **Equation 6-4** is only valid for monodisperse particles. For heterodisperse suspensions, the value of V_{rms} should be summed over the various types of particles present.

In practice the ratio of V_{rms} / V is the most useful parameter for flocculation kinetics evaluation. This ratio which is usually called the "Ratio Value" or the "Flocculation Index" is used because it is not affected by electronic drift. The electronic drift affects both the V and the V_{rms} in the same proportion, and therefore does not affect their ratio.

The PDA has a wide range (1-1000) of magnification for the ac voltage that results from the random variation of the number of particles in a specific volume of the suspension.

(which is converted to the V_{rms}). This magnification allow for even the smallest responses to be compared. The magnification is controlled by setting a knob on the PDA called the "RMS Gain" to a value between 1 to 1000; 1 being low magnification while 1000 represents a very high magnification. In the present study, the following magnifications were used depending on the clay concentration:

clay concentration (mg/L)	RMS Gain value
5	500
25 or 50	50
100	20

6.4 Experimental Methods

Figure 6-5 is a schematic of the experimental setup used in performing all of the experiments reported herein. A constant flow of about 15 mL/min from the reactor to the PDA optical sensor was maintained through the use of a tubing system and a peristaltic pump. This flow then passed through a 2.5 mm internal diameter glass tubing fixed between the light source and the photodiode in the PDA and then back to the reactor through the tubing system. The flow stream was withdrawn from the same level as the impeller and was recirculated back near the bottom of the reactor. The outputs of the pH meter, the PDA, and the thermocouple were transferred and stored at 5 seconds intervals into a 5.25 inch floppy disk through the use of a personal computer based data acquisition and control system (Strawberry Tree Computers, Sunnyvale, CA).

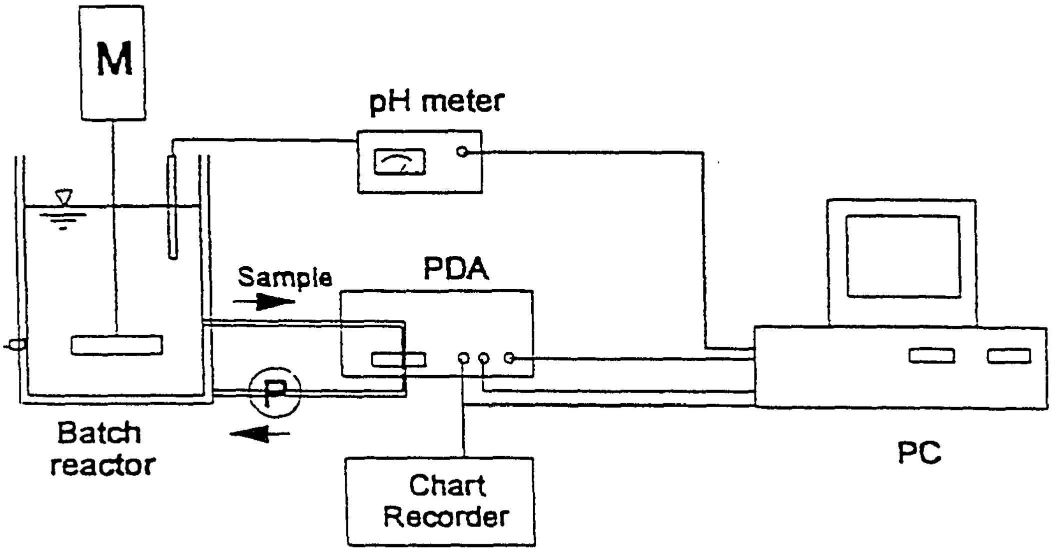


Figure 6-5: Schematic of the experimental setup.

The following is a representative procedure for an experiment conducted using the 18 L reactor. For the 2 L reactor experiments, a similar procedure was followed except that turbidity was measured only after 10 minutes of settling.

1. The PDA, the Turbidimeter, and the clay mixing pump are turned on. The warm up periods for the PDA and the Turbidimeter are 10 minutes and 1 hour, respectively. The stock clay mixing time should continue for at least 30 minutes to insure the homogeneity of the clay suspension.
2. The reactor is connected to the PDA through the tubing system. Distilled water is added to the reactor until water flows through the tubing system and through the PDA. The PDA is then calibrated by adjusting the DC gain to give a value of 10.00 mV for the distilled water.
3. Sodium nitrate, sodium carbonate and bicarbonate (if required), sodium sulfate (if required), and the required amount of the stock clay suspension are added to the reactor. The volume of the suspension is then brought to 18 L. Mixing of the suspension in the reactor starts at about 200 rpm. Fine tuning of the pH using NaOH or HNO_3 is then performed.
4. For low temperature experiments, the dilution water had been cooled to 5 °C by storage for 2 days in the constant temperature room. After adding the chemicals and clay, the temperature is somewhat above 5 °C. The temperature is brought down to 5 °C using an appropriate amount of very cold water (by storing it in the freezer) mainly to compensate for the warm temperature of the stock clay sample which is not stored in the constant temperature room.

5. A sample is taken by a # 13 gauge needle connected to a 60 mL syringe to measure the initial zeta potential and the initial turbidity value.

6. The required volumes of the cationic polymer solution (if any), the ferric nitrate coagulant (if any) and the chemically equivalent amount of NaOH are then filled into appropriate syringes.

7. The mixing intensity is brought to the required value by adjusting the impeller rpm. The data acquisition system is ordered to start storing data. The required amounts of ferric nitrate, NaOH and the cationic polymer solution are added in the desired sequence for the experiment. Ferric nitrate and NaOH are added simultaneously. Rapid mixing continues for the required time. Mixing intensity is then brought to the desired flocculation intensity by readjusting the impeller rpm.

8. A sample is then immediately taken from the sampling port closed by a rubber septum, using a 60 mL syringe for zeta potential measurement.

9. During the whole rapid mixing and flocculation periods, the pH readings, the temperature, and the outputs from the PDA including the "Ratio values" (i.e. the "Flocculation Index" values) are stored every 5 seconds on a floppy disk.

10. After 30 minutes of flocculation, the suspension is allowed to settle for 30 minutes. Supernatant turbidity values at the prescribed depth are measured after 10, 20, and 30 minutes of settling.

6.5 Charge Density Determination For Polymers

Charge density is one of the most important characteristics of cationic polymers. The method that has usually been used for charge density determination is the titration method (Dentel et al. 1989, Toei and Kohara 1976). A solution containing the polymer with the unknown charge density is titrated with a standard polymer solution of opposite charge whose charge density is already known. The point at which equivalent amounts of the two oppositely charged polymers have reacted is determined by an indicator which changes its color at that point.

In the present study, Cat-Floc TL, a cationic polymer, was titrated with a standard anionic polymer titrant, polyvinyl sulfate potassium salt (PVSK), (Eastman Kodak Company, Rochester, New York). PVSK monomer has the formula $C_2H_3O_4SK$. The charge density value for PVSK reported by Schell and Bernhardt (1986) (in Haarhoff 1988) was used. A solution of 32.4 mg/L PVSK was prepared which has a charge value of 0.0002 equivalent (i.e. 0.0002 meq/mL).

Toluidine Blue O (TBO), which has the formula, $C_{15}H_6ClN_3S$ (Sigma Chemical Company), was used as the colorimetric indicator. The TBO colorimetric indicator turns from blue to purple (red-violet) when the polymer reagent charge changes from positive to negative. It has an indistinct color change when the reagent charge changes from negative to positive.

The cationic polymer (Cat-Floc TL) solution with a concentration of 10 mg/L in 100 mL volume was titrated with the 32.4 mg/L PVSK after 3 drops of Toluidine Blue O was added to the cationic polymer solution. The titration was terminated once the color of the solution being titrated (the cationic polymer with added TBO) changed from blue to purple. The charge density of the cationic polymer (meq/mg) is then calculated as: (mL of the PVSK solution added)(0.0002). For Cat-Floc TL, the charge density was calculated as equal to 1.96 meq/g of polymer as supplied (3.92 meq/g of active polymer). No charge density measurements for Cat-Floc L or Magnifloc 573 C were made. The charge density for Magnifloc 573 C is equal to 8.5 meq/g of active polymer (Edzwald et al. 1987).

It should be noted that in the titration method for charge density determination, the titrant should be the anionic polymer solution, PVSK, and the indicator should be added to a solution with a cationic reagent. In addition to the indistinct color change when the polymer reagent charge changes from negative to positive, the TBO indicator which has a positive charge can form an indicator-reagent complex if added to an anionic polymer solution (Dentel et al. 1989). Therefore, when the charge density of an anionic polymer is sought, a known volume of a standardized cationic polymer solution should be added to the anionic polymer solution until it becomes positively charged. Then TBO is added and the solution is back titrated by PVSK as is the case with cationic polyelectrolytes. The charge on the anionic polymer is then calculated from the difference between the amount of PVSK added and the amount needed to neutralize the cationic polymer alone. The preferable cationic polymer that is added to change the anionic polymer solution to cationic is polybrene since it retains a constant charge density regardless of solution pH.

6.6 Molecular Weight Determination For Polymers By Viscosity Method

Polymers are normally a mixture of molecules with a range of molecular weights. This is due to the statistical nature of the polymerization process. A number of methods to determine the average molecular weight of polymers have been developed. The viscosity method is one of the easiest methods for this purpose.

The viscosity method is based on the fact that the viscosity of a polymer solution increases with increasing the volume of the polymer molecules, and consequently with the molecular weight of the polymer. The viscosity of the polymer solution, however, also depends on the concentration of the polymer. In order to eliminate the effect of the concentration on the viscosity, a viscosity parameter that is independent on the concentration has been introduced. This parameter has been called the limiting viscosity (η_{lim}) or the intrinsic viscosity. The limiting viscosity is defined as (Cooper 1989):

$$\eta_{lim} = \lim_{C \to 0} \frac{\eta_{sp}}{C} \qquad (6\text{-}5)$$

where:

η_{lim} = limiting viscosity (dimensionless)

C = concentration of polymer in the solution (mass/volume)

η_{sp} = the specific viscosity (dimentionless). η_{sp} is defined as:

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} \qquad (6\text{-}6)$$

where:

η = the viscosity of the polymer solution (N.s/m^2)

η_s = the solvent viscosity (N.s/m^2)

The value of η_{sp} is always greater than zero, because the viscosity of the polymer solution is always greater than the viscosity of the solvent.

The limiting viscosity (η_{lim}) is related to the average molecular weight (M_v), determined by the viscosity method, through the Mark-Houwink-Sakundra (MHS) equation, as follows (Cooper 1989, Schroder et al. 1989):

$$\eta_{lim} = kM_v^a \tag{6-7}$$

where k and a are constants.

The value of the average molecular weight of the polymer, M_v, depends on the temperature and the solvent characteristics used for the measurement. Some of the values of 'a' and 'k' for some of the polymers used in water treatment are listed in **Table 6-1.**

The viscosity is generally measured by capillary, rotation, and drop viscometers. Capillary viscometers are most frequently used to measure the limiting viscosity. There are two types of capillary viscometers: Ostwald type and Ubbelohde type. For a specific capillary viscometer, the viscosities of the solvent and the polymer solution are proportional only to the flow time:

$$\frac{\eta}{\eta_s} = \frac{t}{t_s} \tag{6-8}$$

where:

Table 6-1: Values of Mark-Houwink-Sakundra (MHS) equation constants, ‘a’ and 'k' for poly(DADMAC) polymers at different NaCl concentrations at 20 °C (Butler and Zhang 1991).

salt concentration	“a”	“k”
0.1 M NaCl	0.66	3.98×10^{-4}
0.2 M NaCl	0.638	2.512×10^{-4}
0.3 M NaCl	0.620	2.510×10^{-4}
0.4 M NaCl	0.542	1.390×10^{-4}
0.5 M NaCl	0.566	3.98×10^{-4}

η = viscosity of the polymer solution,

η_S = viscosity of the solvent,

t = flow time between the two fiducial marks in the polymer solution, and

t_S = flow time between the two fiducial marks in the solvent.

The value of η/η_S is usually referred to as the relative viscosity, η_r. From η_r, the value of the specific viscosities ($\eta_{sp}=\eta_r - 1$) for different polymer concentrations can then be determined. The value of the limiting viscosity can be obtained by drawing a graph between the reduced viscosity (η_{sp}/C) vs C and extrapolate the graph to C = 0. The equation governing the calculations is (Schroder et al. 1989):

$$\frac{\eta_{sp}}{C} = \eta_{lim} + k\eta_{lim}^2 C \tag{6-9}$$

Figure 6.6 shows the figure between η_{SP} and C for Cat-Floc TL polymer used in the present work. The limiting viscosity is the Y intercept of this figure and was equal to 0.183 L/g.

Figure 6.6 was obtained by charging 5 mL of Cat-Floc TL polymer solution with different polymer concentration (1.0 to 10.0 g/L) into a size 25 viscometer tube (Cannon-Fenske Routine, Fisher Scientific, Pittsburg, PA). Flow time of the polymer solution dissolved in distilled water with added 0.1 M NaCl at different concentrations between two fiducial marks on the viscometer was measured along with the flow time of water with a dissolved 0.1 M NaCl.

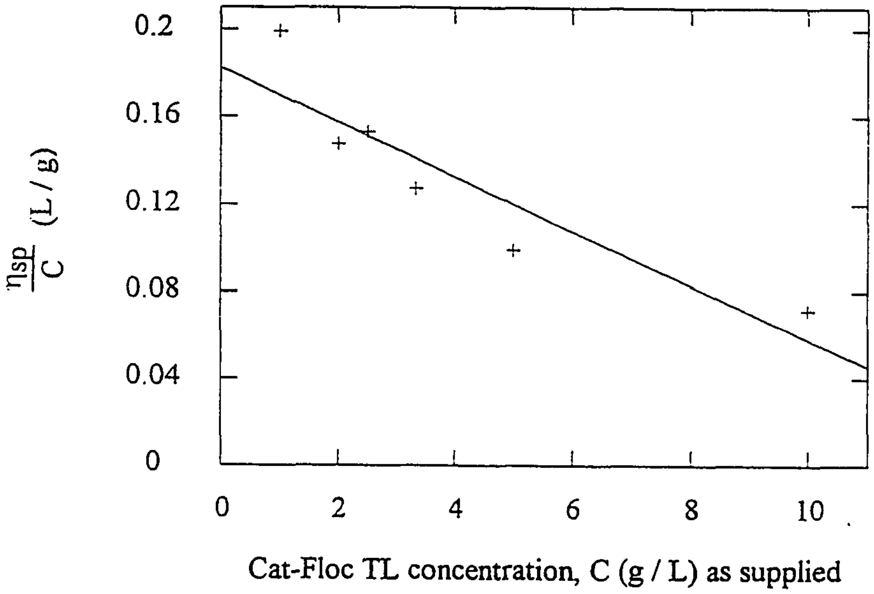


Figure 6.6: graphical determination of the limiting viscosity (η_{lim}) for Cat-Floc TL.

After the intrinsic viscosity is calculated, the viscosity average molecular weight can be calculated using MHS equation, if the values of 'a' and 'k' are known for the particular polymer. If 'a' and 'k' are not known, a rough idea of the relative molecular weights of polymers can be obtained using comparisons of intrinsic viscosites.

In the case of Cat-Floc TL, the molecular weight was calculated using MHS equation using "a" and "k" values from Table 6-1 to be equal to about 11,000 g/mole. For Cat-Floc L, the limiting viscosity was found to be 1.27 L/g, and the molecular weight was calculated to be about 200,000 g/mole.

The measurement of the molecular weight and charge density of the polymer were conducted to check any changes in the polymer characteristics with time. Within one year, the molecular weight for one batch of the cationic polymer was measured twice, and found to be similar.

7. RESULTS AND DISCUSSION

7.1 General

The experimental results are presented in this chapter along with the pertinent discussion in four stages. First, the preliminary results are presented, upon which most of the following three sections are based. This includes the determination of the different optimum coagulant dosages under different experimental conditions. The difference between the sole use of cationic polymers and ferric nitrate at different pH and clay concentration values is also addressed.

The second section focuses on the effects of rapid mixing intensity and duration on flocculation kinetics. This includes results of using ferric nitrate and the cationic polymer as sole coagulants as well as a combination thereof. The third section is about the addition sequence effects. In addition the benefits of using dual coagulants (dual coagulants in this discussion refers to the combined use of the inorganic coagulant and the cationic polymer, unless stated otherwise) by comparing their performance to the performance of ferric nitrate as sole coagulant are presented. The fourth and last section addresses the effects of water temperature on flocculation kinetics using ferric nitrate, cationic polymers, and dual coagulants.

Sulfate effects are not presented here in a separate section. Instead, its effects on the other variables examined in this study are discussed. In other words sulfate effects will be discussed as part of the other sections.

The results are shown in graphical formats. The X axis of all figures represents the mixing time variable. This includes both rapid mixing time and slow mixing time. Rapid mixing time is represented by negative time. The zero time point is the seperation between the rapid mixing time and slow mixing time. The Y axis represents the "Ratio" value recorded by the Photometric Dispersion Analyzer (PDA). In this work the "Ratio" value is called the "Flocculation Index" to give it a more descriptive term. The results obtained using the Automatic Image Analyzer (AIA) are shown in the appendix, and will not be discussed here.

As was mentioned in the methods section, the steeper the rising limb of the Flocculation Index curve, the better the flocculation kinetics and the bigger are the resulting flocs. It should be noted that the initial Flocculation Index values, perhaps for the first 10 to 15 minutes of flocculation, are the most important values. This is because after the passage of the first 10 to 15 minutes, the flocs become big and start settling. Therefore the effects of the large flocs, which are no longer in suspension, on the Flocculation Index value are lost.

It should be noted that the problem of settling was serious in the 2 L reactor when the mixing intensity in the second half of the tapered flocculation period was reduced from 60 rpm to 30 rpm. Large flocs, especially when dual coagulants were used, settled and their effect on the Flocculation Index value was lost. Therefore, the Flocculation Index value for experiments where large flocs were formed decreased after the mixing intensity was reduced to 30 rpm. To reduce the problem of settling, the flocculation mixing intensity regime in the 18 L reactor was changed to become 15 minutes at 60 rpm followed by 15 minutes at 45 rpm for clay concentrations of 5, 25, and 50 mg/L. For experiments with clay concentration of 100 mg/L, the flocculation mixing intensity continued at 60 rpm for the whole 30 minutes. **Table 7.1** is a summary of the mixing intensity values and durations used in this study.

The majority of experiments reported in this chapter were conducted in the 18 L reactor. Only a limited number of the experiments conducted in the 2 L reactor are presented here, since most of the results obtained using the 2 L reactor are redundent. Therefore, in all the figures presented in this chapter, the results are reported for the 18 L reactor experiments, unless stated otherwise.

Table 7.1: Mixing intensity regimes used for different experimental conditions.

Variable	Parameter	Description
Clay concentration = 5,25, and 50 mg/L in the 18 L reactor	Flocculation mixing intensity	15 min. at 60 rpm (G = 56 s^{-1} at 23 °C) followed by 15 min. at 45 rpm (G = 37 s^{-1} at 23 °C)
Clay concentration = 100 mg/L in the 18 L reactor	Flocculation mixing intensity	30 min. at 60 rpm
2 L reactor experiments	Flocculation mixing intensity	15 min. at 60 rpm (G = 60 s^{-1} at 23 °C) followed by 15 min. at 30 rpm (G = 22 s^{-1} at 23 °C)
2 L reactor experiments	Rapid mixing intensity	250 rpm (G = 500 s^{-1} at 23 °C)
All experiments in the 18 L reactor except where rapid mixing intensity was evaluated	Rapid mixing intensity	250 rpm (G = 450 s^{-1} at 23 °C)
All experiments where rapid mixing intensity was evaluated	Rapid mixing intensity	2 values; either 250 rpm (G = 450 s^{-1} at 23 °C) or 400 rpm (G = 900 s^{-1} at 23 °C)

7.2 Iron (III) and Cationic Polymer Use as Sole Coagulants

Before the advantages of dual coagulants and the effects of the different variables on the flocculation kinetics were studied, preliminary studies were conducted using each coagulant as the sole coagulant. This provided a basis for the selection of the dosages in dual coagulant experiments. It also provided a basis for comparison between dual coagulant use and the sole use of each coagulant.

The experiments conducted in the present work were conducted either at pH 6.0 or 7.8. For experiments conducted at pH 7.8, sodium bicarbonate and sodium carbonate were added to get the required pH. The presence of bicarbonate at this pH had a substantial effect on the zeta potential of the particles in suspension after the coagulant addition; making it more negative. In all these experiments (conducted at pH 7.8), the zeta potential of the suspension after the coagulant, or coagulants, addition were substantially negative. Therefore, the zeta potential after the coagulat addition for these experiments will not be presented for each experimet. Instead, an average value of zeta potential for each set of experimental conditions is presented in **Table 7.2**. It should be noted that the change in zeta potential from one experiment to another (for the same coagulant dose and clay suspension) was small (± 2 mV). Zeta potential values for experiments conducted at pH 6.0 (and when it was necessary at pH 7.8) are presented as part of the figures.

First of all, the optimum dosages of the cationic polymer (Cat-Floc TL) at 5, 25, 50 and 100 mg/L kaolin clay concentration were determined. The optimum dose of Cat-Floc L for the 25 mg/L kaolin clay concentration was also determined. **Figure 7.1** shows the results

Table 7.2: Average zeta potential values for experiments conducted at pH 7.8.

Coagulant Dosage (mg/L)	Clay Concentratiom (mg/L)	Zeta Potential (mV)
2.5 ferric nitrate alone	5	-6
	25	-23
	50	-25
	100	-29
2.5 ferric nitrate + 0.1 Cat-Floc TL	25	-21
	50	-24
2.5 ferric nitrate + 0.02 Car-Floc TL	5	-6
2.5 ferric nitrate + 0.3 Cat-Floc TL	100	-20
5.0 ferric nitrate alone	5	0.0
	25	-16
	50	-20
	100	-25

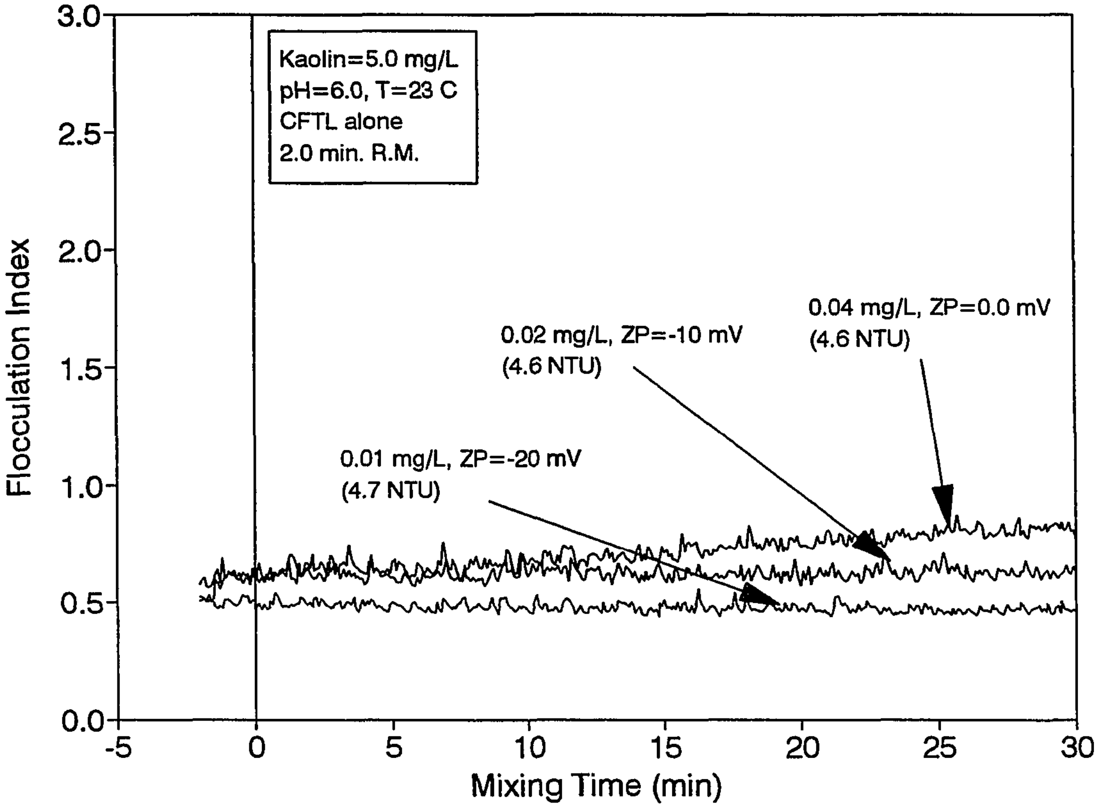


Figure 7.1: Optimum cationic polymer (CFTL) dosage determination for 5.0 mg/L kaolin clay suspension. Only supernatant residual turbidities after 30 min. of settling are presented (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

obtained using 5.0 mg/L kaolin clay concentration at pH 6.0 using Cat-Floc TL (CFTL on the figures) as the cationic polymer coagulant. It can be seen that the different coagulant doses used did not have any impact on the Flocculation Index values nor on the residual turbidity after 30 minutes of settling (NTU values shown in parantheses). The residual turbidities were the same as those of the initial turbidity values before the coagulant addition. It should be noted at this point that the magnification value (the RMS Gain reading) was set at 500 in order to measure any small increase in the Flocculation Index at this low clay concentration. **Figure 7.1** shows that the PDA or the residual turbidity could not detect any changes in the particle size distribution of the suspension at this low clay concentration suspension coagulated with a cationic polymer. It is not known whether such a growth did not occur or that the PDA could not detect such small changes in the diameter of particles. As was shown by Kang and Cleasby (1994) with 25 mg/L clay concentration, the AIA measured a change in the number of particles as high as 50 % after rapid mixing, while the PDA reading change was only about 10 %. In other words, the effects of the small particles on the Flocculation Index value is much smaller than the effect of the larger particles. The residual turbidity also is indicative of the settleability of the formed flocs. If the flocs are not large enough to settle, then the residual turbidity is a useless measure of particle growth. No optimum dose could be obtained from this figure. However, 0.02 mg/L Cat-Floc TL was picked for use in dual coagulant experiments based on the fact that 0.10 mg/L was the optimum dose for the 25 mg/L clay concentration (see below).

Experiments conducted to determine the optimum dose for the 25 mg/L kaolin clay concentration using Cat-Floc TL (CFTL in the figures) are shown in **Figure 7.2**. As shown, the optimum dose, 0.10 mg/L, produces a suspension with zeta potential value of less than zero. As a matter of fact, two doses (0.05 mg/L and 0.10 mg/L) giving zeta potential values of -18 mV and -12 mV gave better performance than a dose giving a zero zeta potential (0.20 mg/L). Similar results were observed with 50 and 100 mg/L clay concentration. In **Figure 7.3**, three doses of Cat-Floc TL producing a suspension with zeta potential values ranging from -16 mV to -21 mV gave better performance than a dose producing a zeta potential value of -8 mV for 50 mg/L clay suspension. As can be seen from this figure, three doses (0.1, 0.15, and 0.20 mg/L) gave almost similar Flocculation Index values as well as residual turbidity values (residual turbidity after 10, 20, and 30 minutes of settling are shown in paranthesis with "NTU" following these residual turbidity values). The optimum value for use in dual coagulant experiments at this clay concentration was chosen to be 0.10 mg/L. This was also based on experimental work with dual coagulants where 0.10 mg/L Cat-Floc TL produced similar Flocculation Index values and slightly better residual turbidity than 0.15 mg/L when added simultaneously with 2.5 mg/L ferric nitrate (F.N. in the figures) **(Figure 7.4)**.

Despite the fact that both the 25 and 50 mg/L kaolin clay suspensions have the same optimum Cat-Floc TL dosage at pH 6.0 and 23 °C (as shown in **Figures 7.2 and 7.3**), it should be asserted that this is by no means a contradiction to the stoichiometry concept. **Figures 7.2 and 7.3** show that there was a range of optimum coagulant doses, not only one.

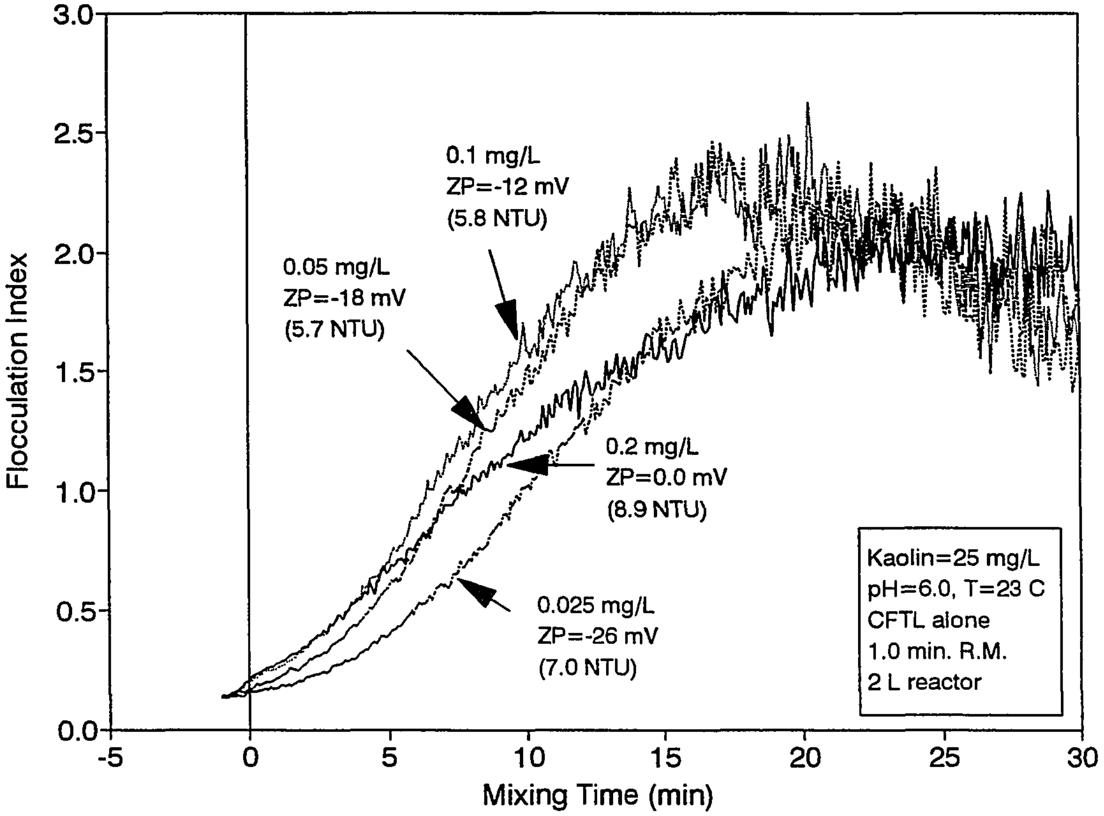


Figure 7.2: Optimum cationic polymer (CFTL) dosage determination for 25 mg/L kaolin clay suspension. Only supernatant residual turbidities after 10 min. of settling are presented in these experiments conducted using the 2 L reactor (rapid mixing = 1.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 30 rpm).

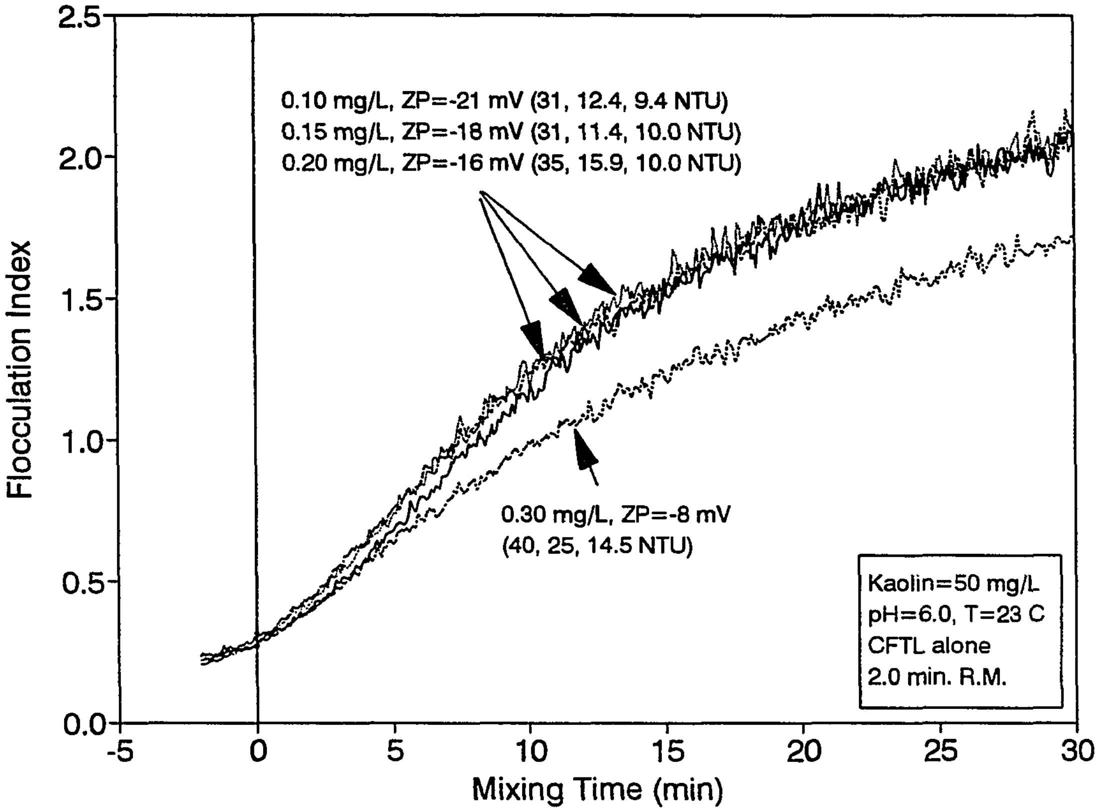


Figure 7.3: Optimum cationic polymer (CFTL) dosage determination for 50 mg/L kaolin clay suspension (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

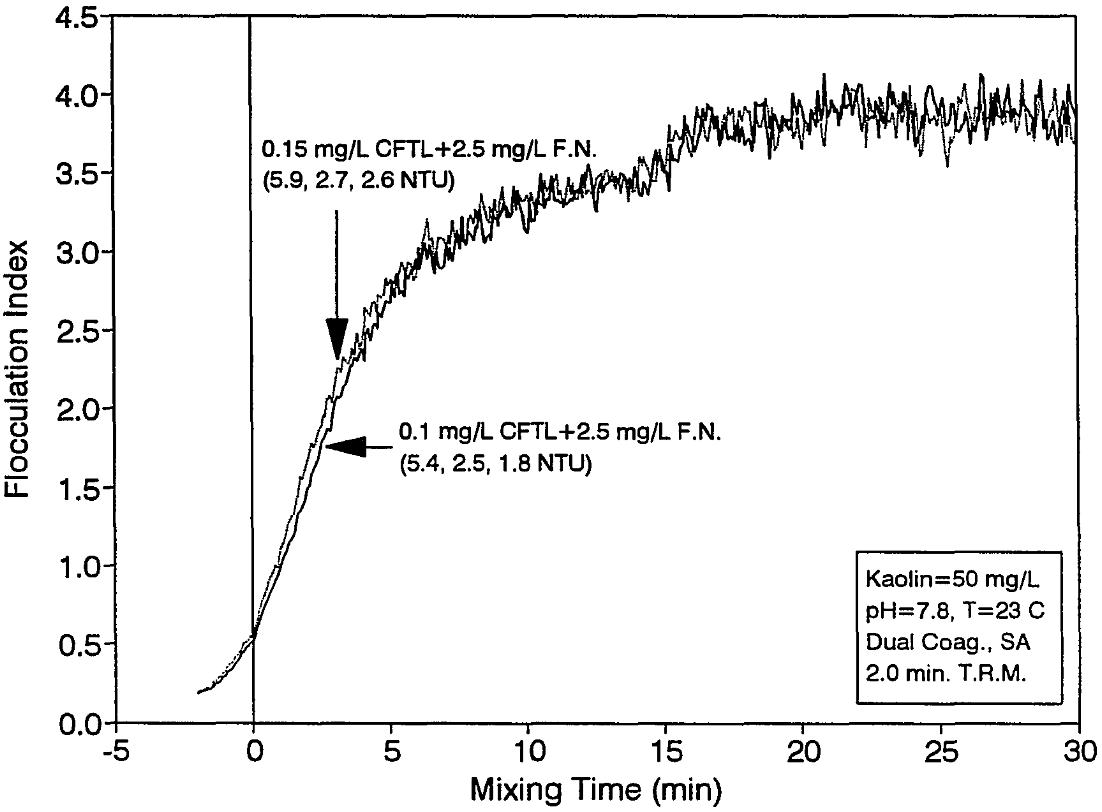


Figure 7.4: Confirmation of the Optimum cationic polymer (CFTL) dosage for 50 mg/L kaolin clay suspension using dual coagulants added simultaneously (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

In other words, one could just as easily pick 0.075 mg/L and 0.15 mg/L as optimum dosages of Cat-Floc TL for the 25 and 50 mg/L clay suspensions, respectively. Similarly, 0.10 and 0.20 mg/L cationic polymer dose for the 25 and 50 mg/L clay suspensions is a second possible combination. In short, because there was a range of possible optimum doses, the writer picked these two values (0.1 mg/L Cat-Floc TL for 25 mg/L clay suspension, and 0.1 mg/L Cat-Floc TL for the 50 mg/L clay suspension) as a best estimate for use in the remaining dual coagulants experiments.

Figure 7.5 shows the optimum Cat-Floc TL dose for the 100 mg/L clay suspension. Again, the optimum dose (0.30 mg/L) reduces the zeta potential of the suspension from about -32 mV to only -15 mV at pH 6.0. Dosages that reduce the zeta potential to values closer to zero did not perform as well.

The occurrence of the optimum performance at zeta potential values less than zero when using cationic polymers has also been observed with Cat-Floc L (a cationic polymer with higher molecular weight than Cat-Floc TL). The optimum dose of 0.10 mg/L produced a suspension with zeta potential of about -13 mV at pH 6.0 and 25 mg/L clay concentration (**Figure 7.6**) and -23 mV at pH 7.8. Cat-Floc L was only used with clay concentrations of 25 mg/L.

Preliminary experiments done using an EPI/DMA cationic polymer (Magnifloc 573 C, American Cynamid Company, Wayne, New Jersey) had an optimum dose of 0.1 mg/L that produced a suspension with near zero zeta potential (about -4 mV) at pH 6.0 and 25

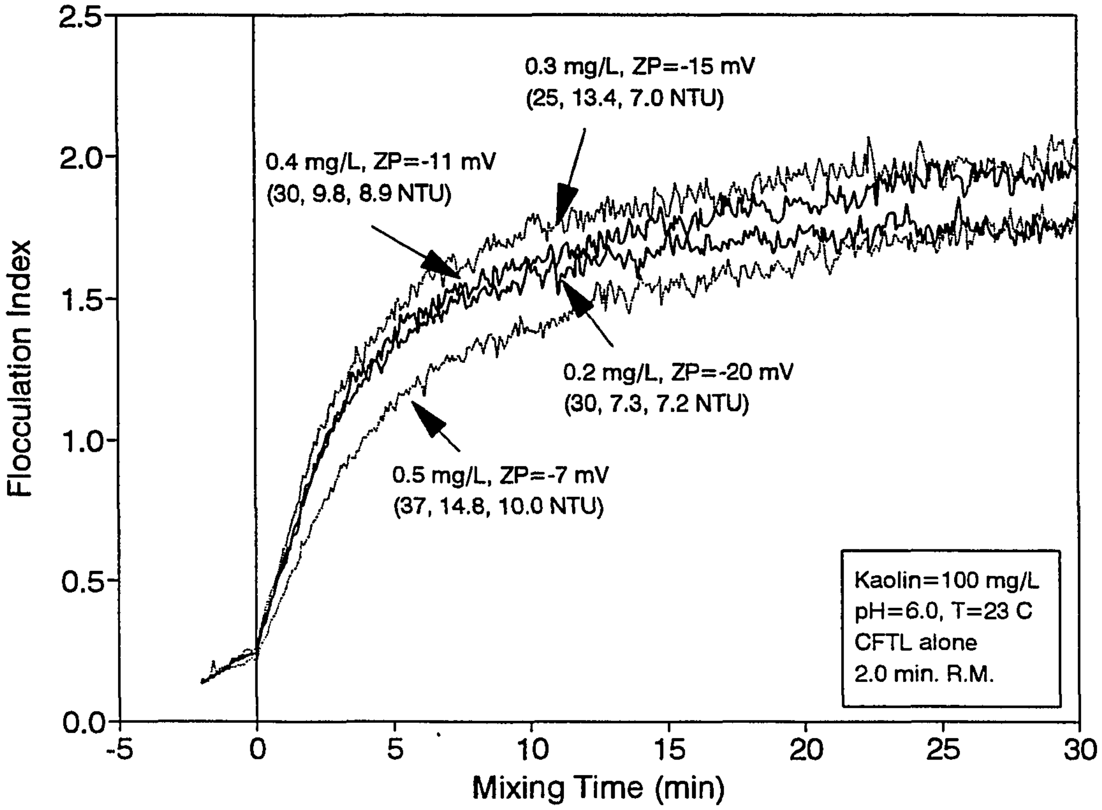


Figure 7.5: Optimum cationic polymer (CFTL) dosage determination for 100 mg/L kaolin clay suspension (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

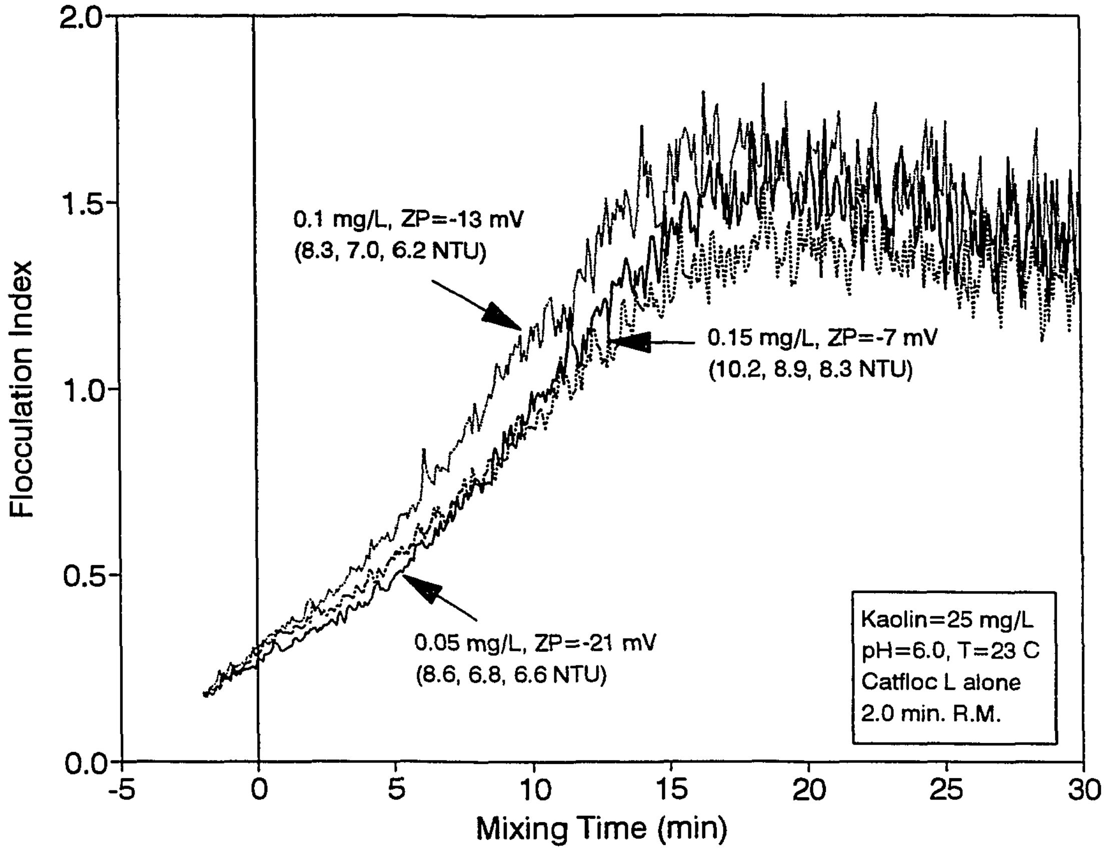


Figure 7.6: Optimum cationic polymer (CFL) dosage determination for 25 mg/L kaolin clay suspension (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

mg/L clay concentration. This same dosage was the optimum at pH 7.8 and 25 mg/L clay concentration, but the zeta potential value was about -14 mV.

It should be noted that the optimum dosages selected in all the previous figures with cationic polymers were determined at pH 6.0. The reason is that the flocculation index values at pH 7.8 and 6.0 track an almost identical path for the same cationic polymer dose, and therefore the same optimum dose was observed for the two pH values. Better residual turbidity values were observed at pH 6.0 than at pH 7.8 (residual turbidity after 10, 20, and 30 minutes of settling are shown in paranthesis in Figure 7.7 and all the figures that follow), probably due to the less negative zeta potential at pH 6.0. This is shown in **Figure 7.7** for the 25 mg/L clay suspension case.

The occurrence of optimum cationic polymer dosages that produce suspensions with zeta potential values well below zero is in agreement with some prior studies (Black and Vilaret 1969, Mohtadi and Rao 1973, Nakris et al. 1991) and contradicts other studies reported in the literature (Gregory 1976, Gregory and Lee 1990, Ghosh et al. 1985, Lindquist and Stratton 1976). Other studies found that different amounts of cationic polymer charge were needed for optimum flocculation performance of the same suspension depending on the cationic polymer charge density and molecular weight (Yeh and Ghosh 1981, Leu and Ghosh 1988).

In the present study, the molecular weights of the cationic polymers used, especially Cat-Floc TL, were not high enough to induce coagulation by bridging. Therefore, the bridging mechanism can not be used to explain the fact that optimum coagulation occurred

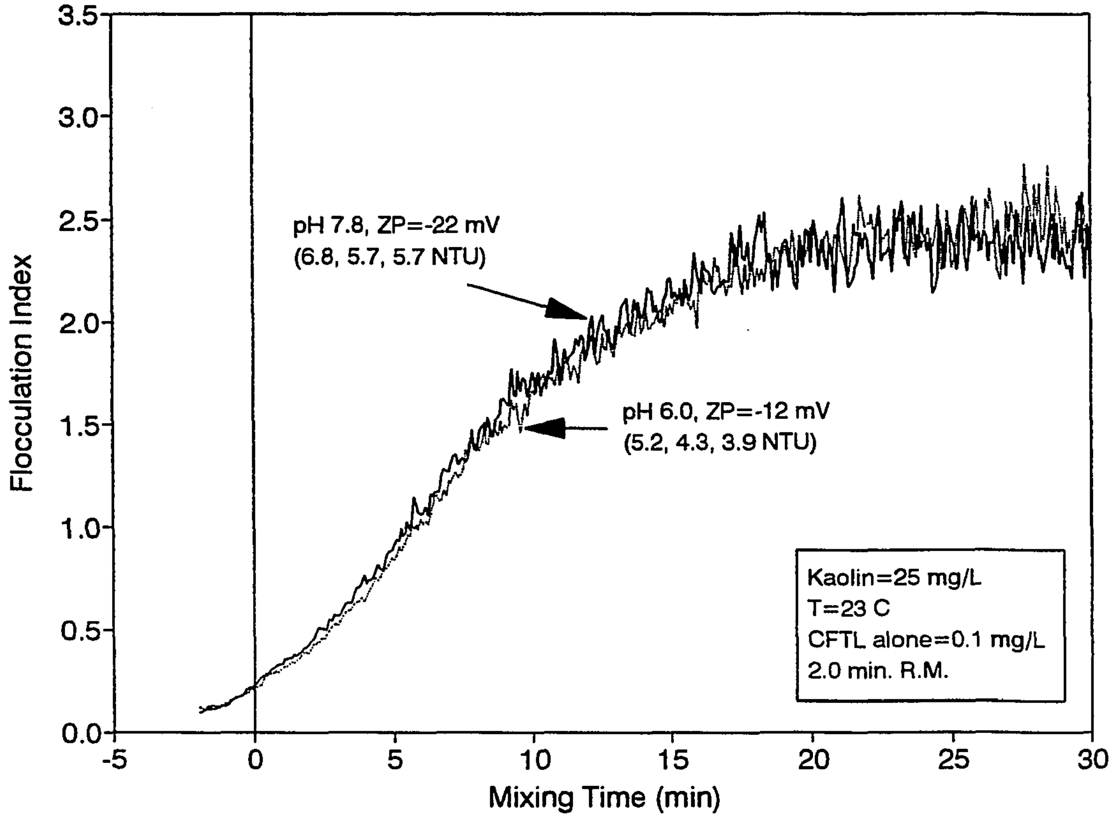


Figure 7.7: Effect of pH change on flocculation kinetics using a cationic polymer (CFTL) for 25 mg/L kaolin clay suspension (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

when the zeta potential of the suspended particles was well below zero. The writer hypothesized that the fractional coverage of the particles surface by the adsorbed cationic polymer could be used to explain such behavior.

Smellie and La Mer (1958) and Healy and La Mer (1962) proposed that (for polymer bridging between colliding particles) the collision efficiency between particles with adsorbed polymer depends on the fractional coverage of the solid surface by the adsorbed polymer. Specifically, the following equation was introduced:

$$E = \theta (1 - \theta) \tag{7-1}$$

where:

E = Collision efficiency factor by polymer bridging between colliding particles.

θ = Fractional coverage of the solid surfaces by adsorbed polymer.

From Equation 7-1, the maximum collision efficiency factor occurs when θ is equal to 0.5, with a maximum efficiency of 0.25. It should be noted that this equation was introduced for high molecular weight polymers that induce aggregation by bridging.

Hogg (1984) criticized Equation 7-1 on both theoretical and experimental bases. He stated that since collisions between an appropriately oriented patch of adsorbed polymer on one particle and a bare surface on the other particle, as well as the reverse situation, can lead to aggregation, the right hand side of Equation 7-1 should be multiplied by 2. He also stated that there is experimental evidence that optimum flocculation occurs at fractional coverages significantly less than 0.5 with collision efficiency closer to 1.0 than to 0.25. Also, optimum flocculation occurs over a broad range of polymer dosages, unlike Equation 7-1 which suggests the presence of a distinct optimum dosage.

Whether optimum collision efficiency occurs when the fractional coverage, θ, is equal to 0.5 or not, the fractional coverage plays a major role in determining the optimum dose for polymers that act by bridging. The "patch" concept (discussed earlier) when cationic polymers are used plays a significant role in determining the collision frequency factor as well as the strength of the flocs. Therefore, the fractional coverage of the solid particles with the cationic polymer should be an important parameter in determining the flocculation efficiency. If only collisions between an adsorbed cationic polymer patch on one particle and a bare surface on the other particle can lead to aggregation or at least to strong aggregation, then the fractional coverage concept, and its effect on the collision efficiency (Equation 7.1) could also be appropriate with cationic polymers. The difference would be that the overall charge on the colliding particles with adsorbed cationic polymer is also an important factor in determining the collision efficiency, unlike nonionic polymers.

The writer believes that if the optimum surface coverage of a particle by a cationic polymer is reached before the zeta potential of the particles is reduced to zero, the optimum flocculation occurs at zeta potential value less than zero. If, on the other hand, zero zeta potential of the colliding particles is reached before the optimum surface coverage is exceeded, optimum coagulation occurs at zero zeta potential. The optimum surface coverage value in the case of cationic polymer should be different than that for non charged polymers because the overall charge of the particles is also an important factor for cationic polymers. In other words, the combined effects of the fractional surface coverage and the zeta potential value of the particles determines the optimum cationic polymer dose.

In the present study, the cationic polymers used were not able to reduce the zeta potential value to zero before the optimum surface coverage was exceeded. Only Magnifloc 573 C (the highest charge density polymer used in this study) was able to reduce the zeta potential value to near zero at pH 6.0 before the optimum surface coverage was exceeded.

Once the optimum dosages for the cationic polymer were determined, it was necessary to determine the ferric nitrate optimum dosages at various clay concentration and different pH values (ferric nitrate dosages in all the figures and discussion that follow are expressed as $Fe(NO_3)_3.9H_2O$). Optimum ferric nitrate dosages at pH 7.8 could not be determined. The reason is that higher ferric nitrate dosages always gave better performance than smaller dosages, whithin the range of dosages utilized in this research (1.0 mg/L to 10 mg/L as $Fe(NO_3)_3.9H_2O$). Therefore, the dosages of ferric nitrate at pH 7.8 were randomly selected to try to avoid the sweep floc region, and to provide a basis for evaluating the effects of the different variables studied. With high ferric nitrate dosages, it would be difficult to detect the effects of the other variables such as mixing and sequence of coagulant addition.

The optimum dose of ferric nitrate for suspensions with pH values of 6.0 and no sulfate concentration was taken as that dosage that produced a suspension with zero zeta potential, despite the fact that higher dosages, in some cases, gave better performance. The optimum ferric nitrate performance (at optimum dosages giving zero zeta potential) were compared to the performance of cationic polymer as sole coagulant at similar pH, clay concentration and sulfate concentration.

Figure 7.8 presents the difference in flocculation kinetics using ferric nitrate alone and the cationic polymer alone at pH 6.0 and zero sulfate concentration. The experiments were performed in the 2 L reactor with kaolin clay concentration of 25 mg/L and room temperature. The figure shows that the cationic polymer performed better than ferric nitrate eventhough the zeta potential values were zero for ferric nitrate experiment and -26 to -12 mV for the cationic polymer experiments. Similar results were obtained in the 18 L reactor and 5 °C under similar experimental conditions (**Figure 7.9**). In **Figure 7.9** the zeta potential values were not corrected for temperature change because the writer believes that the experimental error in determining the zeta potential values is larger than the temperature correction. A change of temperature from 23 to 5 °C would decrease the zeta potential value by less than 20 %. In other words, for a zeta potential of -20 mV at 23 °C, the laser zee meter measures a value of ~ -16 mV at 5 °C.

The better performance of the cationic polymer than ferric nitrate in coagulating suspensions at pH 6.0 and zero sulfate concentration was also observed using 50 mg/L kaolin clay concentration, as shown in **Figure 7.10**. In this figure, the optimum cationic polymer dose producing a suspension with negative zeta potential outperformed the zero zeta potential suspension produced by using ferric nitrate alone.

For the 100 mg/L clay suspension at pH 6.0 and zero sulfate concentration, the ferric nitrate dose that was necessary to obtain zero zeta potential was about 5.0 mg/L. **Figure**

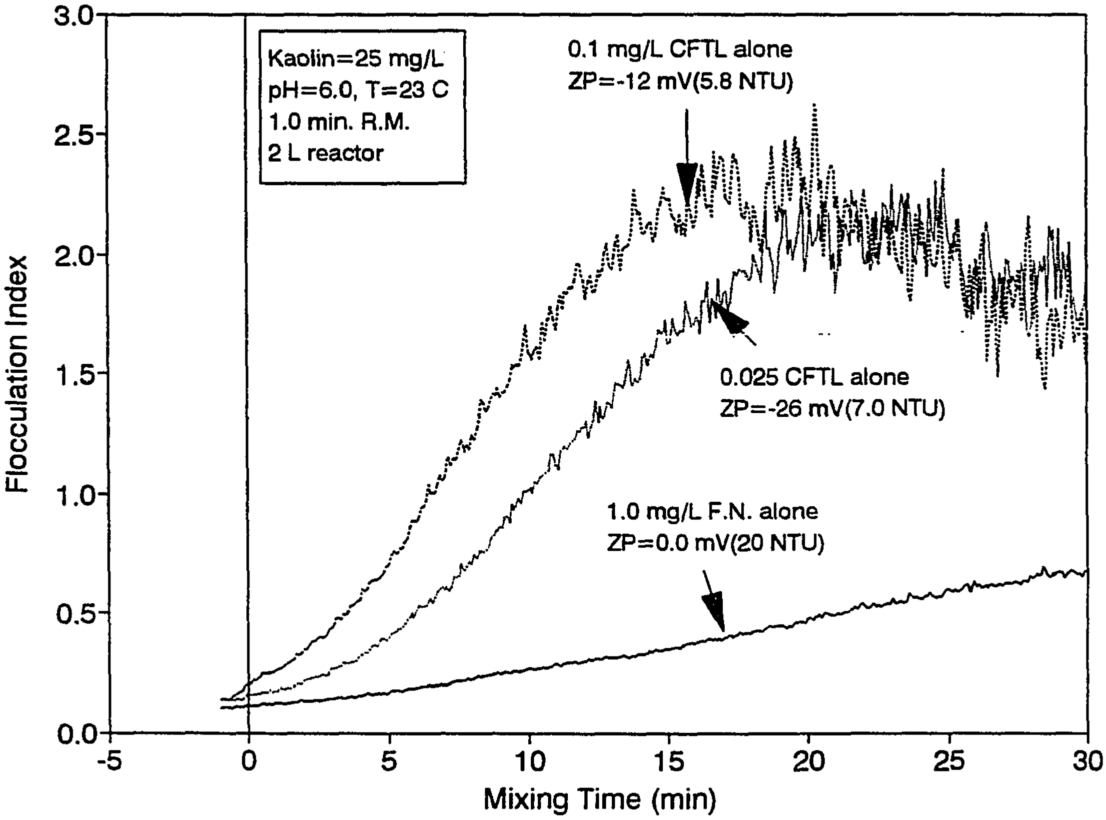


Figure 7.8: Comparison between flocculation kinetics using a cationic polymer (CFTL) alone or ferric nitrate (F.N.) alone at pH 6.0 and zero sulfate concentration, for 25 mg/L kaolin clay suspension at 23 °C. Only supernatant residual turbidity after 10 min. of settling are presented in these experiments conducted using the 2 L reactor (rapid mixing = 1.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 30 rpm).

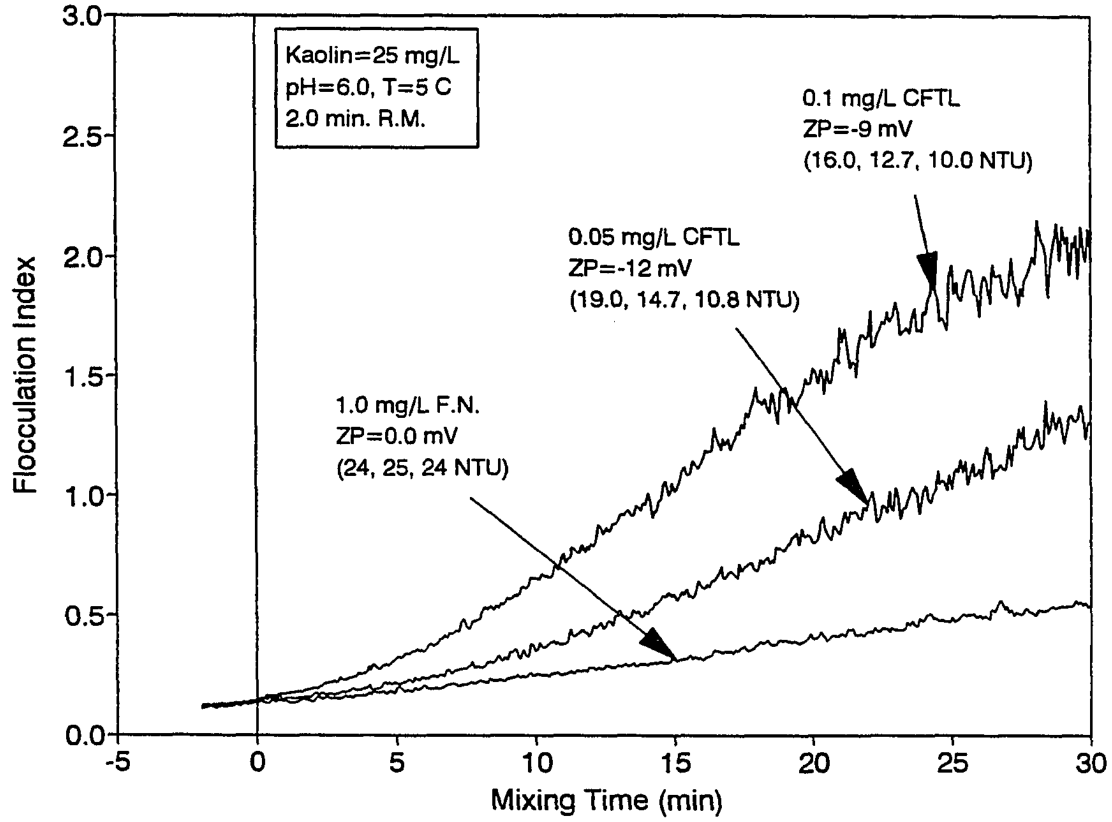


Figure 7.9: Comparison between flocculation kinetics using a cationic polymer (CFTL) alone or ferric nitrate (F.N.) alone at pH 6.0 and zero sulfate concentration, for 25 mg/L kaolin clay suspension at 5 °C (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

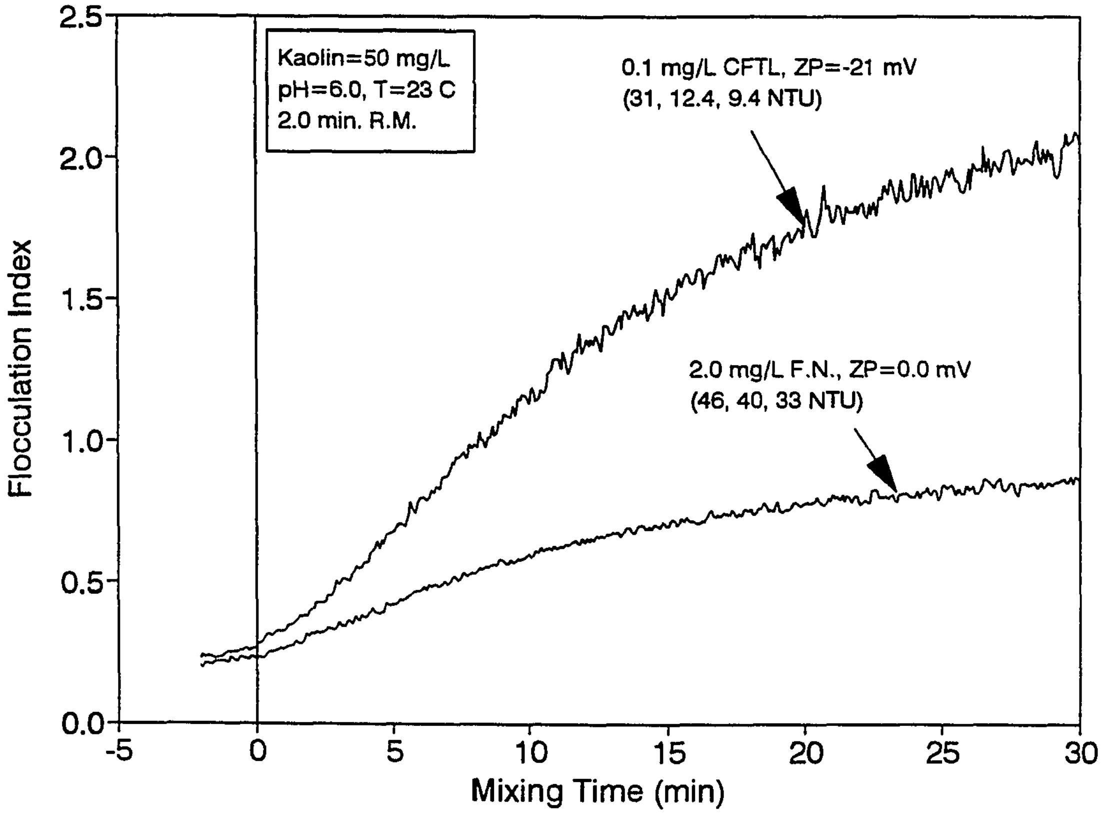


Figure 7.10: Comparison between flocculation kinetics using a cationic polymer (CFTL) alone or ferric nitrate (F.N.) alone at pH 6.0 and zero sulfate concentration, for 50 mg/L kaolin clay suspension. (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

7.11 shows a comparison between the optimum cationic polymer dose along with two ferric nitrate dosages. The figure shows that, unlike the 25 and 50 mg/L clay concentration, the 5.0 mg/L ferric nitrate dose outperformed the use of the cationic polymer alone. This is obviously due to the high ferric nitrate dose that produced a large amount of precipitate, thus improving the flocculation kinetics.

In **Figure 7.12**, both the cationic polymer and ferric nitrate each used alone at pH 6.0 and 5.0 mg/L kaolin clay concentration could not produce any increase in the flocculation index or reduce the homogenized turbidity even after 30 minutes of settling. The experiments were done in the absence of sulfate. **Figure 7.12** also shows that a 2.5 mg/L ferric nitrate at pH 7.8 was able to increase the flocculation index and produce a residual turbidity value lower than the homogenized turbidity value. This stresses the important benefit of the ferric precipitates in increasing the amount of solids present at this low clay concentration. This benefit can not be achieved using cationic polymers.

It should be noted that the above results with ferric nitrate were obtained when sulfate concentration was equal to zero. However, in the presence of 0.001 M sulfate, the results become similar to those at pH 7.8. **Figure 7.13** shows that the flocculation kinetics improves substantially in the presence of 0.001 M sulfate, and become almost similar to the case where the suspension has a pH of 7.8 for the same coagulant dosage.

From the results presented thus far, one can conclude that zero zeta potential does not necessarily produce the best flocculation kinetics. In the case where the cationic polymers were used alone, zero zeta potential produced the best results only at pH 6.0 when

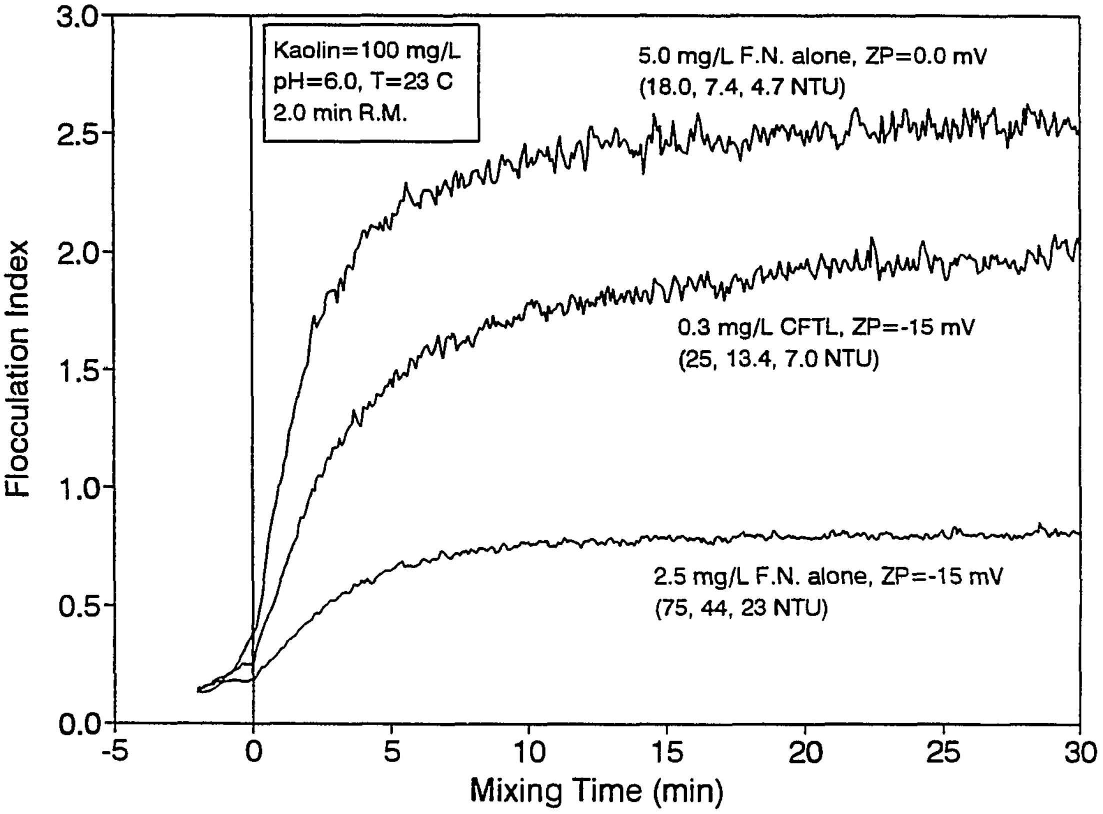


Figure 7.11: Comparison between flocculation kinetics using a cationic polymer (CFTL) alone or ferric nitrate (F.N.) alone at pH 6.0 and zero sulfate concentration, for 100 mg/L kaolin clay suspension. (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

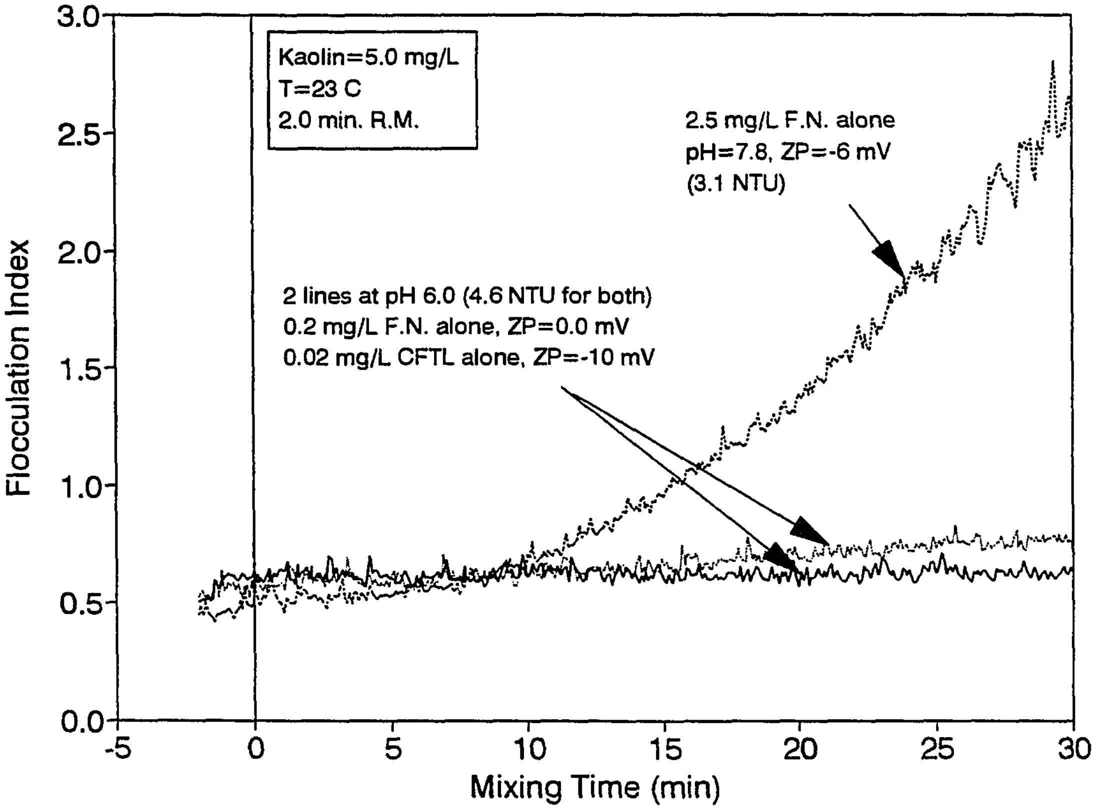


Figure 7.12: Comparison between flocculation kinetics at pH 6.0 (using either a cationic polymer (CFTL) alone or ferric nitrate (F.N.) alone with zero sulfate concentration) and pH 7.8 (using ferric nitrate alone) for 5.0 mg/L kaolin clay suspension. Only supernatant residual turbidity after 30 min. of settling are presented (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

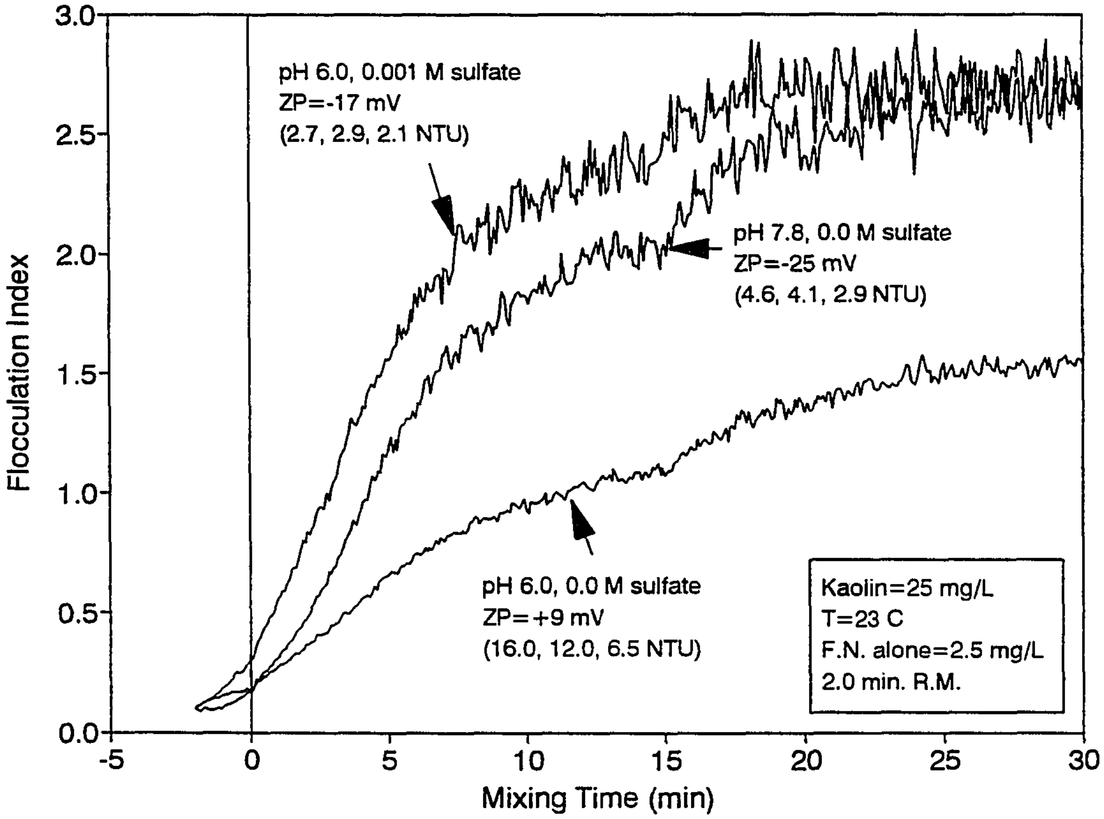


Figure 7.13: Comparison between flocculation kinetics using ferric nitrate (F.N.) alone at pH 6.0 and 0.001 M sulfate concentration, and the flocculation kinetics at pH 6.0 or 7.8 without sulfate for 25 mg/L kaolin clay suspension (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

Magnifloc 573 C was used. On the other hand, less than zero zeta potential produced the optimum flocculation kinetics when Cat-Floc TL was used. In addition, at clay concentration of 25 and 50 mg/L, the use of cationic polymers at pH 6.0 and zero sulfate concentration was superior than the use of ferric nitrate alone, despite the fact that ferric nitrate produced suspensions with zero zeta potential. This can again be explained by the "patch" theory. At pH 6.0 with zero sulfate concentration and clay concentration of 25 and 50 mg/L at zero zeta potential, the mode of coagulation is charge neutralization (i.e. there is, almost, no precipitation of ferric hydroxide due to the low dosage of ferric nitrate required to reach zero zeta potential). Therefore, the collision frequency between particles should be the same whether ferric nitrate or the cationic polymer (each used as sole coagulant) is used. This means that any differences between the flocculation kinetics is due to the collision efficiency and strength of the flocs formed. When cationic polymers alone are used, the interaction between the positive polymer patches and the original negative surface patches on adjacent particles increases the collision efficiency as well as the floc strength. This interaction is not present in the case of ferric nitrate due to the much smaller, and more numerous, hydrolysis product molecules of Fe(III).

For the 5.0 mg/L clay concentration suspension at pH 6.0 and zero sulfate concentration, neither the cationic polymer nor ferric nitrate were successful in increasing the Flocculation Index or reducing the turbidity of the suspension. This is because, the particle collision frequency is the rate limiting step at this low clay concentration. Additional particles from the precipitation of ferric hydroxide were necessary to increase the frequency of particle collisions, as was observed at pH 7.8 and 2.5 mg/L ferric nitrate dose (**Figure 7.12**).

For the 100 mg/L clay concentration at pH 6.0 and zero sulfate concentration, the ferric nitrate dosage necessary to reduce the zeta potential value to near zero was large enough (5.0 mg/L) to produce substantial ferric hydroxide precipitate. This, in combination with the already high clay concentration, improved the flocculation kinetics.

In the presence of sulfate, Kang (1994) found that the improved flocculation kinetics at acidic pH values was mainly due to an increase in the rate and extent of ferric hydroxide precipitation, thus increasing the collision frequency between particles. The improved flocculation kinetics observed at pH 6.0 in the presence of 0.001 M sulfate in the present study (**Figure 7.13**) are in agreement with Kang's findings.

7.3 Rapid Mixing Effects

Results of rapid mixing intensity and duration effects on flocculation kinetics using dual coagulants are presented in this section. But first, rapid mixing effects on flocculation kinetics using each coagulant alone are presented, since it is expected that these results would help interpret the results using dual coagulants.

It should be noted that in experiments conducted at room and cold temperatures, the mixing rpm value was kept constant. This leads to a different G value at each temperature, but the energy input per unit mass will be constant at both temperatures. Another point of difference in the following figures presenting the effects of rapid mixing duration should be kept in mind. In these figures, the Flocculation Index curves will start at the same time on the "Mixing Time" abscissa regardless of the rapid mixing duration applied for each experiment. The negative time (which represents rapid mixing time in figures other than those that discuss rapid mixing time effects) is the rapid mixing time provided for the longest rapid mixing period applied for the experiments presented in the figure. The Flocculation Index curves for experiments with less rapid mixing time are started at the same time by shifting the flocculation results to the left by an appropriate time interval. This will allow for a comparison between the Flocculation Index results as a function of total time of mixing regardless of whether it was rapid mixing or slow mixing.

Figures 7.14 through 7.17 present results obtained using the cationic polymer Catfloc TL. **Figure 7.14** shows the effects of rapid mixing time on the flocculation kinetics at 5 °C and pH 6.0 using 25 mg/L clay suspension. The rapid mixing intensity was 250 rpm ($G \cong 350\ s^{-1}$ at 5 °C). As can be seen, for a 25 mg/L clay concentration, the rapid mixing time had only a slight effect on the flocculation kinetics using a cationic polymer (for the range investigated and at the rapid mixing intensity used). Both the Flocculation Index curves and the residual turbidity values were slightly better at 2.0 minutes of rapid mixing time at this rapid mixing intensity (250 rpm).

Figure 7.15 compares between the results obtained by mixing at either 400 rpm (~700 s^{-1} at 5 °C) or 250 rpm (~350 s^{-1} at 5 °C) during a 2.0 minutes rapid mixing period when Catfloc TL was used alone. The experimental conditions are 25 mg/L clay concentration at 5 °C and pH 6.0. Both the Flocculation Index curves and the residual

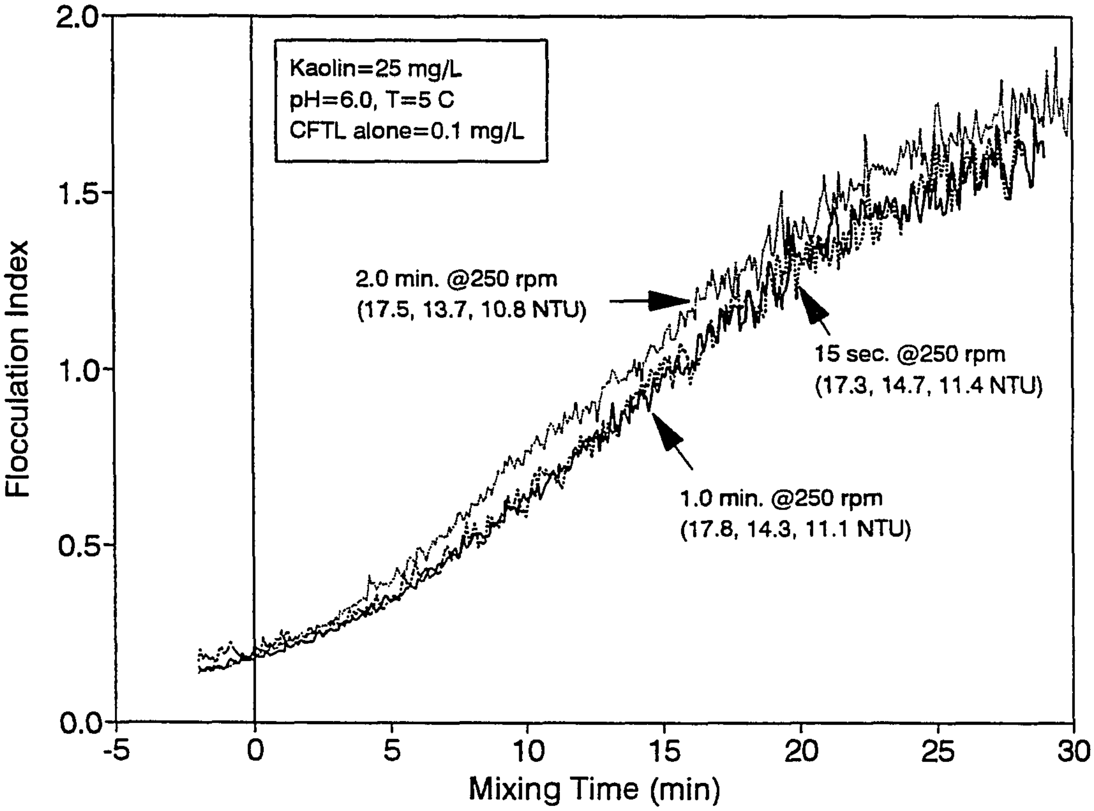


Figure 7.14: Effects of rapid mixing duration on flocculation kinetics using a cationic polymer (CFTL) alone for 25 mg/L kaolin clay suspension at 5 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

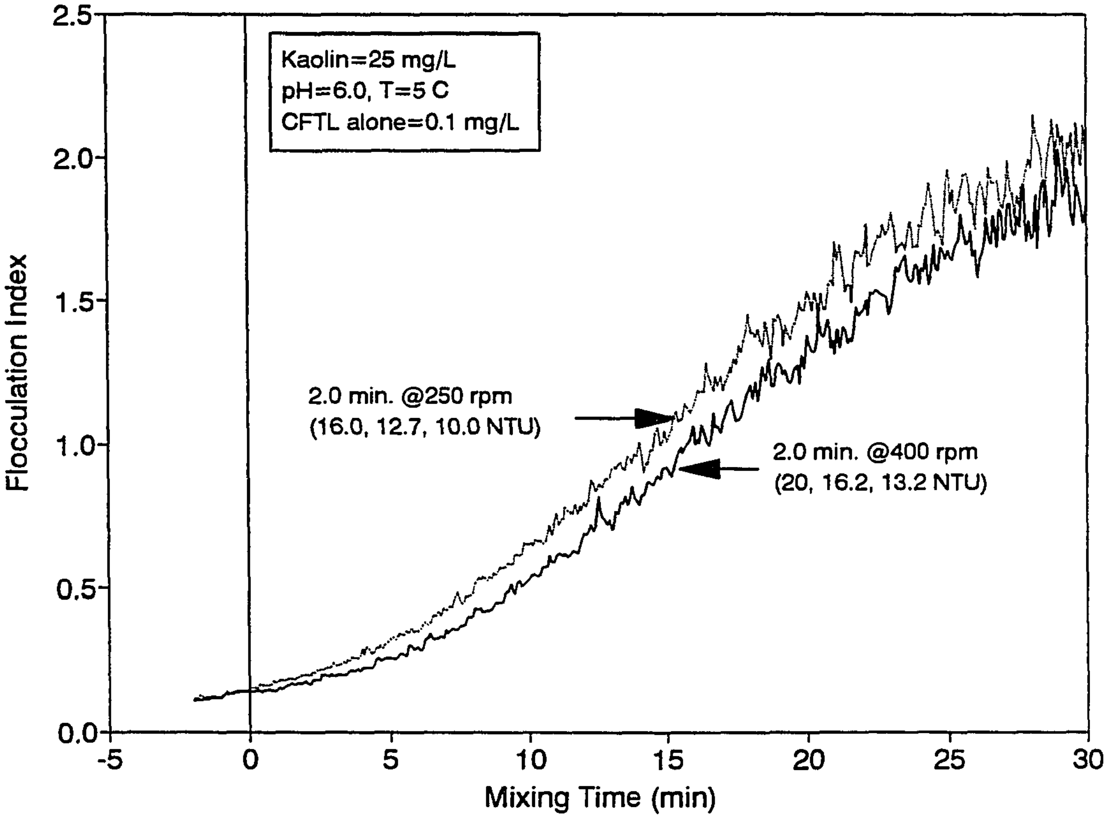


Figure 7.15: Effects of rapid mixing intensity on flocculation kinetics using a cationic polymer (CFTL) alone for 25 mg/L kaolin clay suspension at 5 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

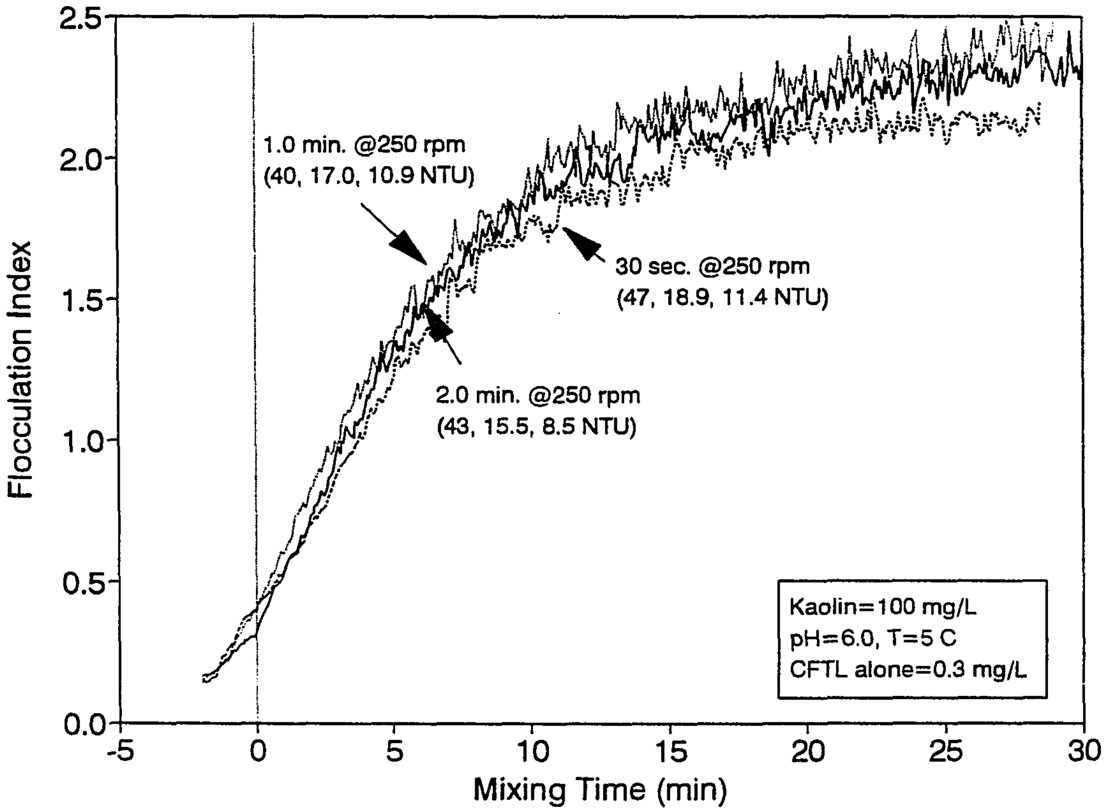


Figure 7.16: Effects of rapid mixing duration on flocculation kinetics using a cationic polymer (CFTL) alone for 100 mg/L kaolin clay suspension at 5 °C (slow mixing = 30 min. at 60 rpm).

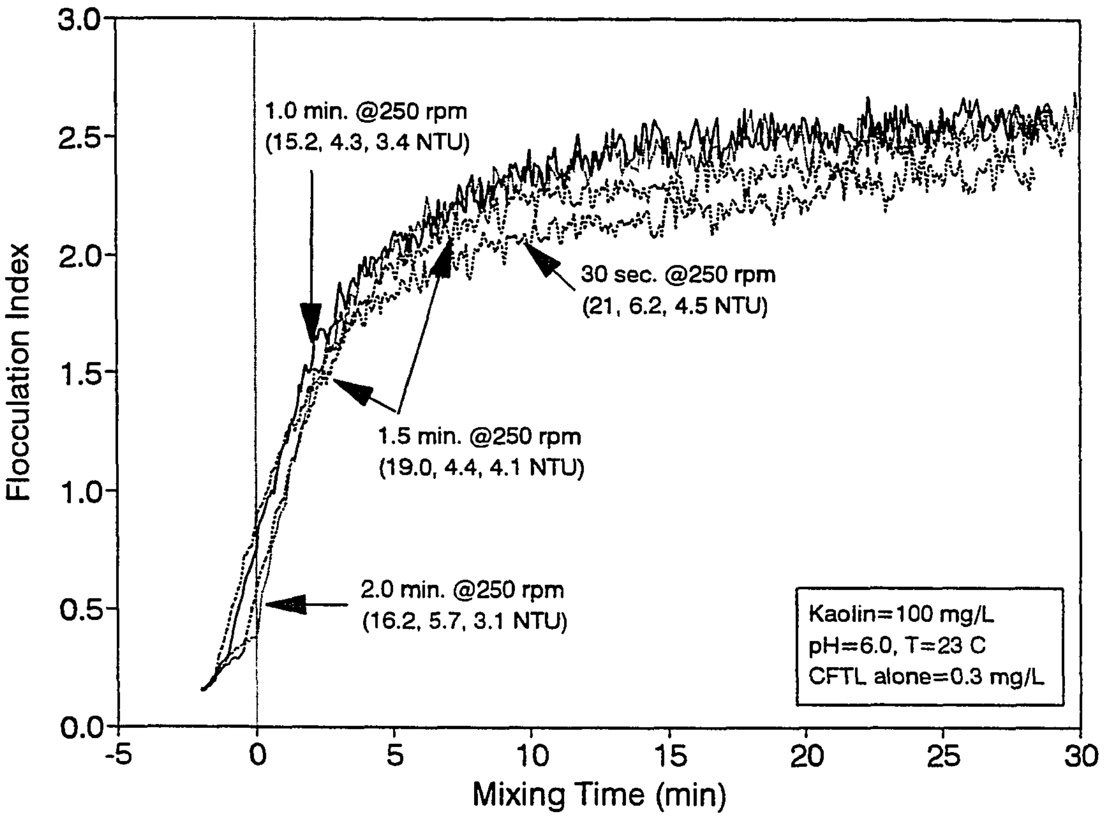


Figure 7.17: Effects of rapid mixing duration on flocculation kinetics using a cationic polymer (CFTL) alone for 100 mg/L kaolin clay suspension at 23 °C (slow mixing = 30 min. at 60 rpm).

turbidity values after 10, 20, and 30 minutes of settling were slightly better when 250 rpm mixing intensity was applied.

Figures 7.16 and 7.17 were obtained using 100 mg/L Kaolin clay suspension coagulated with Catfloc TL alone at 5 °C and room temperature, respectively. In both these figures, rapid mixing times between 30 seconds and 2.0 minutes were applied at 250 rpm (~ 450 s^{-1} at 23 °C and ~ 350 s^{-1} at 5 °C). From these figures, it can be seen that, although there were some slight differences in the residual turbidity and Flocculation Index curves, the extended rapid mixing time (2.0 min.) neither had a beneficial nor a detrimental effect on the flocculation kinetics at this clay concentration.

The effects of rapid mixing time on the flocculation kinetics using ferric nitrate alone at room temperature are shown in **Figures 7.18 through 7.20** at clay concentrations of 25, 50, and 100 mg/L, respectively. The ferric nitrate dosage was 2.5 mg/L as $Fe(NO_3)_3.9H_2O$ in all the three figures. The zeta potential values were less than -20 mV in these figures, since the pH was 7.8 and the buffer system was used (see Table 7.2).

Figure 7.18 reveals the benefits of extended rapid mixing time (within the range investigated) when ferric nitrate alone was used with 25 mg/L clay suspension. Rapid mixing for 2.0 minutes at 250 rpm significantly outperformed the shorter rapid mixing periods as evidenced by the higher Flocculation Index values. Residual turbidity values were also lower when 2.0 minutes of rapid mixing was used, but the differences were not as clear as the Flocculation Index values. The reason for that is probably the settling of the large flocs during the flocculation process as evidenced by the falling limb of the Flocculation Index

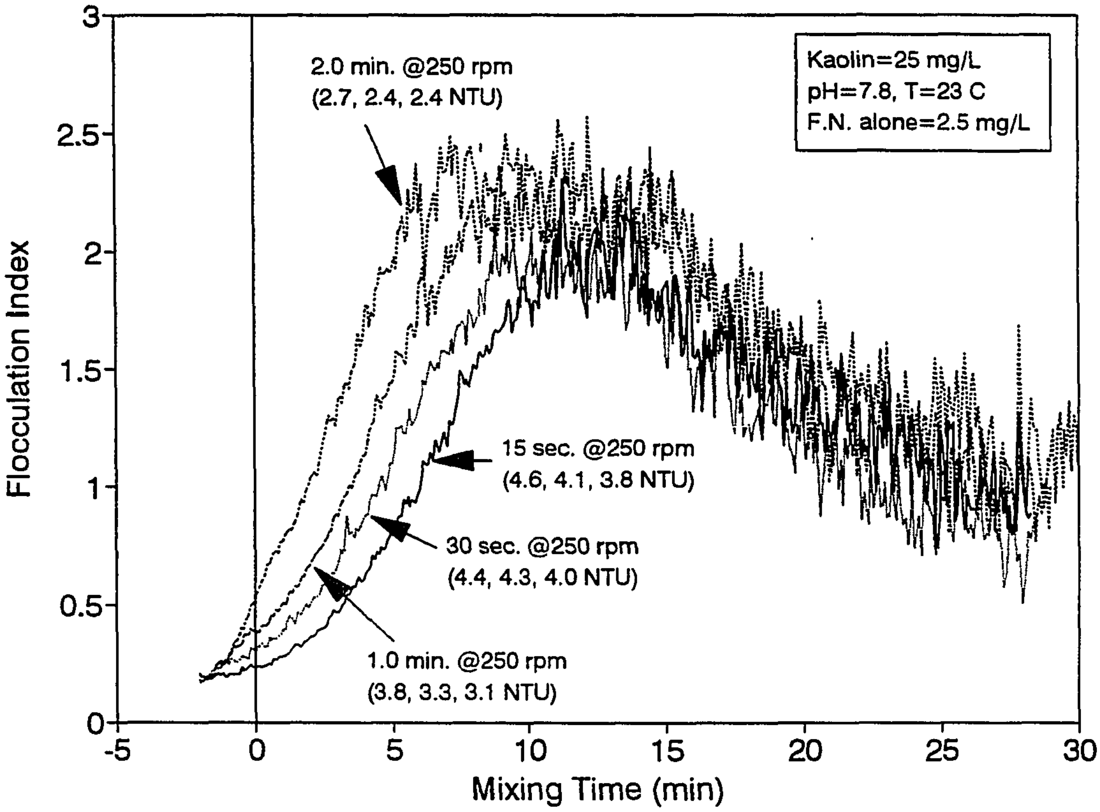


Figure 7.18: Effects of rapid mixing duration on flocculation kinetics using ferric nitrate (F.N.) alone for 25 mg/L kaolin clay suspension at 23 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

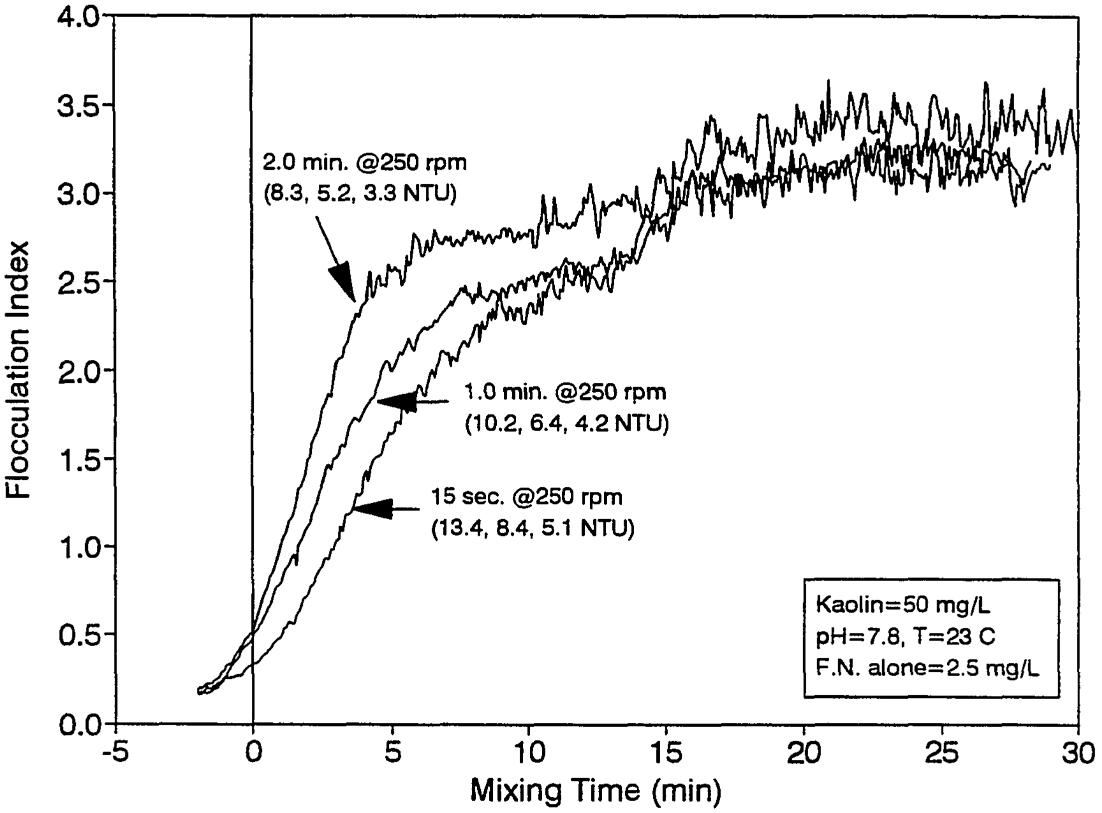


Figure 7.19: Effects of rapid mixing duration on flocculation kinetics using ferric nitrate (F.N.) alone for 50 mg/L kaolin clay suspension at 23 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

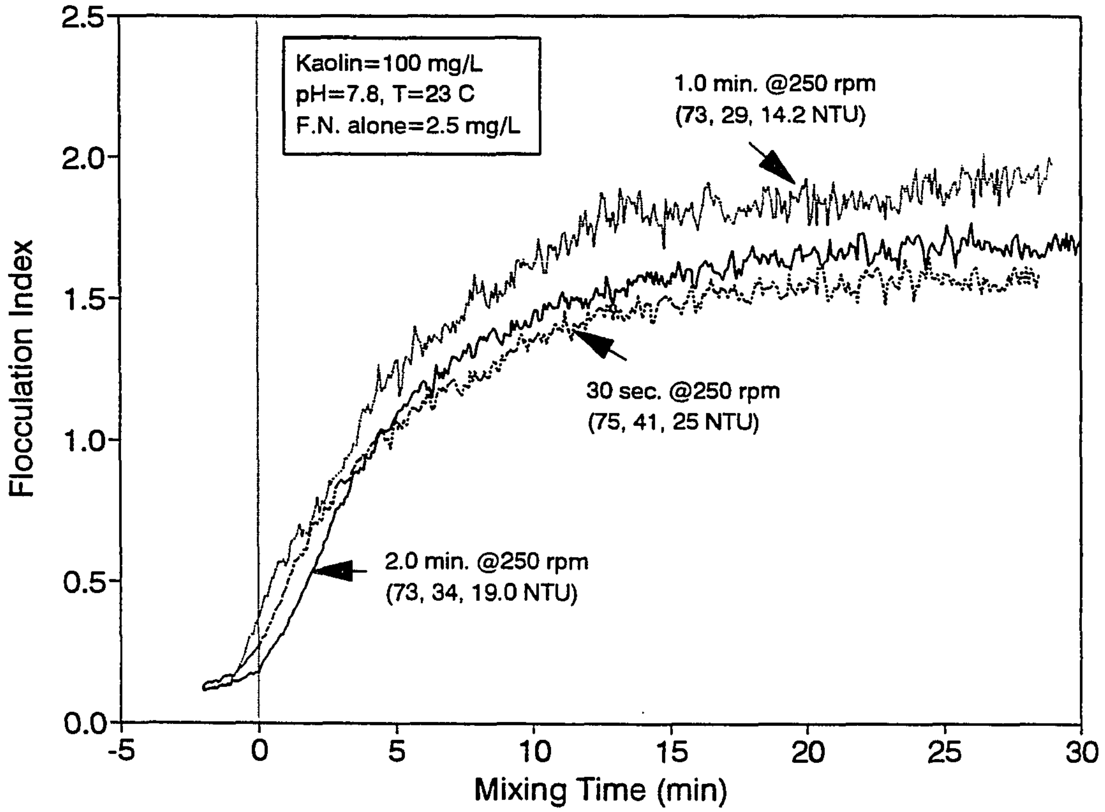


Figure 7.20: Effects of rapid mixing duration on flocculation kinetics using ferric nitrate (F.N.) alone for 100 mg/L kaolin clay suspension at 23 °C (slow mixing = 30 min. at 60 rpm).

curve. The settling of flocs is detrimental to turbidity removal, since the flocs that are supposed to pick up the smaller particles by colliding with them are lost. The settling of the flocs occurred in these experiments because the clay suspension had a higher tendency for coagulation in the this clay batch than the other batches as was mentioned earlier in chapter 6 about the changing behavior of the clay suspension.

The improvement in flocculation kinetics with extended rapid mixing when ferric nitrate alone is used was also obtained using 50 mg/L clay concentration (**Figure 7.19**). In these experiments, which were obtained using 2.5 mg/L ferric nitrate at pH 7.8, 2.0 minutes of rapid mixing at 250 rpm was superior to shorter rapid mixing times at the same mixing intensity. This was clear by both the residual turbidity and the Flocculation Index values.

The influence of rapid mixing time on flocculation kinetics with high turbidity (100 mg/L clay) suspension using ferric nitrate alone is demonstrated in **Figure 7.20**. These experiments were again conducted at pH 7.8 and room temperature with 2.5 mg/L ferric nitrate. In contrast to the previous two figures (using 25 or 50 mg/L clay concentration), 2.0 minutes of rapid mixing at 250 rpm did not outperform all shorter rapid mixing times. Rapid mixing for 1.0 minute was the best duration (among those tried) at this high clay concentration. Rapid mixing for 2.0 minutes was detrimental in this case.

This interesting feature of having different optimum rapid mixing durations with ferric nitrate depending on the clay concentration is worth discussing before any data about rapid mixing effects on dual coagulants are presented. The absence of such feature in coagulation with cationic polymers is also discussed.

The occurrence of different optimum rapid mixing durations (optimum duration is used here to indicate the best duration among the durations investigated) at different clay concentrations can be explained by investigating the Flocculation Index values in the "negative mixing time" range on the mixing time abscissa. The negative mixing time is the rapid mixing duration for the longest rapid mixing duration experiment used in constructing the figure. For example, in **Figure 7.18**, rapid mixing for the curve labeled :1.0 min. @ 250 rpm" starts at -2.0 min. and ends at -1.0 min. on the Mixing Time basis. Similarly, the curve labeled "15 sec. @ 250 rpm" had 15 seconds of rapid mixing, but it starts at -2.0 min. and ends at -1.75 min. on the Mixing Time basis. In short, the "-2.0" min. mark on Figure 7.18 represents the start of rapid mixing of all the experiments. The "0" mark represents the end of 2.0 minutes of mixing (whether rapid mixing alone or a combination of rapid plus slow mixing).

To make the discussion clearer, the first 4.0 minutes of mixing (from -2.0 to +2.0 min. on the Mixing Time basis) of **Figures 7.18, 7.20, and 7.17** are presented in **Figures 7.21, 7.22, and 7.23**, respectively.

In **Figure 7.21**, it can be seen that the Flocculation Index (which is a measure of floc sizes) after 2.0 minutes of rapid mixing time was higher than the other experiments where only part of the 2.0 minutes mixing time was rapid mixing (15, 30, and 60 seconds) and the remaining time of the 2.0 minutes was slow mixing at 60 rpm. In other words, particle growth during rapid mixing occurred at a higher rate than slow mixing for these initial stages of particle growth when ferric nitrate is used to coagulate a 25 mg/L clay suspension. The

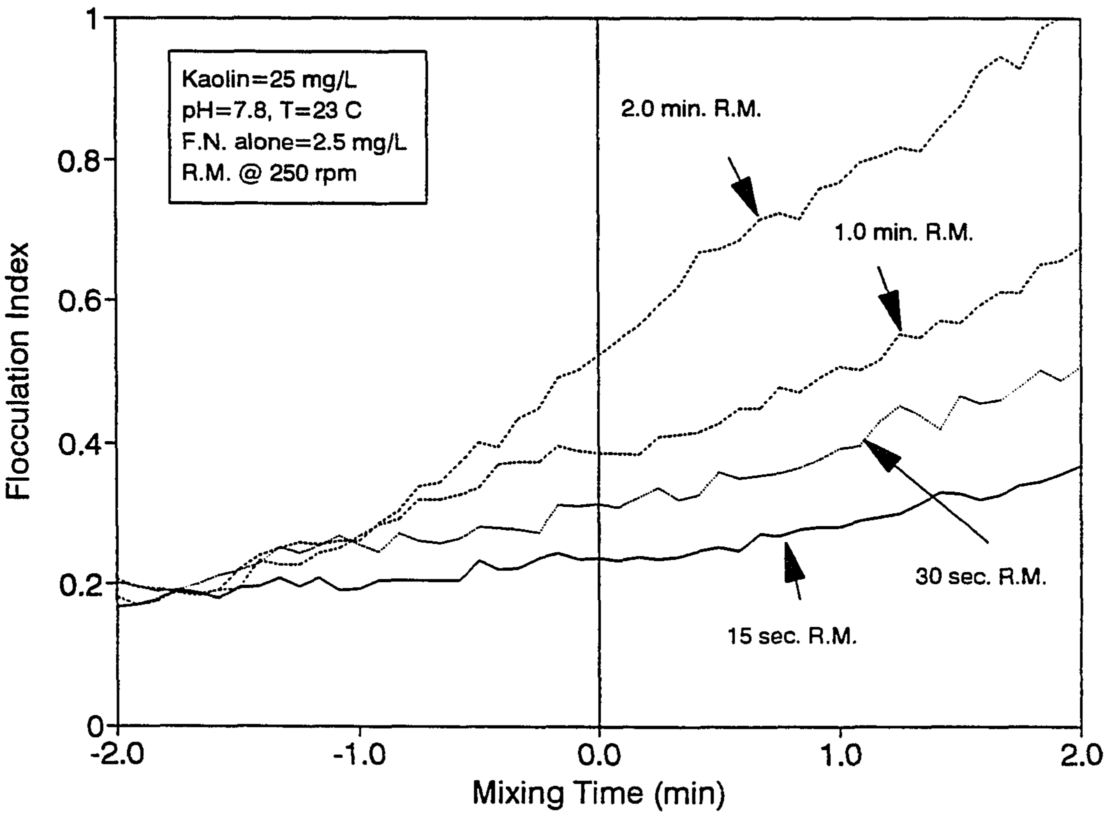


Figure 7.21: Effects of rapid mixing duration on flocculation kinetics in the initial stages of mixing using ferric nitrate (F.N.) alone for 25 mg/L kaolin clay suspension at 23 °C.

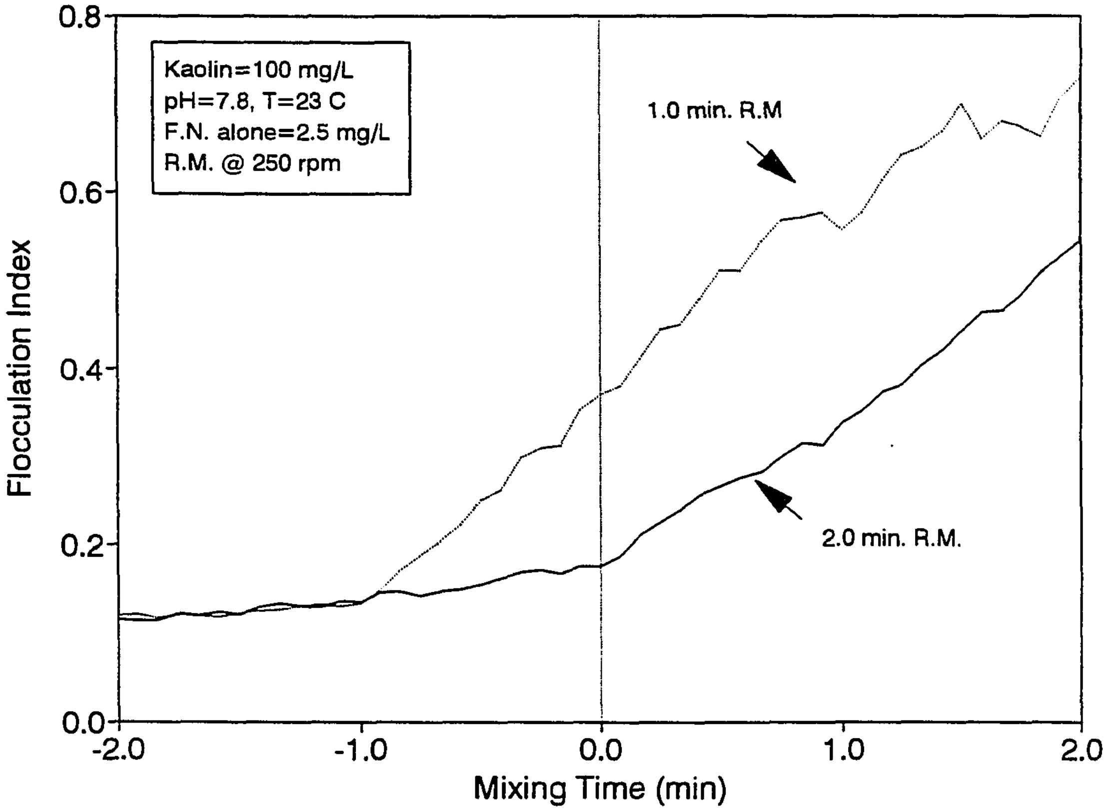


Figure 7.22: Effects of rapid mixing duration on flocculation kinetics in the initial stages of mixing using ferric nitrate (F.N.) alone for 100 mg/L kaolin clay suspension at 23 °C.

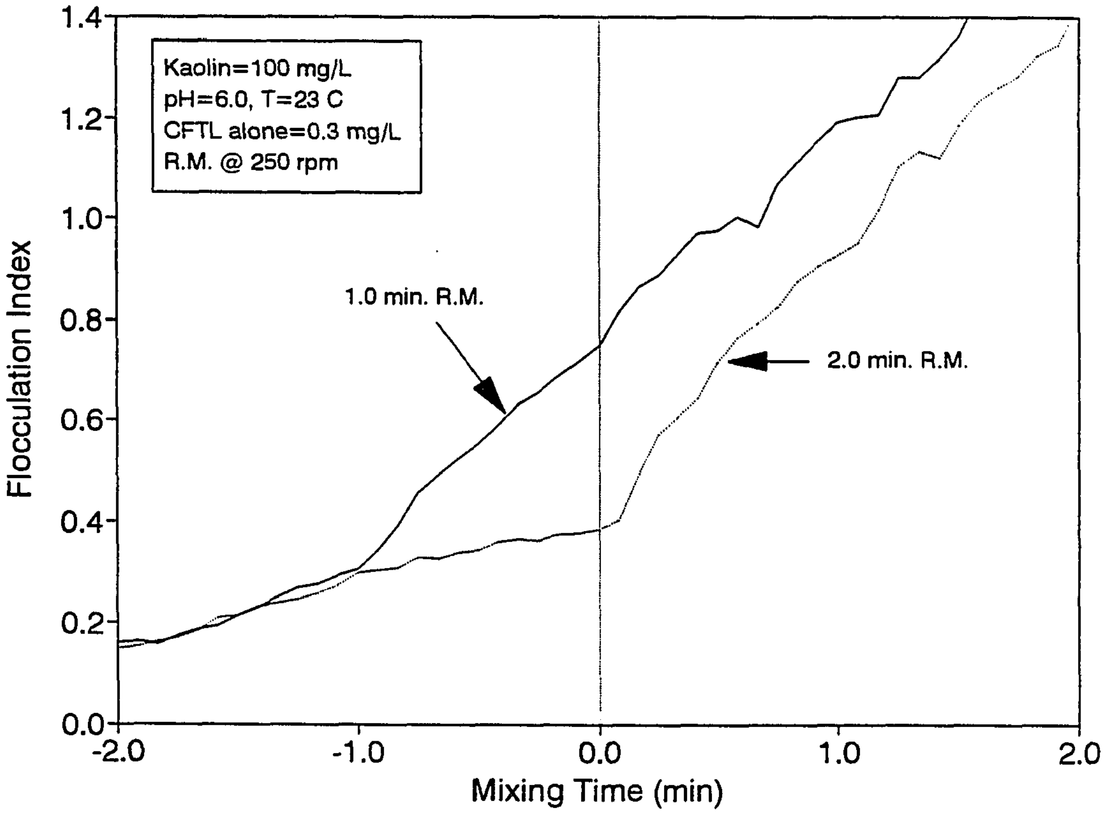


Figure 7.23: Effects of rapid mixing duration on flocculation kinetics in the initial stages of mixing using a cationic polymer (CFTL) alone for 100 mg/L kaolin clay suspension at 23 °C.

perpetuation of the higher Flocculation Index during most of the slow mixing (the first 10 to 15 minutes are the most important in interpreting the Flocculation Index results) for the experiment with 2.0 minutes of rapid mixing is an indication that the growth of particles under high mixing intensity is very important. It can affect both the flocculation process as well as the sedimentation process.

Figure 7.22 demonstrates why 1.0 minute of rapid mixing was the optimum and why 2.0 minutes of rapid mixing was detrimental at 100 mg/L clay concentration when ferric nitrate is used alone. As can be seen, after the 1.0 minute rapid mixing period ended (for the case where 1.0 minute rapid mixing duration was applied), the Flocculation Index grew rapidly. By the end of another 1.0 minute of slow mixing, the Flocculation Index reached a appreciable value. On the other hand, for the 2.0 minutes rapid mixing period experiment, the Flocculation Index for the first 1.0 minute was identical with the case where 1.0 minute of rapid mixing was applied. Rapid mixing for the second minute, however, did not allow the particles to grow as rapidly as 1.0 minute of slow mixing at 60 rpm (the second minute in the 1.0 minute rapid mixing experiment). The second rapid mixing minute prevented the flocs formed during rapid mixing from growth and probably started breaking up of these flocs. Particles that result from breakage of flocs have a lower tendency to agglomerate. At this high clay concentration (100 mg/L) particles collide at a higher rate than at lower clay concentration (25 or 50 mg/L) and therefore needs a shorter time to reach a specific diameter. Rapid mixing should continue until this specific diameter (probably a fraction of the equilibrium diameter) is reached.

Figure 7.23 shows a comparison between the first 4.0 minutes of mixing using cationic polymers (Catfloc TL) and 100 mg/L suspension. Only 1.0 minute and 2.0 minutes of rapid mixing time curves are presented for clarity. At this high clay concentration, again 2.0 minutes of rapid mixing prevented the particles from growth (and probably caused breakage of the flocs) during the second minute of rapid mixing. However, unlike the case where ferric nitrate was used, the Flocculation Index after 2.0 minutes of rapid mixing has passed increased rapidly and rapidly reached the 1.0 minute curve. It seems that the second rapid mixing minute did not hurt the flocs formed with cationic polymers at the end of the first minute of rapid mixing as much as it did with flocs coagulated with ferric nitrate alone.

The effects of rapid mixing time on the flocculation kinetics using dual coagulants for 25 mg/L clay suspension and pH 7.8 are shown in **Figures 7.24 through 7.26** at 23 °C. **Figure 7.24** presents the results obtained using a combination of 0.1 mg/L Catfloc L and 2.5 mg/L ferric nitrate added simultaneously. The simultaneous addition was found to be the best addition sequence (see section 7.4), and therefore only rapid mixing effect on dual coagulants when added simultaneously will be discussed here. Rapid mixing for 2.0 minutes in Figure 7.24 outperformed the shorter rapid mixing times (30 sec. and 1.0 min.) investigated. The higher Flocculation Index for the 2.0 minutes rapid mixing curve at the "0" time mark is obvious. Again, particles grew at a higher rate during the rapid mixing period of 2.0 minutes at 250 rpm with dual coagulants than at a lower mixing intensity (rapid mixing for either 1.0 min. or 30 sec. and slow mixing at 60 rpm for the remaining of the 2.0 minutes). The anomaly in the residual turbidity values is related to the settling of the big

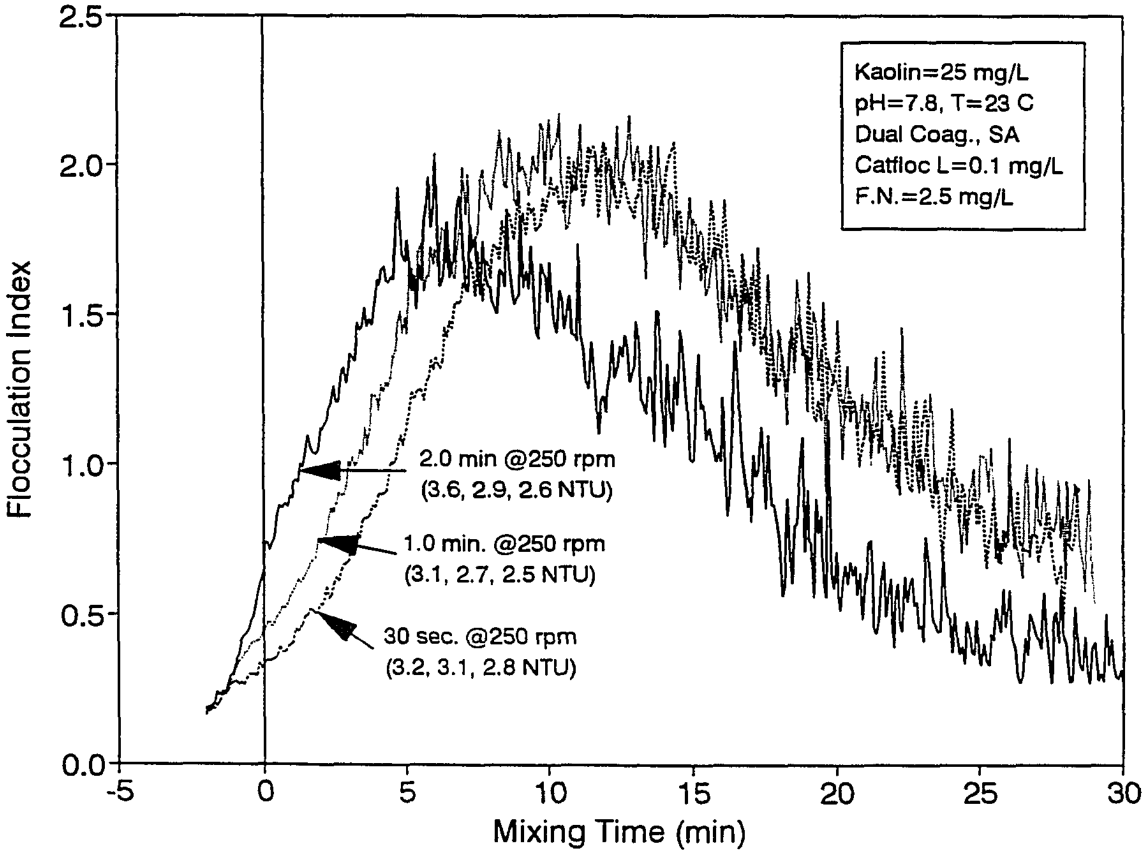


Figure 7.24: Effects of rapid mixing duration on flocculation kinetics using dual coagulants (CFL (a higher molecular weight polymer than CFTL) + F.N.) added simultaneously for 25 mg/L kaolin clay suspension at 23 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

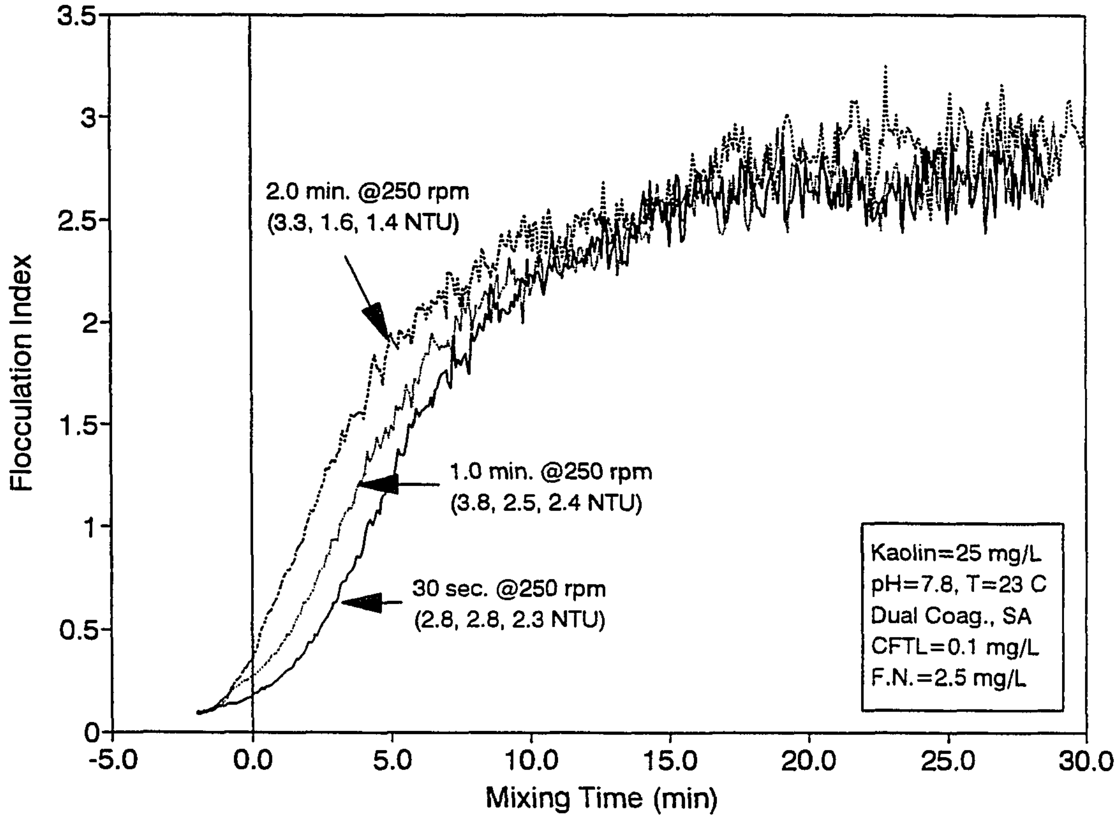


Figure 7.25: Effects of rapid mixing duration on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 25 mg/L kaolin clay suspension rapid mixed at 250 rpm at 23 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

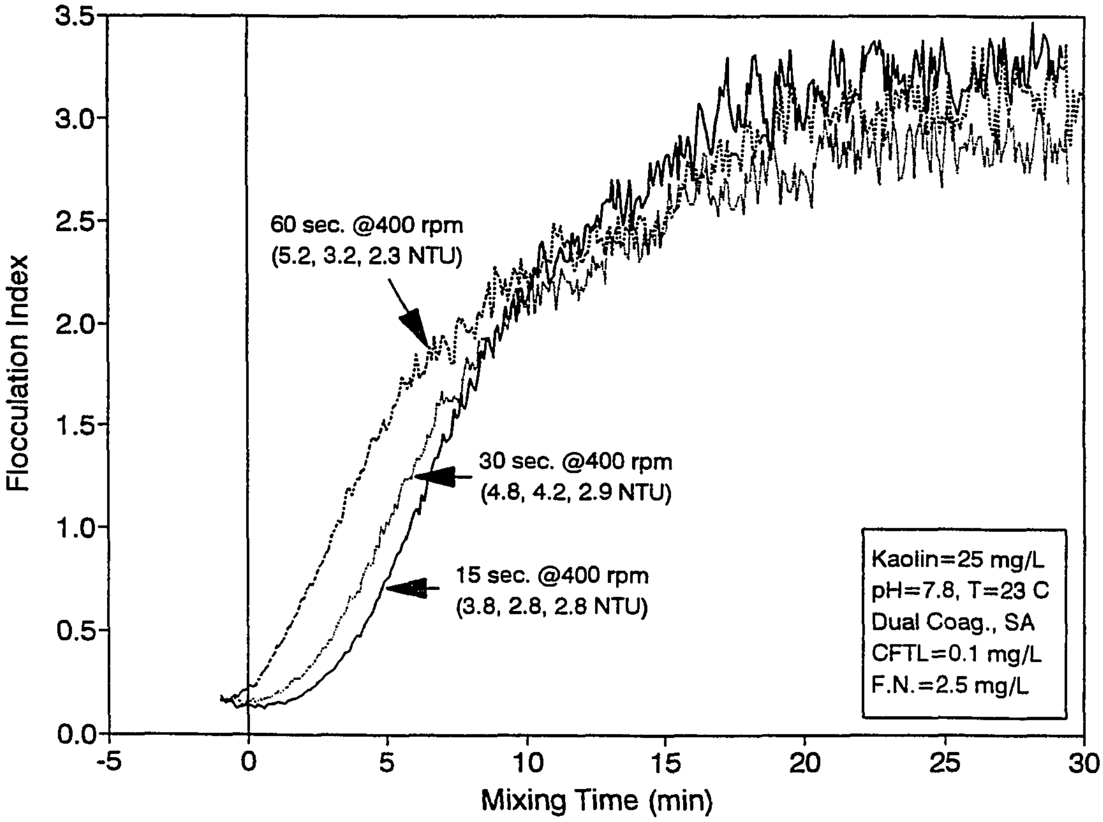


Figure 7.26: Effects of rapid mixing duration on flocculation kinetics using dual coagulants (CFL + F.N.) added simultaneously for 25 mg/L kaolin clay suspension rapid mixed at 400 rpm at 23 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

flocs during slow mixing as evidenced by the falling limb of the Flocculation Index curve, as discussed previously in connection with **Figure 7.18**.

Figures 7.25 and 7.26 show the rapid mixing period effects using Catfloc TL and ferric nitrate added simultaneously for 25 mg/L clay suspension, using 250 rpm and 400 rpm mixing intensities, respectively. In both these figures, longer rapid mixing time (60 sec. for 400 rpm experiments and 2.0 minutes for 250 rpm experiments) outperformed the shorter mixing periods, within the ranges studied. This was evidenced by both the Flocculation Index curves and the residual turbidity values after 10, 20, and 30 minutes of settling. Again, the higher value of the Flocculation Index at the "0" time mark for the longer rapid mixing period curves is evident.

For 50 mg/L clay suspension, **Figure 7.27** shows that 2.0 minutes of rapid mixing at 250 rpm was superior to the shorter periods. These experiments were conducted using 0.1 mg/L Catfloc TL added simultaneously with 2.5 mg/L ferric nitrate at pH 7.8 and room temperature.

Figures 7.28 and 7.29 present the influence of rapid mixing duration on flocculation kinetics using dual coagulants at 100 mg/L clay concentration at 5 °C and 23 °C , respectively. Catfloc TL (0.3 mg/L) and ferric nitrate (2.5 mg/L) were added simultaneously at pH 7.8 in both these figures. The optimum rapid mixing time was 1.0 minute in experiments conducted at 5 °C (**Figure 7.28**), whereas 1.0 and 2.0 minutes of rapid mixing gave similar Flocculation Index results at 23 °C (**Figure 7.29**) but better turbidity removal for 2.0 minutes rapid mixing. The detrimental effect of 2.0 minutes rapid mixing at 5 °C is

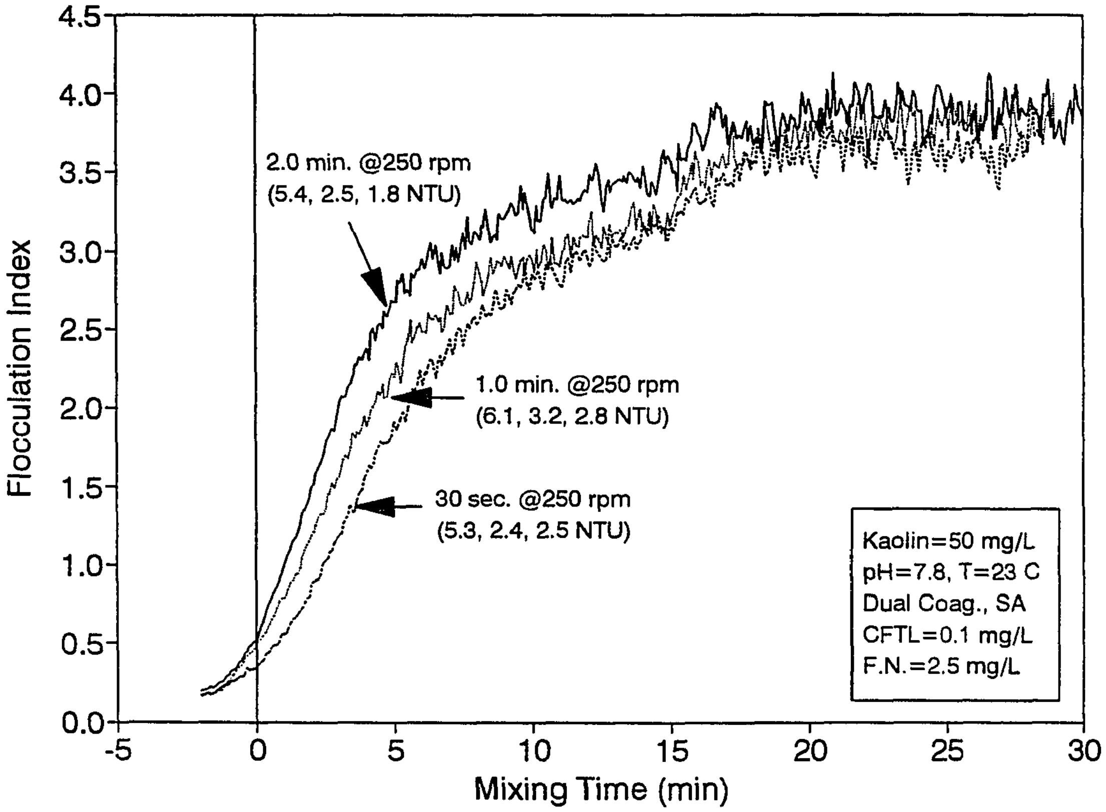


Figure 7.27: Effects of rapid mixing duration on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 50 mg/L kaolin clay suspension at 23 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

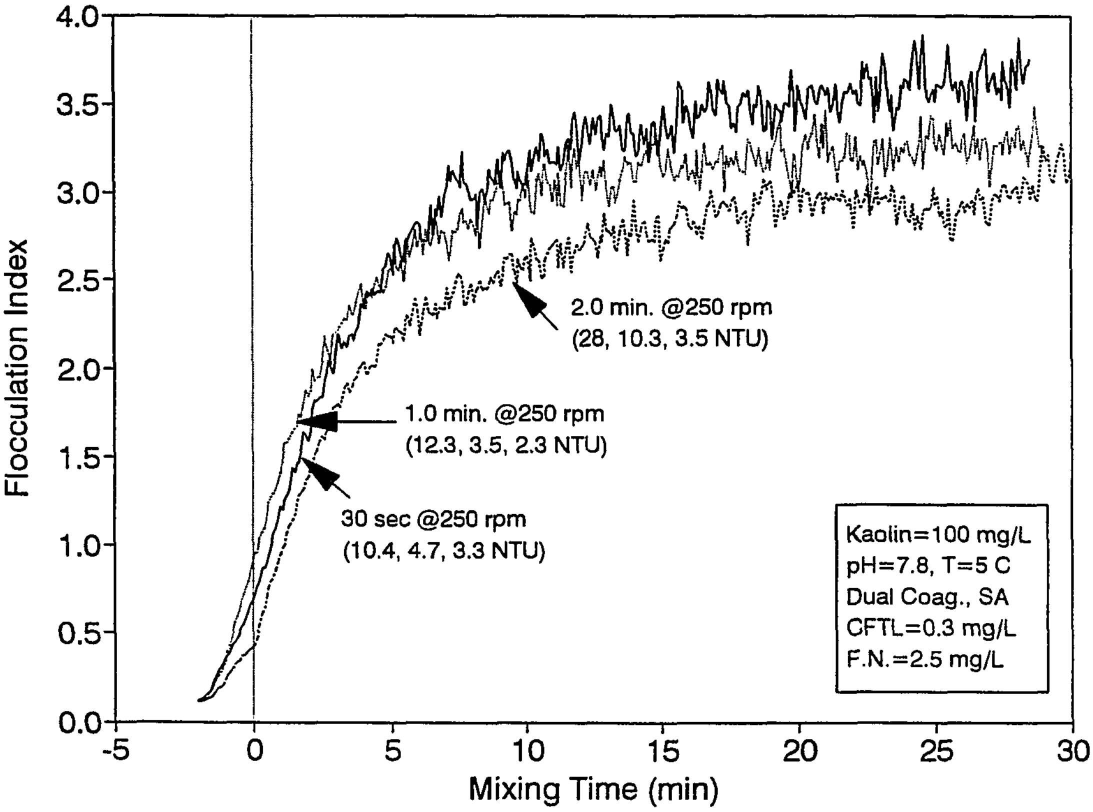


Figure 7.28: Effects of rapid mixing duration on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 100 mg/L kaolin clay suspension at 5 °C (slow mixing = 30 min. at 60 rpm).

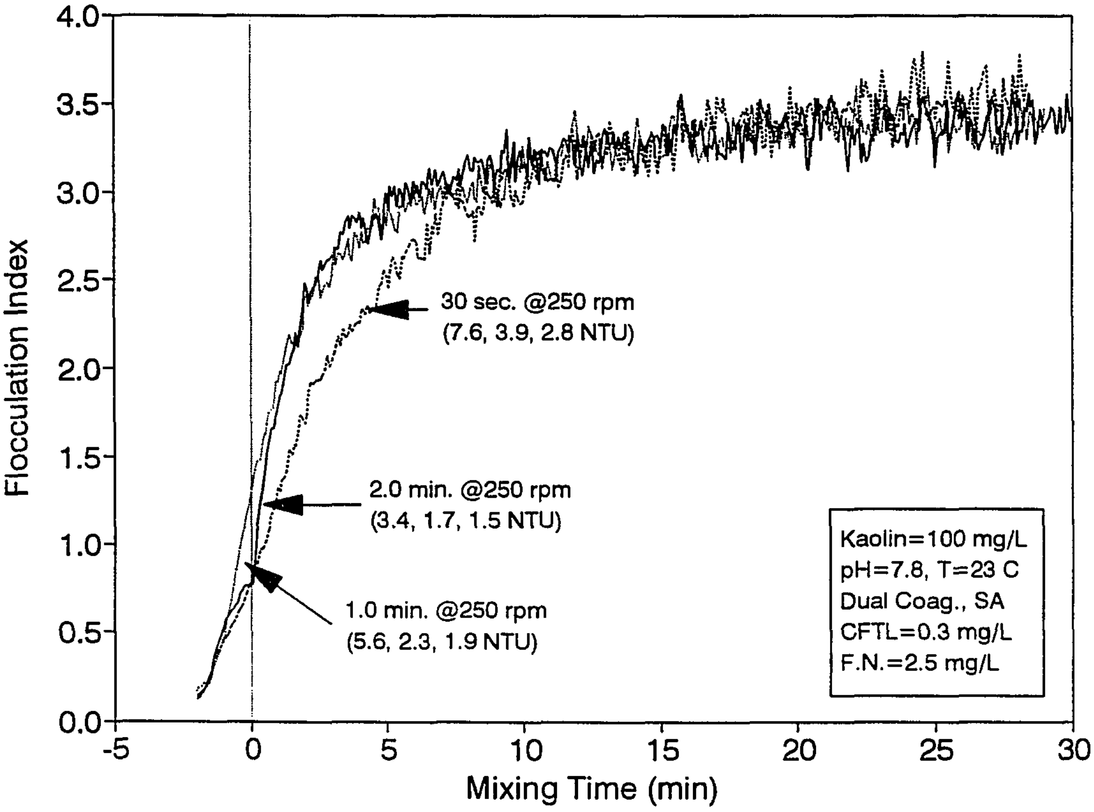


Figure 7.29: Effects of rapid mixing duration on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 100 mg/L kaolin clay suspension at 23 °C (slow mixing = 30 min. at 60 rpm).

pronounced, especially when residual turbidity values after 10 minutes (28 vs 12.3 NTU) and 20 minutes (10.3 vs 3.5 NTU) of settling are compared. Even 30 seconds of rapid mixing outperformed the 2.0 minutes rapid mixing time as the residual turbidity values and the Flocculation Index values show. The 1.0 minute optimum rapid mixing time for 100 mg/L clay concentration at 5 °C (**Figure 7.28**) is similar to the case when ferric nitrate alone was used at 23 °C (**Figure 7.20**). Again a comparison between the Flocculation Index values in **Figure 7.29** at the "0" time mark proves that the 2.0 minutes rapid mixing time is detrimental.

The slight difference between the flocculation kinetics when either 1.0 minute or 2.0 minutes of rapid mixing period when using dual coagulants at 23 °C for 100 mg/L clay suspension (**Figure 7.29**) is probably due to the formation of stronger flocs at room temperature than at cold temperature. Flocs formed using dual coagulants are also stronger than flocs formed using ferric nitrate alone. Therefore, the Flocculation Index curve for the 2.0 minutes rapid mixing time caught up with the 1.0 minute rapid mixing time curve very quickly (in about 1 or 2 minutes after the "0" time mark) which is similar to the case where the cationic polymer was used alone (**Figures 7.16 and 7.17**).

Now after establishing the importance of rapid mixing time, lets investigate the rapid mixing intensity effects on the flocculation kinetics. Previously (**Figure 7.15**), it was shown that 2.0 minutes of rapid mixing at 400 rpm was inferior to 2.0 minutes of rapid mixing at 250 rpm using Catfloc TL alone at 25 mg/L clay concentration. The effects of rapid mixing intensity on flocculation kinetics using dual coagulants are shown as a comparison between experiments with different mixing intensities but with the same mixing time or as a comparison between experiments done at the same Gt product value. Both of these comparisons are shown in **Figures 7.30 and 7.31** for the 25 mg/L clay suspension at 23 °C and pH of 7.8. **Figure 7.30** compares between experiments conducted at 400 rpm (~ 900 s^{-1}) rapid mixing for 15 or 30 seconds with experiments conducted at 250 rpm (~ 450 s^{-1}) for 30 and 60 seconds with everything else being the same. The figure shows that for the same Gt value, the rapid mixing regime with lower mixing intensity (G) and longer duration outperforms the other alternative in both the Flocculation Index values and the residual turbidity values. For the same rapid mixing duration (30 sec.) but with different mixing intensities (250 vs 400 rpm), the Flocculation Index curves were almost similar, but the residual turbidity values were in favor of using the lower mixing intensity (250 rpm).

Figure 7.31 is similar to **Figure 7.30** but compares between longer rapid mixing times. Rapid mixing times of 30 seconds and 1.0 minute mixed at 400 rpm are compared to 1.0 minute and 2.0 minutes rapid mixing times at 250 rpm. For the same Gt values, experiments with the lower G value and longer mixing times produced better turbidity removal and slightly better Flocculation Index values. When experiments with the same rapid mixing time (1.0 min.) at two rapid mixing intensities (250 or 400 rpm) are compared, the high mixing intensity gave better Flocculation Index values but worse settling turbidity values. It is believed that the reason for this anomaly is that high mixing intensity induces breakup of the flocs thus producing small particles that are harder to reaggregate. These

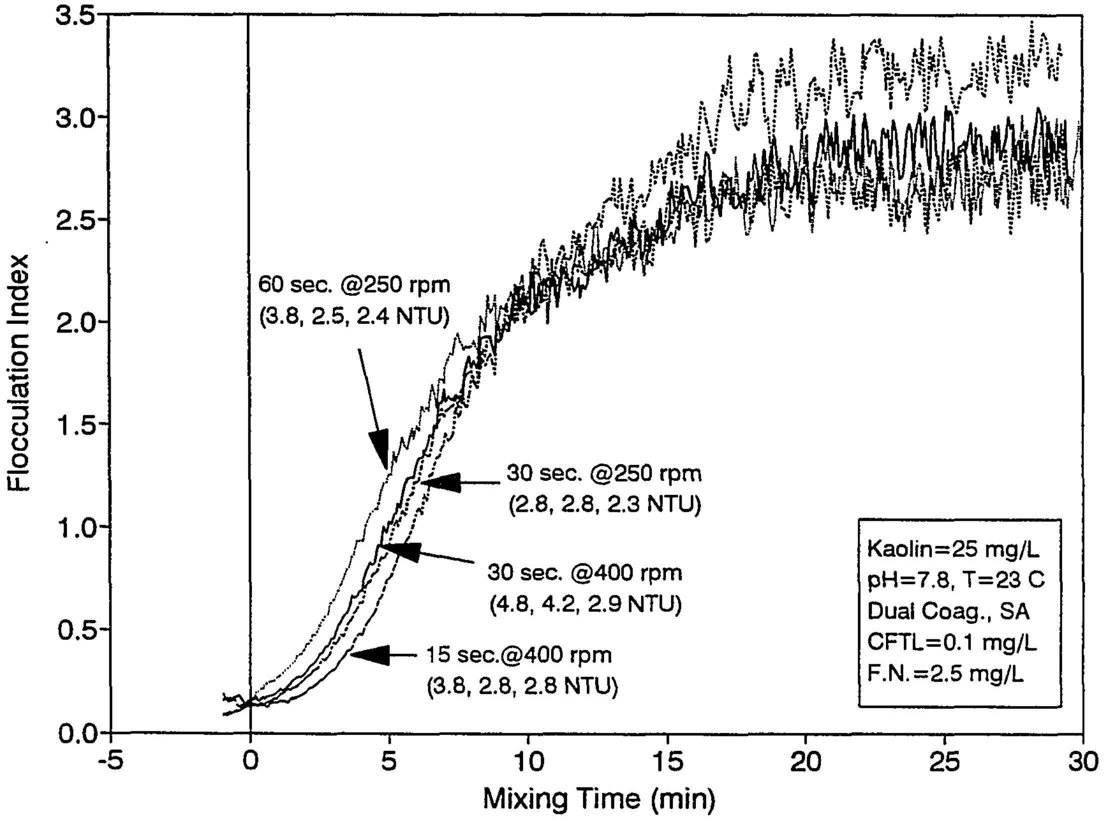


Figure 7.30: Effects of rapid mixing intensity and duration on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for mixing durations from 15 sec. to 60 sec. for 25 mg/L kaolin clay suspension at 23 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

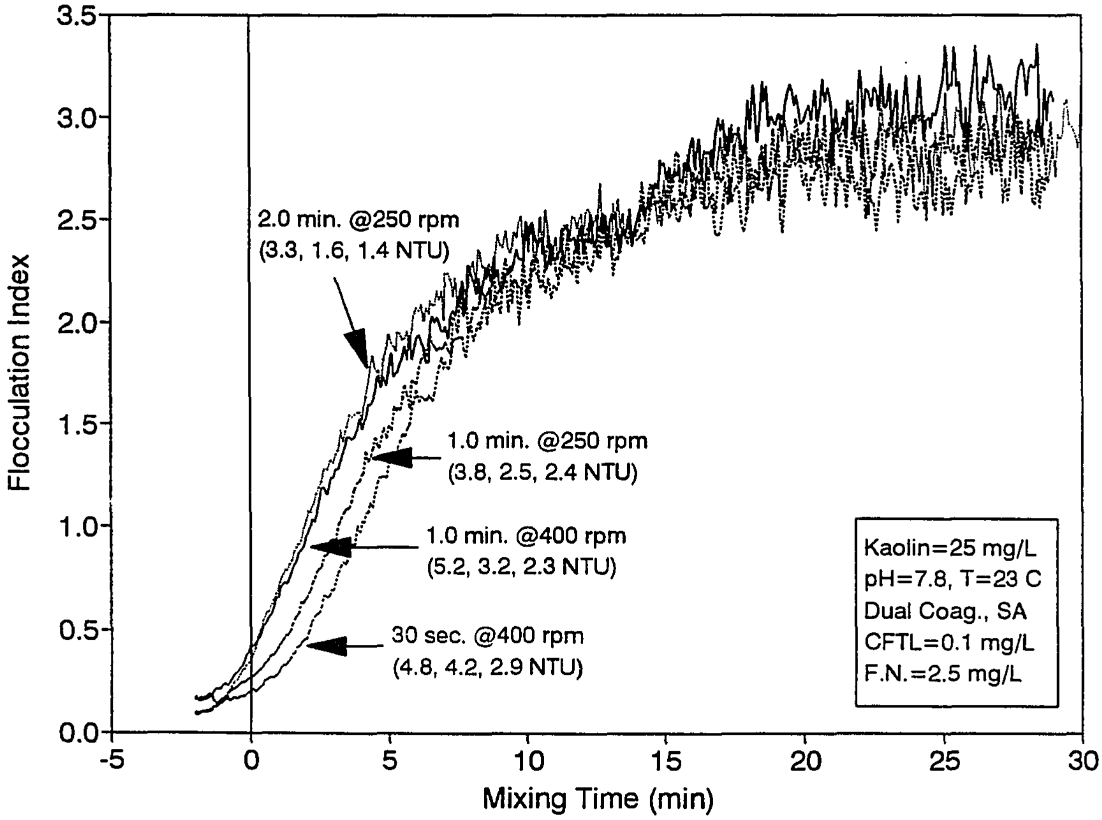


Figure 7.31: Effects of rapid mixing intensity and duration on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for mixing durations from 30 sec. to 2.0 min. for 25 mg/L kaolin clay suspension at 23 °C (slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

small particles have a large effect on the turbidity values but not on the Flocculation Index values which are largely affected by large particles.

The effect of rapid mixing intensity was also investigated using 100 mg/L clay concentration at 5 °C (**Figure 7.32**). Dual coagulants (Catfloc TL + ferric nitrate) added simultaneously were used at pH 7.8. It can be seen that the Flocculation Index values were almost the same, but the lower mixing intensity (250 rpm for 1.0 min.) gave better turbidity removal than the high mixing intensity (400 rpm for 1.0 min.) at this high clay concentration.

In short, for the same Gt product value, lower mixing intensity (250 rpm) and longer rapid mixing time is superior to high mixing intensity (400 rpm) and shorter rapid mixing time. For similar rapid mixing times but different rapid mixing intensities, the higher mixing intensity gave almost similar Flocculation Index values as lower mixing intensity and slightly better in some cases. However, the high mixing intensity rapid mixing did not remove the turbidity as well which could be caused by production of small particles that were left in suspension as a result of the breakup of flocs formed during rapid mixing.

7.4 Addition Sequence Effect For Dual Coagulants

The effect of dual coagulants addition sequence on flocculation kinetics was investigated by comparing the flocculation index changes with mixing time for three different addition sequences. The first addition sequence was the addition of the cationic polymer at the start of the rapid mixing period followed by ferric nitrate after half of the total rapid mixing period (total rapid mixing period refers to rapid mixing period when dual coagulants are used, and it spans the period from the start to the end of rapid mixing regardless of the

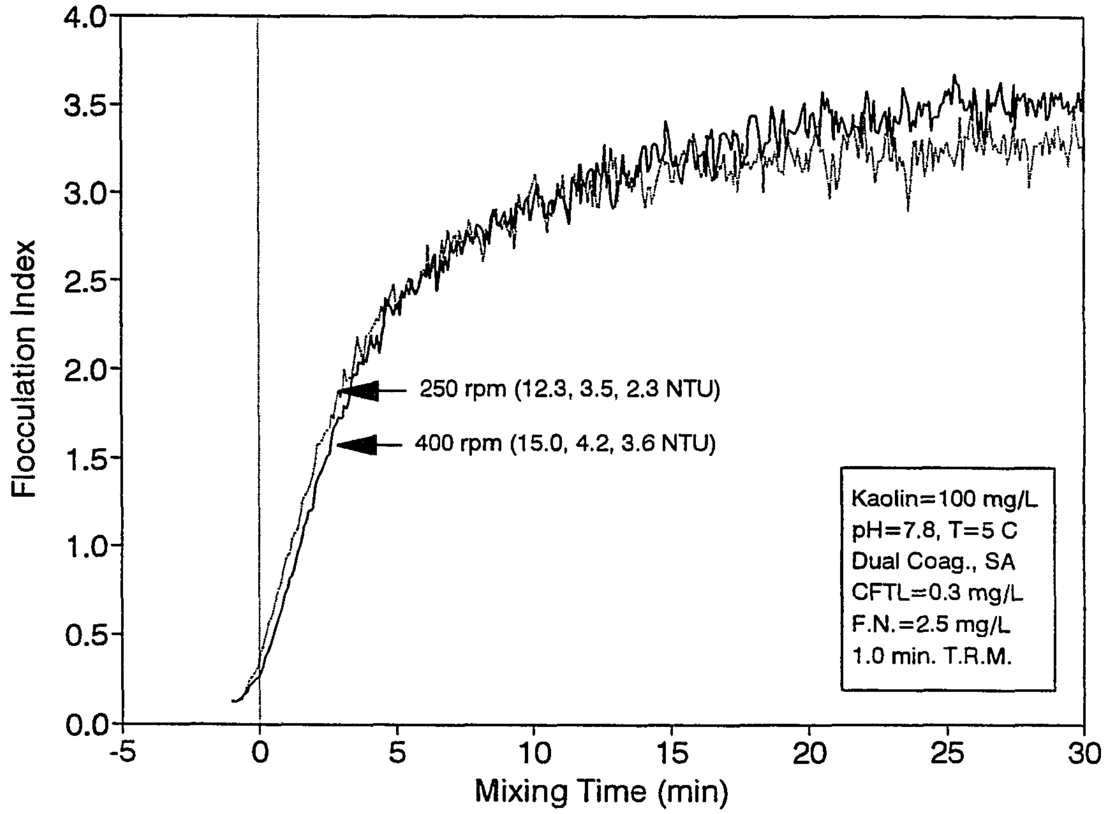


Figure 7.32: Effects of rapid mixing intensity on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 100 mg/L kaolin clay suspension at 5 °C (slow mixing = 30 min. at 60 rpm).

coagulant being mixed). This is referred to in the following discussion as "Polymer First" (PF). For a 2.0 minutes total rapid mixing period, the cationic polymer was added first, and after 1.0 minute of rapid mixing, ferric nitrate was added and rapid mixing continued for an extra 1.0 minute. The second addition sequence which is referred to as "Polymer Second" (PS), starts by adding ferric nitrate. After the passage of half of the total rapid mixing period, the cationic polymer is added and rapid mixing continued for the remaining half of the total rapid mixing period. The third addition sequence is the "Simultaneous Addition" (SA) sequence. Both coagulants were added at the same time and rapid mixing continued for the whole total rapid mixing period. Only experiments with the same total rapid mixing period were compared when addition sequence effects were investigated. The addition sequence effects were investigated using a number of different experimental conditions. These include 4 clay concentrations (5, 25, 50, and 100 mg/L), 2 pH values (6.0 and 7.8), 2 temperature values (room temperature and 5 °C), and 2 sulfate concentrations (0.0 and 0.001 M sulfate).

Figure 7.33 shows the effects of addition sequence at pH 7.8 and kaolin clay concentration of 5.0 mg/L and 23 °C as well as the benefits of using dual coagulants over the sole use of inorganic coagulants. Two doses of ferric nitrate (2.5 and 5.0 mg/L) were compared to dual coagulant use (2.5 mg/L ferric nitrate + 0.02 mg/L Cat-Floc TL) with different addition sequences in the 18 L reactor. It can be seen from this figure that simultaneous addition (SA) was the best addition sequence, as evidenced by both the flocculation index and the residual turbidity after 30 minutes of settling. The addition of

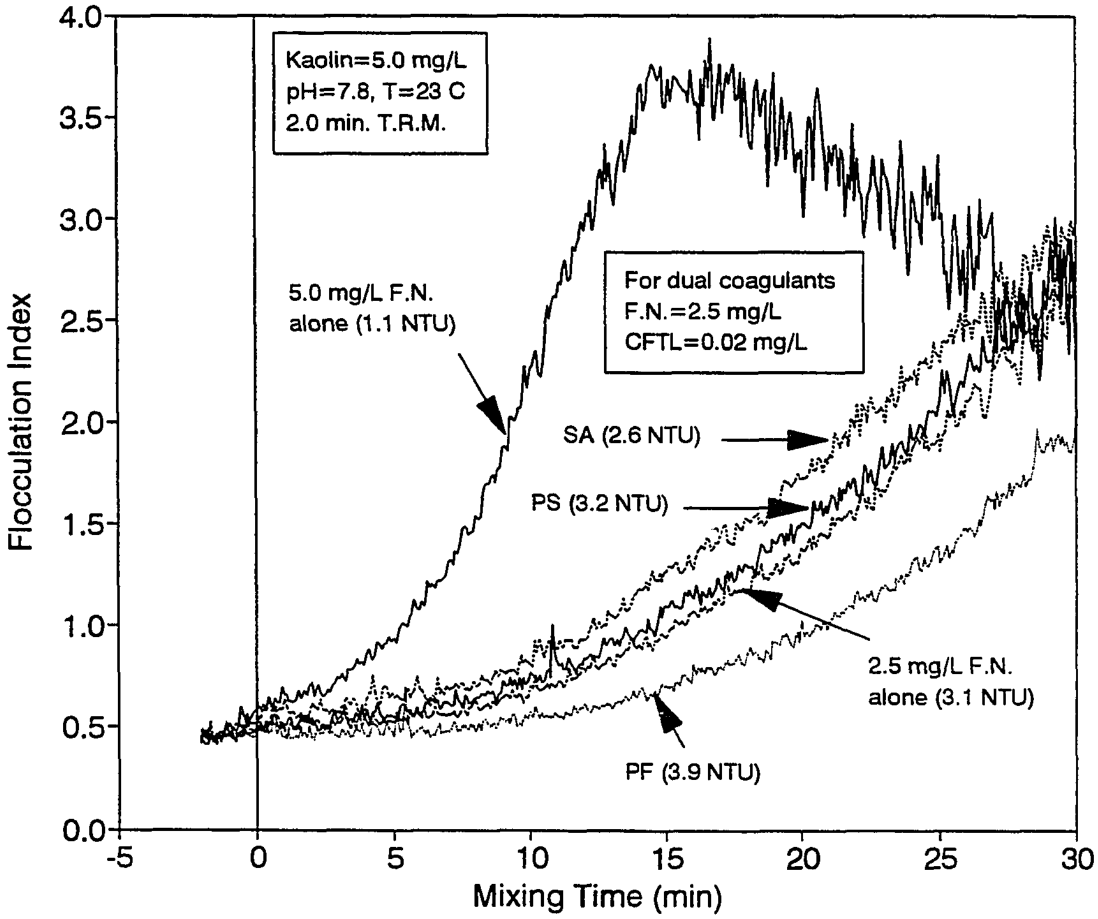


Figure 7.33: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 5.0 mg/L kaolin clay suspension at 23 °C. A comparison between the use of dual coagulants or ferric nitrate (F.N.) alone is also shown (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

cationic polymer after ferric nitrate addition (PS) was second best, while the addition of polymer before ferric nitrate addition (PF) was the worst.

The use of dual coagulants at this low clay concentration only slightly improved the flocculation kinetics when SA was used. It was even detrimental when the PF alternative was used. The use of 5.0 mg/L ferric nitrate dose as sole coagulant was substantially better than the use of dual coagulants. At this low clay concentration, the collision frequency between the suspended particles is the rate limiting step in the flocculation process. The addition of cationic polymers does not enhance the collision frequency because of the lack of a precipitate as compared to the addition of an extra ferric nitrate dose. The detrimental effect of using PF as compared to the use of ferric nitrate alone for the same ferric nitrate dose will be explained later in this section.

Figures 7.34 and 7.35 show the addition sequence effect on the flocculation kinetics at pH 7.8 and clay concentration of 25 mg/L in the 18 L reactor at room temperature and 5 °C, respectively. **Figure 7.34** also compares the use of dual coagulants with the use of ferric nitrate alone. In both these figures, the simultaneous addition (SA) alternative outperforms the other two alternatives, both in the flocculation Index values and the residual turbidity values. The addition of the cationic polymer after the inorganic coagulant (PS) was the second best alternative. It can also be seen from these figures that the difference between the simultaneous addition alternative performance and the other two alternatives was greater at low water temperature compared with room temperature. **Figure 7.34** also shows that the use of dual coagulants outperformed the use of the inorganic coagulant for the same

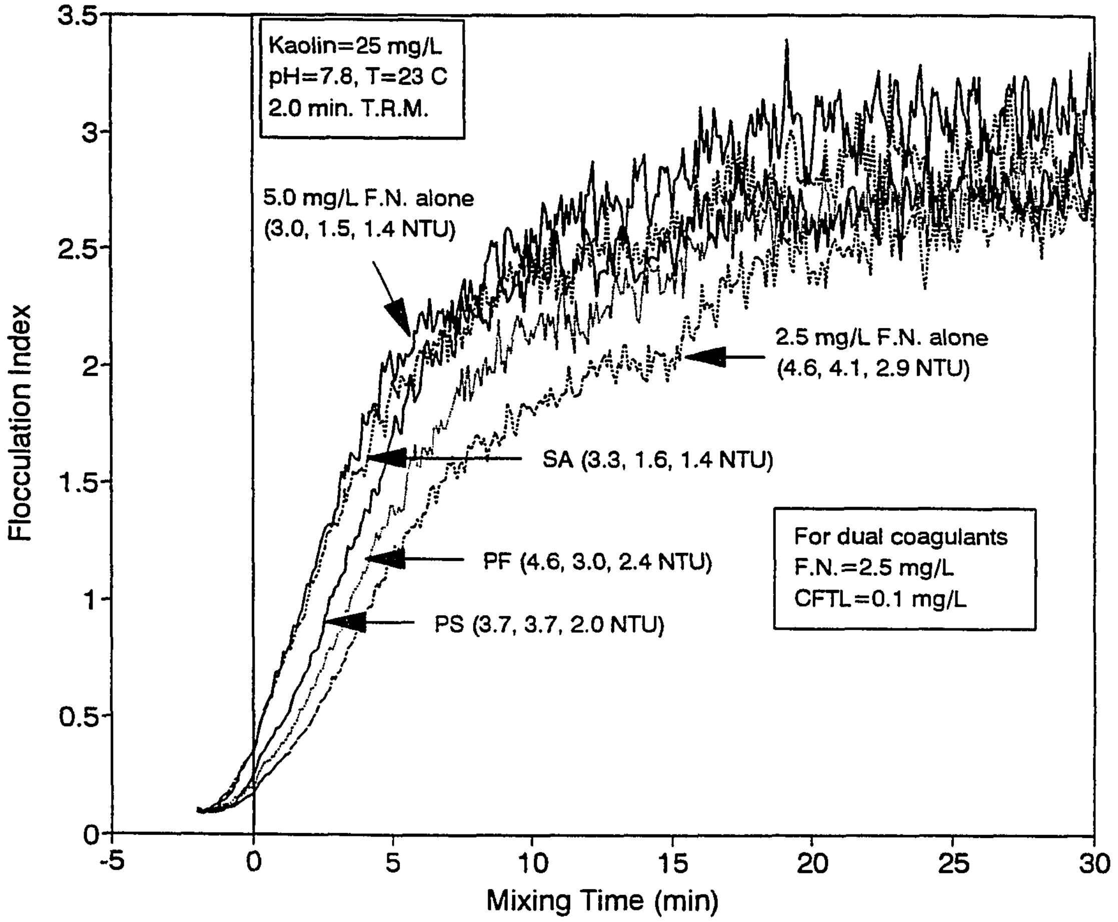


Figure 7.34: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 25 mg/L kaolin clay suspension at 23 °C. A comparison between the use of dual coagulants or ferric nitrate (F.N.) alone is also shown (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

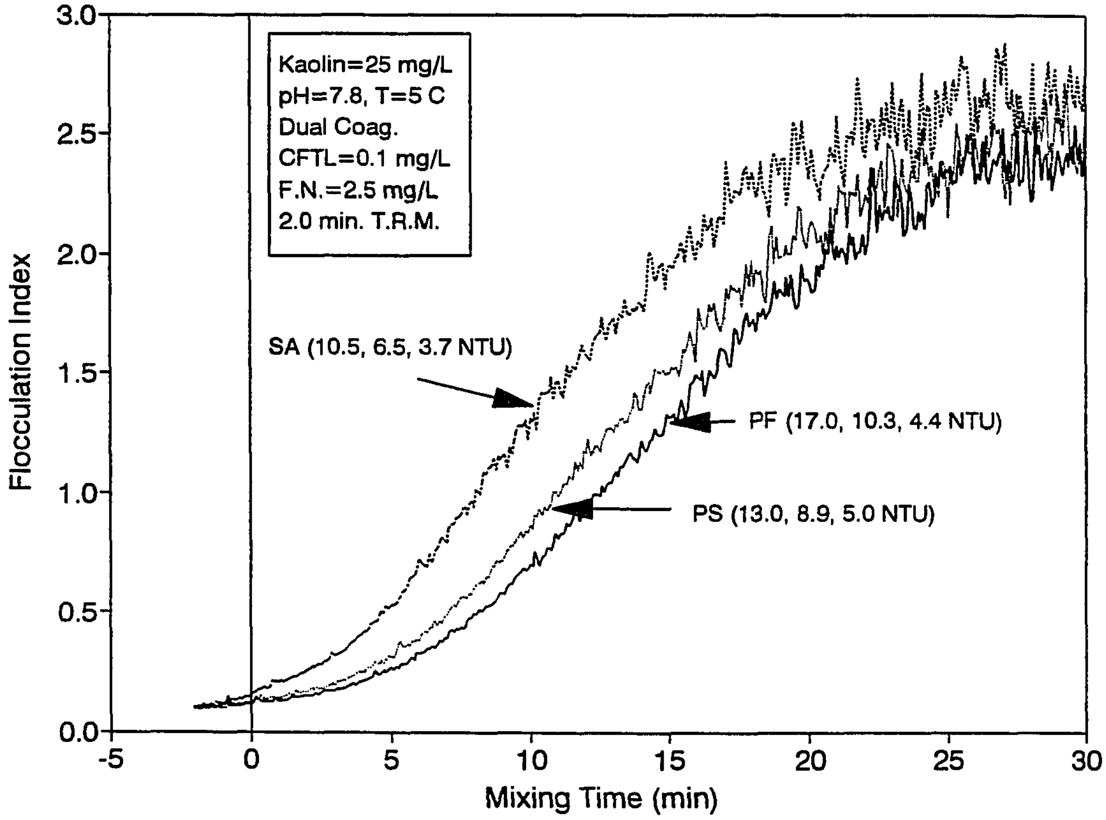


Figure 7.35: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 25 mg/L kaolin clay suspension at 5 °C. (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

inorganic coagulant dose. It also shows that SA sequence (2.5 mg/L ferric nitrate + 0.10 mg/L Cat-Floc TL) performed as well as 5.0 mg/L ferric nitrate coagulant alone as evidenced by both the Flocculation Index and residual turbidity measures. Therefore, the addition of cationic polymers at the same time as the inorganic coagulant can reduce the inorganic coagulant by 50 % without affecting the flocculation kinetics efficiency at this clay concentration.

Figure 7.36 was conducted using similar experimental conditions as used in **Figure 7.34** except that Cat-Floc L (a poly(DADMAC) with higher molecular weight than Cat-Floc TL) and 2.0 minutes of total rapid mixing were used. Simultaneous addition again produced the best flocculation kinetics and residual turbidity values.

The effect of addition sequence was also investigated using 25 mg/L kaolin clay concentration at pH 6.0 using both zero and 0.001 molarity (96 mg/L) sulfate concentration. **Figure 7.37** shows that, at pH 6.0 and zero sulfate concentration, the use of cationic polymers (Cat-Floc TL) in combination with inorganic coagulants is not beneficial regardless of the addition sequence. The experiments were conducted at 5 °C in the 18 L reactor. The use of the cationic polymer alone at these conditions was superior to both dual coagulants use and the sole use of ferric nitrate. Dual coagulant experiments in **Figure 7.37** were conducted using half the optimum dose for ferric nitrate plus half the optimum dose for the cationic polymer Cat-Floc TL. Other experiments (not shown) using a combination of the optimum cationic polymer dose, optimum ferric nitrate dose, half the optimum ferric nitrate dose, as well as half the optimum cationic polymer dose gave similar results to those shown

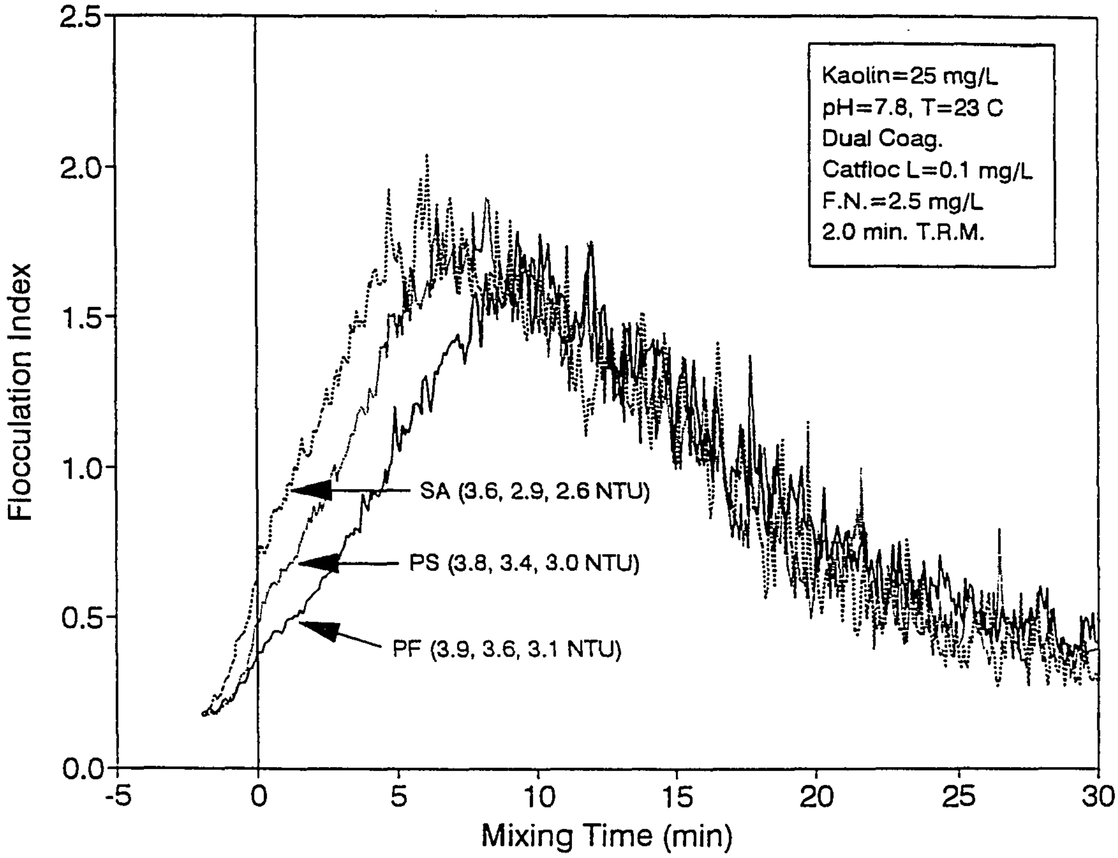


Figure 7.36: Effects of addition sequence of dual coagulants (CFL + F.N.) on flocculation kinetics at pH 7.8 for 25 mg/L kaolin clay suspension at 23 °C. (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

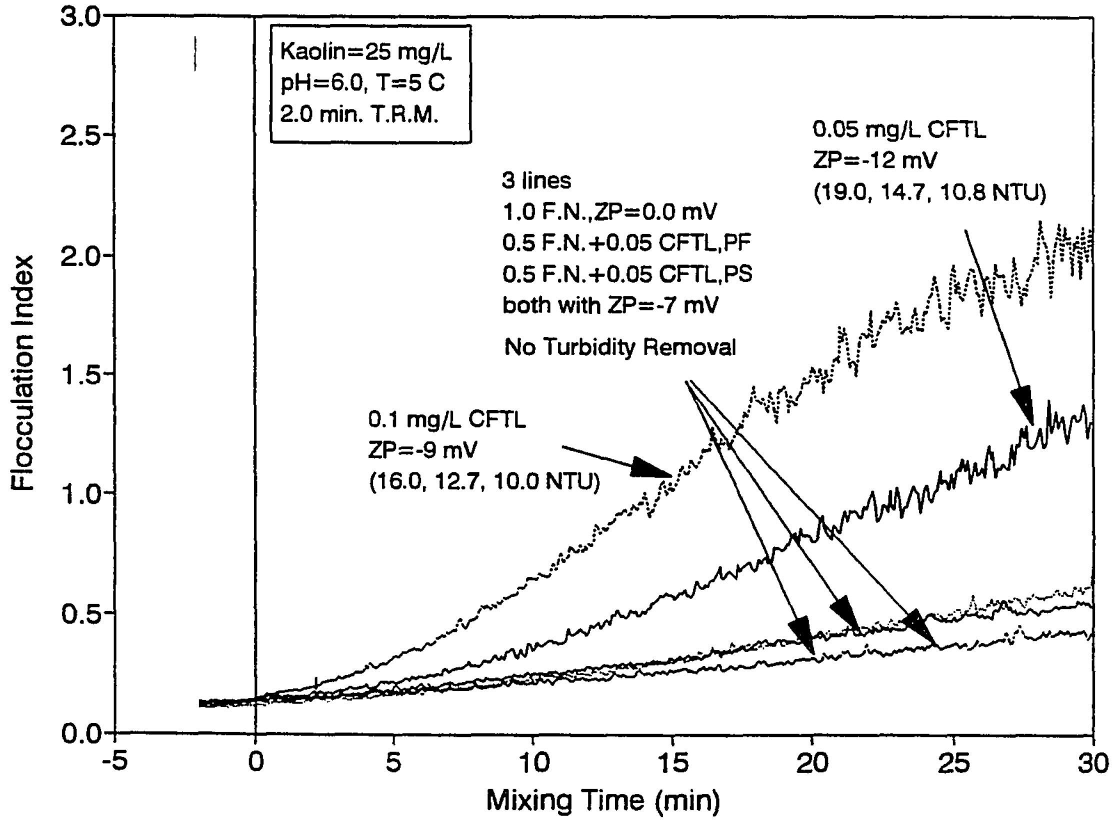


Figure 7.37: Comparison between flocculation kinetics when a cationic polymer (CFTL) alone, ferric nitrate (F.N) alone, or dual coagulants (CFTL + F.N.) are used to coagulate 25 mg/L kaolin clay suspension at pH 6.0 and zero sulfate concentration (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

in **Figure 7.37**. However, in the presence of 0.001 M of sulfate (**Figure 7.38**), the results became similar to those at pH 7.8. At these conditions, the use of dual coagulants improved flocculation kinetics compared to the sole use of the inorganic coagulant. Furthermore, the simultaneous addition sequence proved to be the best addition sequence.

A similar set of experiments was conducted using 50 mg/L kaolin clay concentration. **Figure 7.39** compares the results obtained with different addition sequences at pH 7.8 and room temperature using 50 mg/L clay concentration in the 18 L reactor. **Figure 7.40** shows a similar comparison but at 5 °C along with the results obtained by using 2.5 mg/L and 5.0 mg/L ferric nitrate alone. The effect of addition sequence at pH 6.0 without sulfate and with 0.001 M sulfate for 50 mg/L clay concentration are shown in **Figures 7.41 and 7.42**, respectively. Comparing the figures with 50 mg/L clay concentration to those with 25 mg/L, the similarities are obvious. In both sets of experiments, the use of dual coagulants at pH 6.0 and zero sulfate concentration was inferior to the use of the cationic polymer alone. In the other cases presented, simultaneous addition (SA) was the best addition sequence followed by the addition of the cationic polymer after the addition of ferric nitrate (PS). The addition of the cationic polymer before ferric nitrate (PF) was the worst alternative. Again, the results show that the difference between the simultaneous addition sequence and the other sequences increased at low water temperature. It can also be noted that the difference in results between the simultaneous addition sequence and the other two sequences decreases as the clay concentration increases. The simultaneous addition sequence **(Figure 7.40)** gave

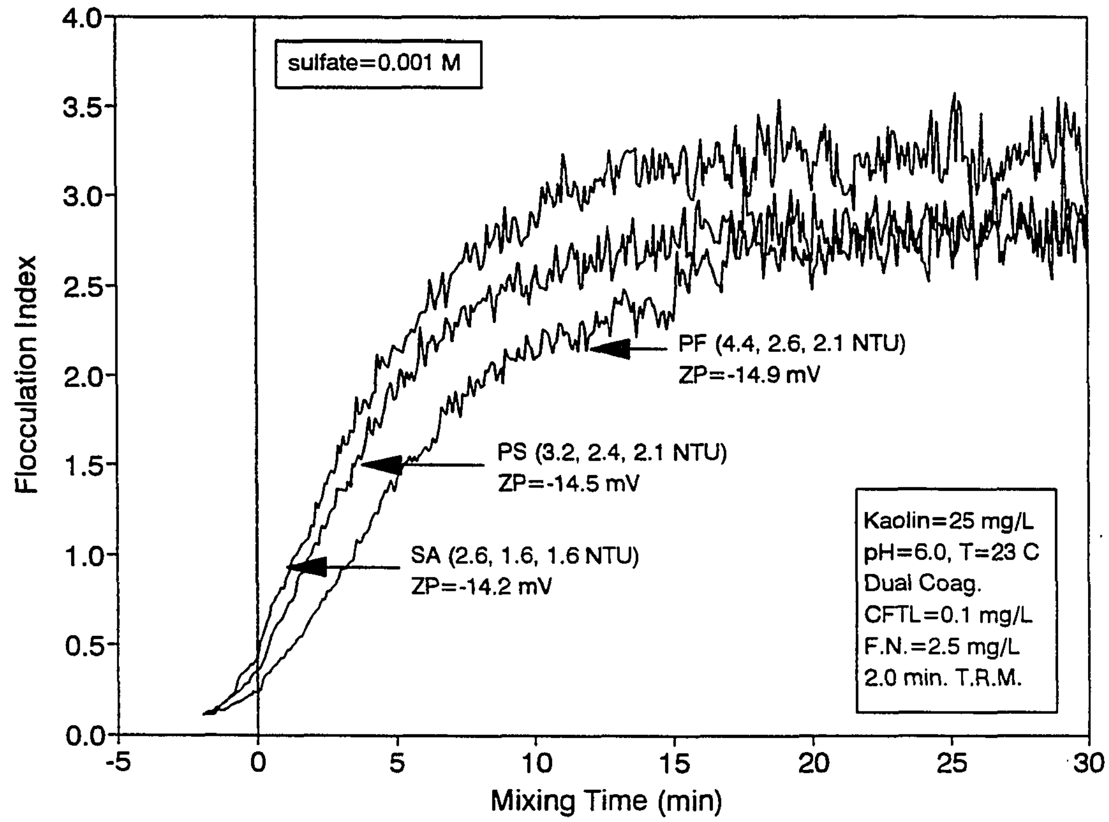


Figure 7.38: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 6.0 and 0.001 M sulfate concentration for 25 mg/L kaolin clay suspension at 23 °C. (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

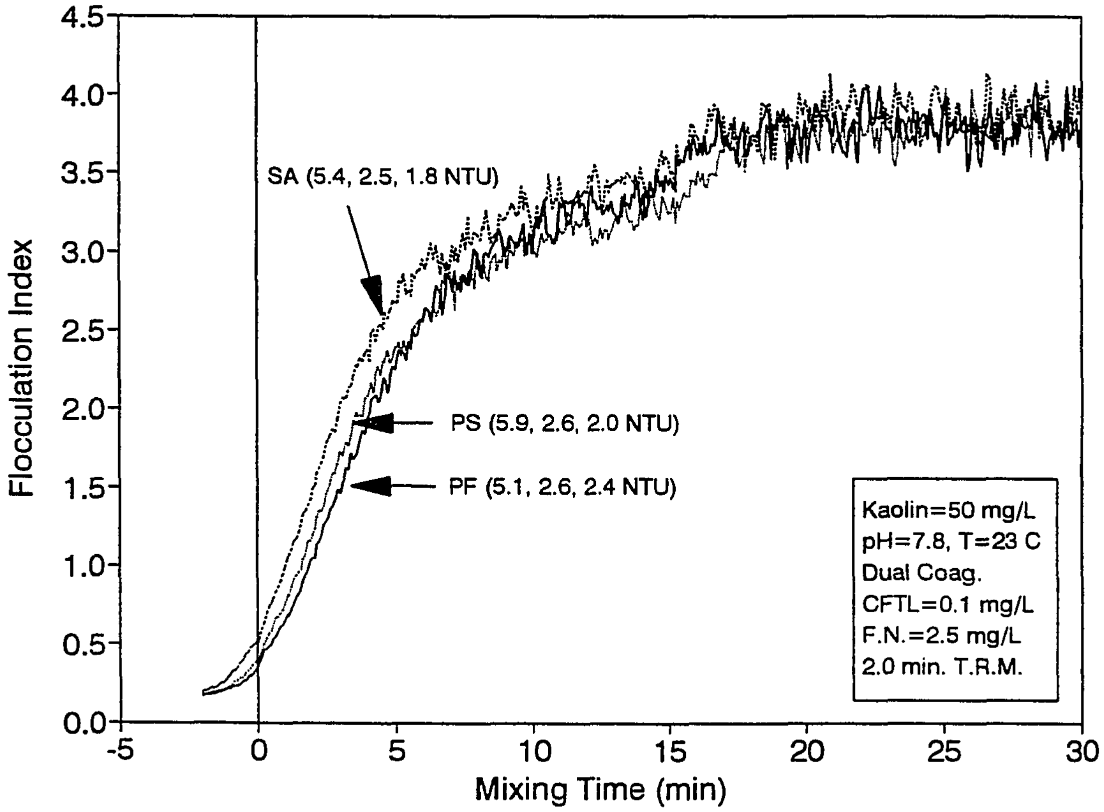


Figure 7.39: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 50 mg/L kaolin clay suspension at 23 °C. (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

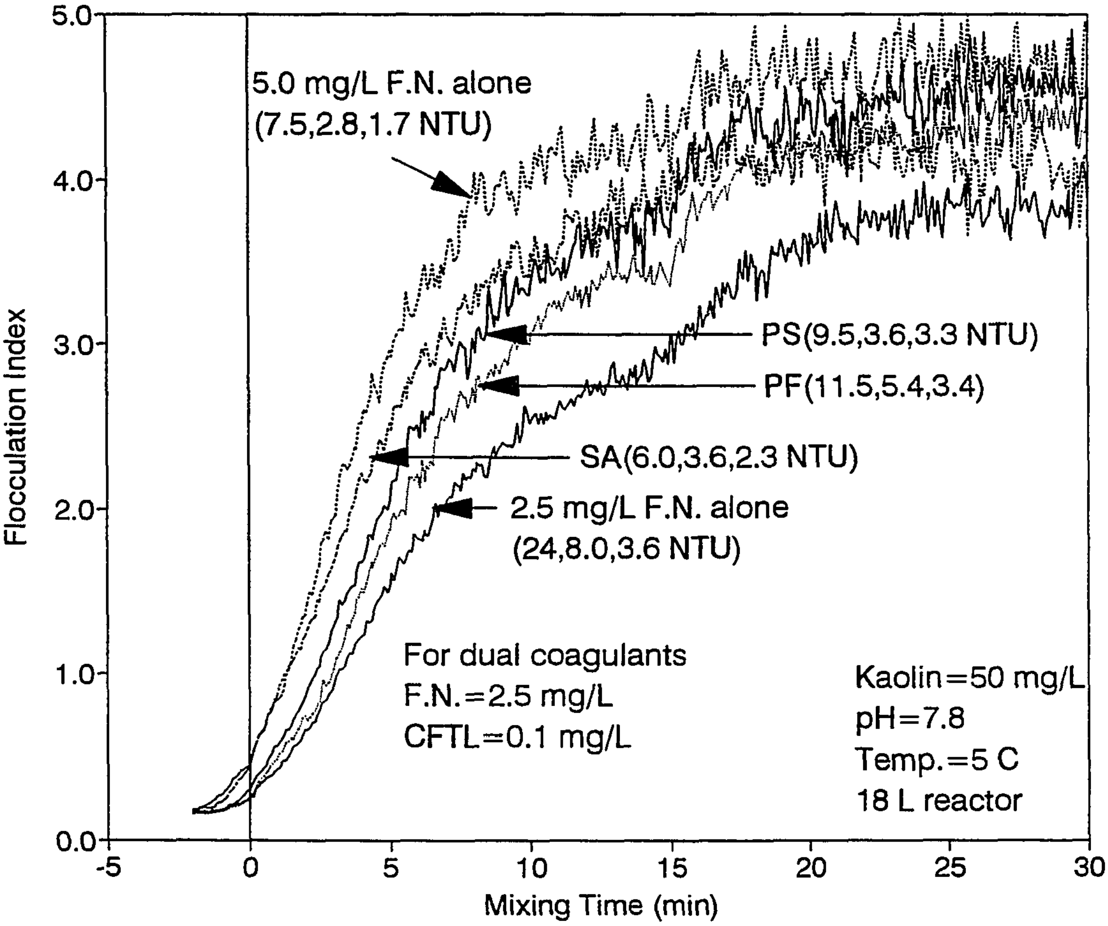


Figure 7.40: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 50 mg/L kaolin clay suspension at 5 °C. A comparison between the use of dual coagulants or ferric nitrate (F.N.) alone is also shown (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

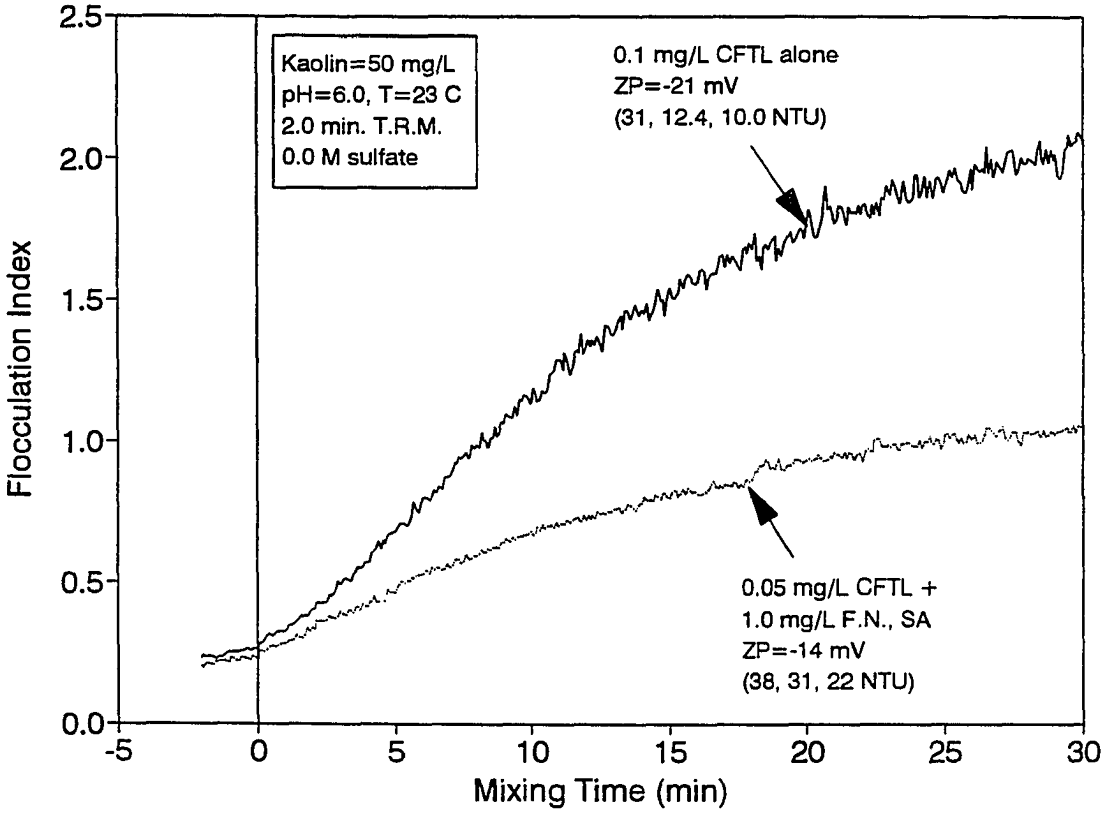


Figure 7.41: Comparison between flocculation kinetics when a cationic polymer (CFTL) alone or dual coagulants (CFTL + F.N.) are used at pH 6.0 and zero sulfate concentration for 50 mg/L kaolin clay suspension at 23 °C. (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

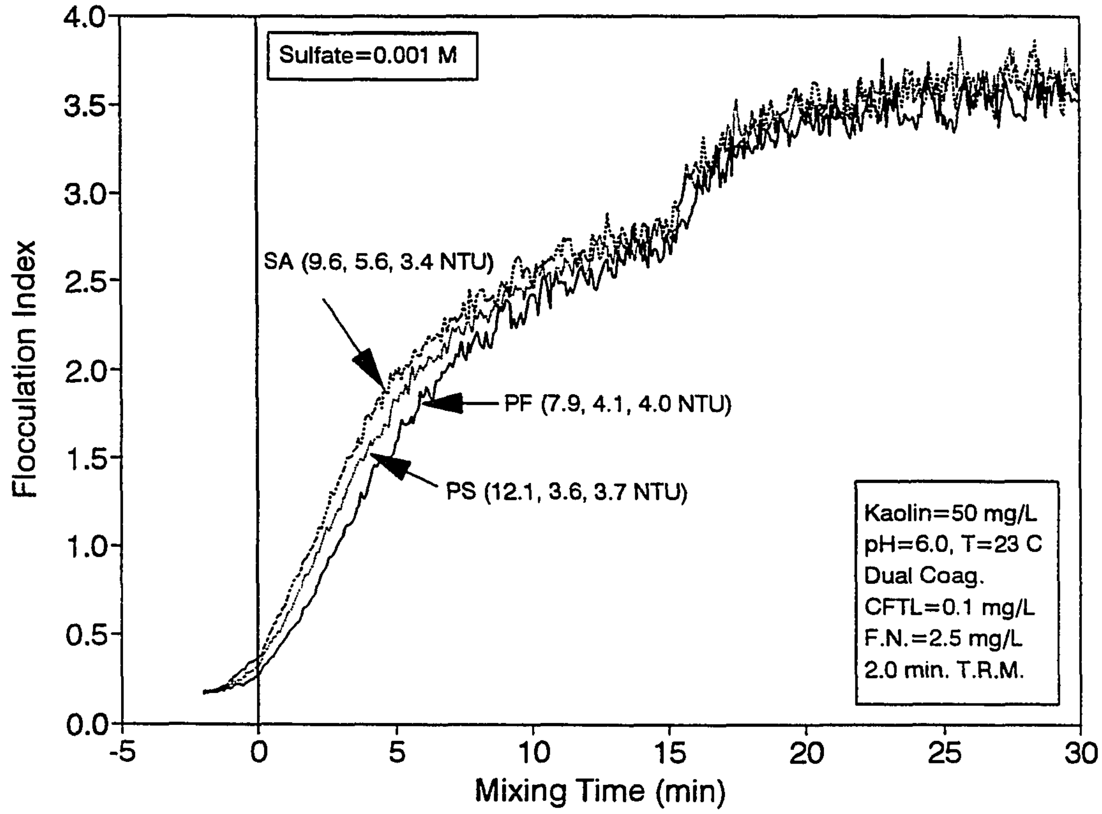


Figure 7.42: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 6.0 and 0.001 M sulfate concentration for 50 mg/L kaolin clay suspension at 23 °C. (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

almost the same results with 2.5 mg/L ferric nitrate as was obtained with a ferric nitrate dose of 5.0 mg/L when used alone.

The effect of addition sequence was also studied using 100 mg/L kaolin clay concentration at pH 7.8. The results are shown in **Figures 7.43 to 7.46**. **Figure 7.43** shows the results at room temperature and 1.0 minute of total rapid mixing at 250 rpm (~ 450/s). The flocculation index and the residual turbidity values after different settling periods prove that there is almost no effect of the addition sequence on flocculation kinetics at these experimental conditions (100 mg/L clay concentration, room temperature, and 1.0 minute of rapid mixing at 250 rpm). This is in agreement with the previous observation that the effect of addition sequence diminishes as clay concentration increases. **Figure 7.44** has the same experimental conditions as **Figure 7.43**, except that the experiments were conducted at low water temperature (5 °C). Here, the simultaneous addition was superior to the other addition alternatives. However, unlike the results with 5, 25, and 50 mg/L clay concentration, the PF alternative performed better than the PS alternative with 100 mg/L clay concentration in these two figures. With 100 mg/L clay concentration, pH 7.8, and 2.0 minutes of rapid mixing (**Figures 7.45 and 7.46**), the simultaneous addition sequence was distinctly superior. Comparing the other two sequences, the PF alternative slightly outperformed the opposite addition sequence (PS) at both room and low temperatures.

A large number of experiments using the 2 L reactor were conducted to study the effects of addition sequence on the flocculation kinetics. **Figure 7.47** is a sample of these experiments. **Figure 7.47** was done at pH 7.8 and clay concentration of 25 mg/L with a total

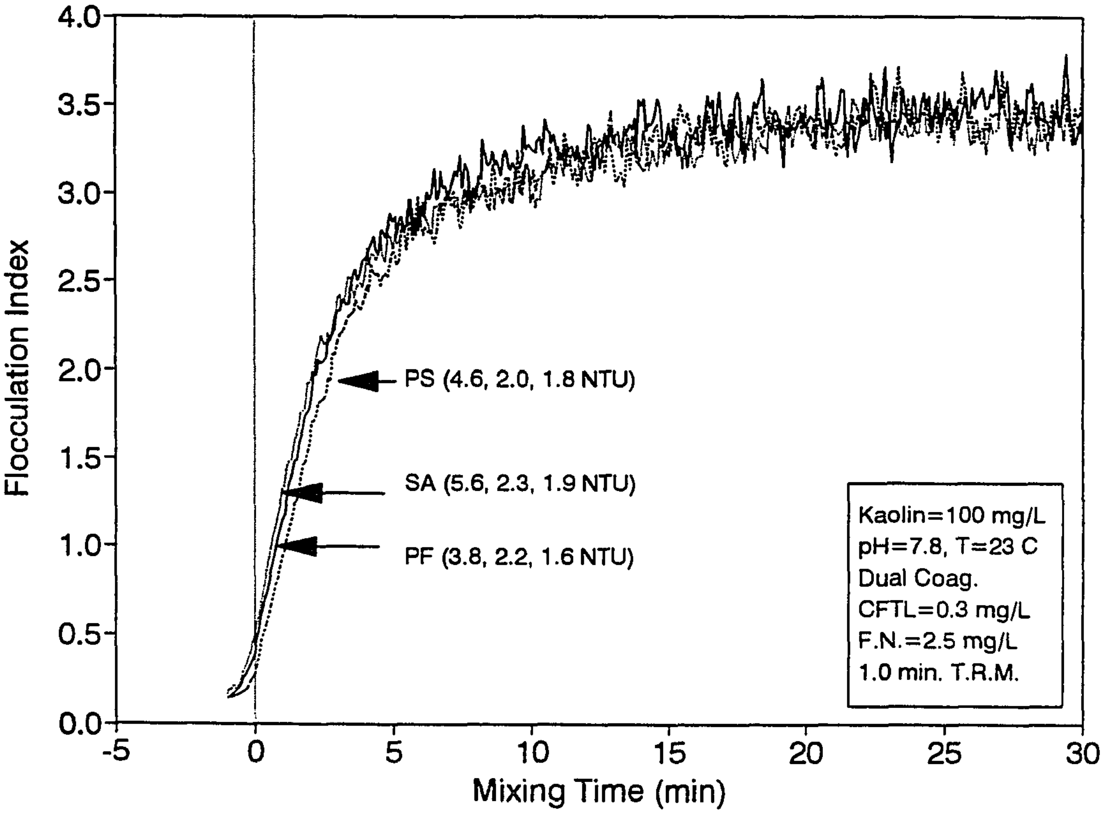


Figure 7.43: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 100 mg/L kaolin clay suspension at 23 °C. (total rapid mixing = 1.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

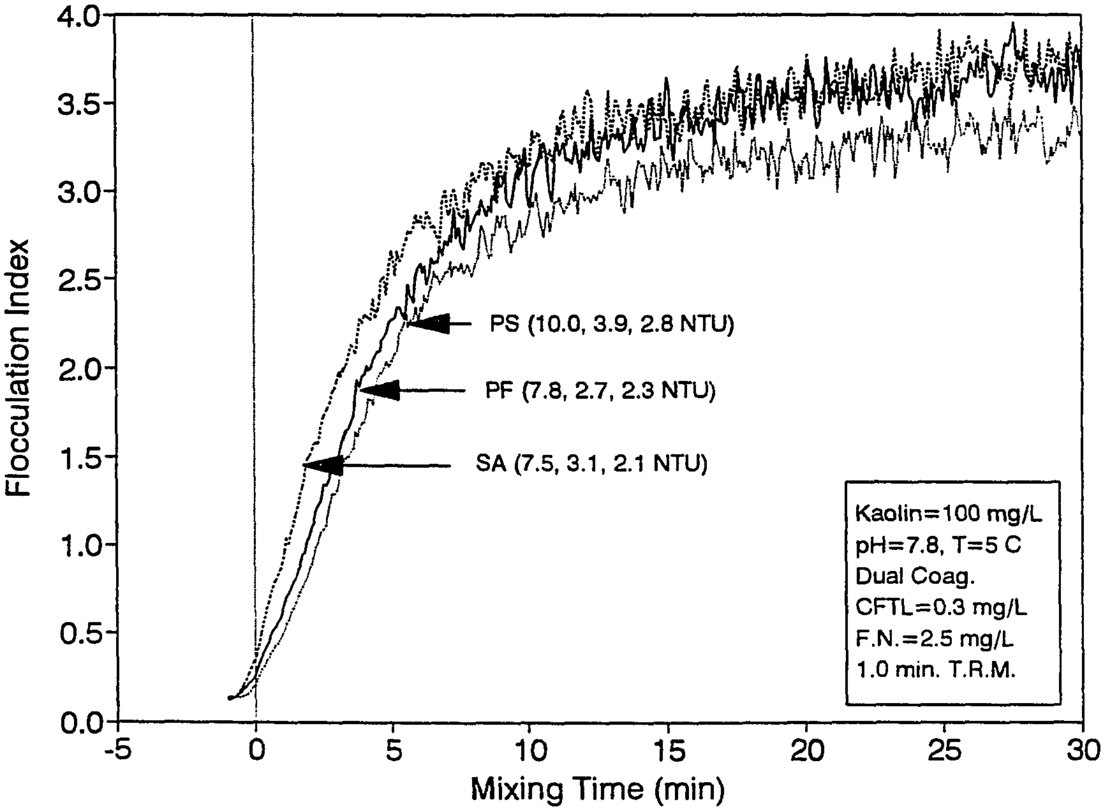


Figure 7.44: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 100 mg/L kaolin clay suspension at 5 °C. (total rapid mixing = 1.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

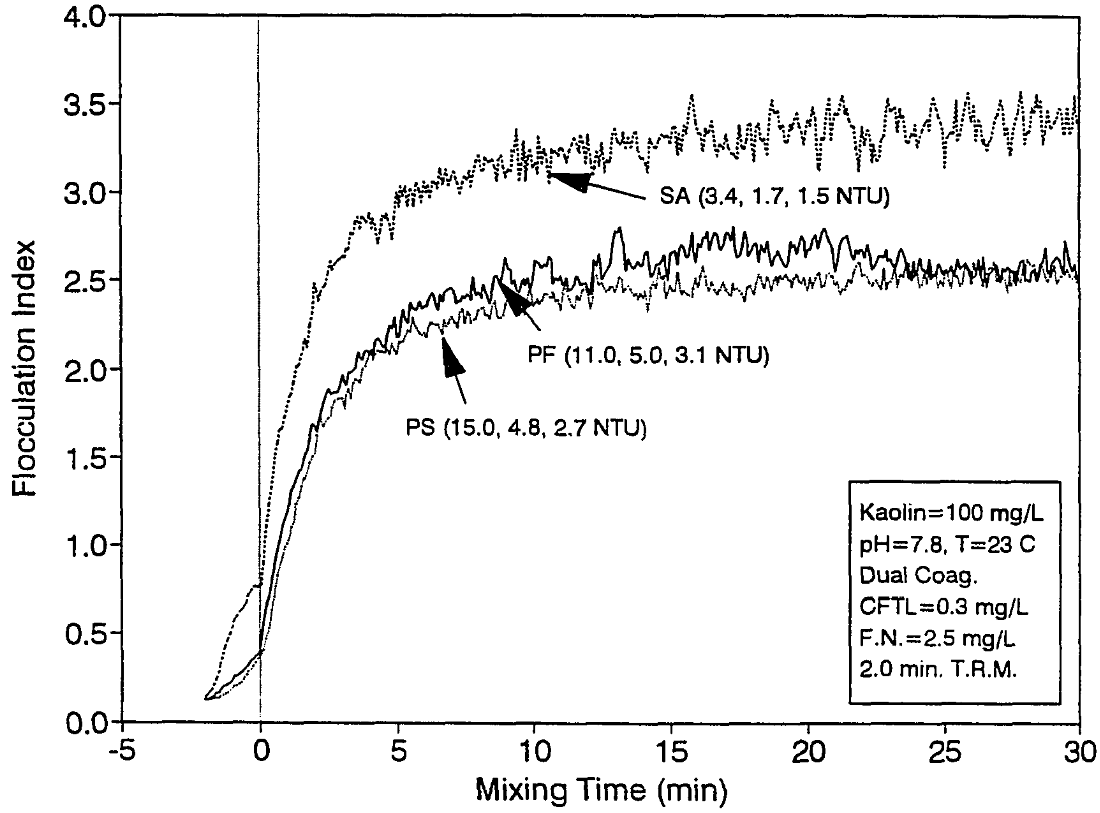


Figure 7.45: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 100 mg/L kaolin clay suspension at 23 °C. (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

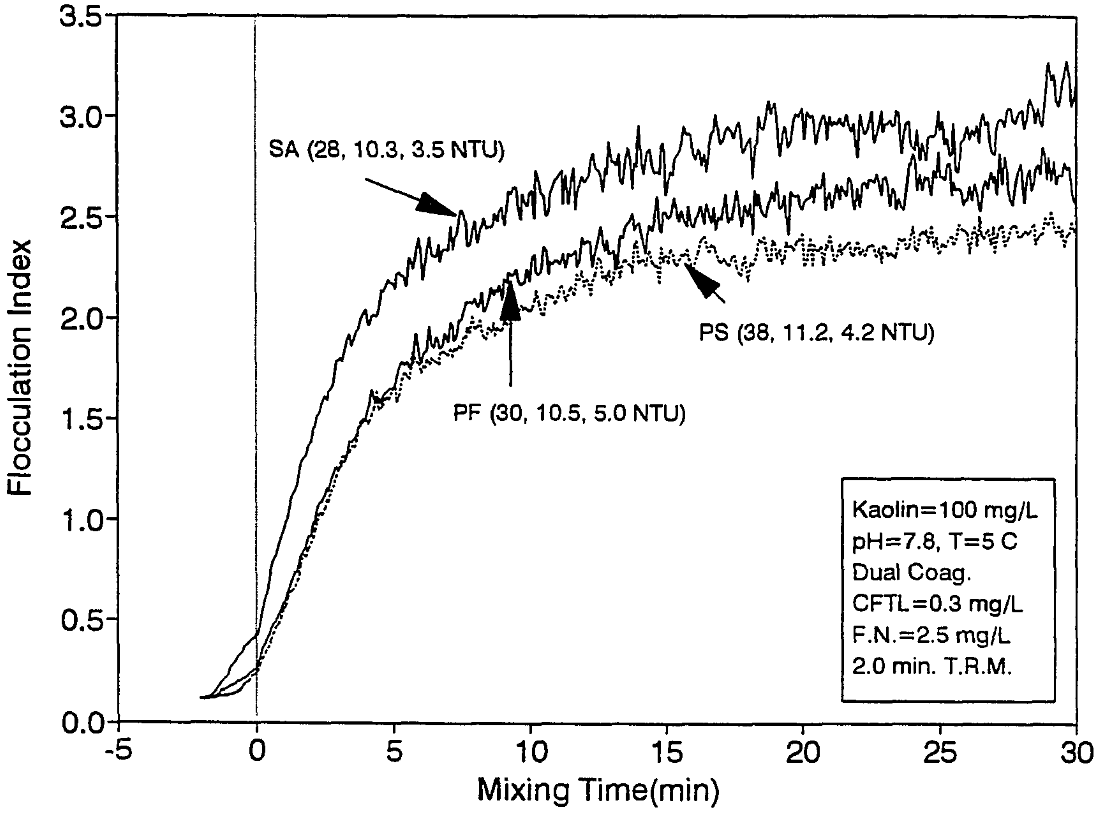


Figure 7.46: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 100 mg/L kaolin clay suspension at 5 °C. (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

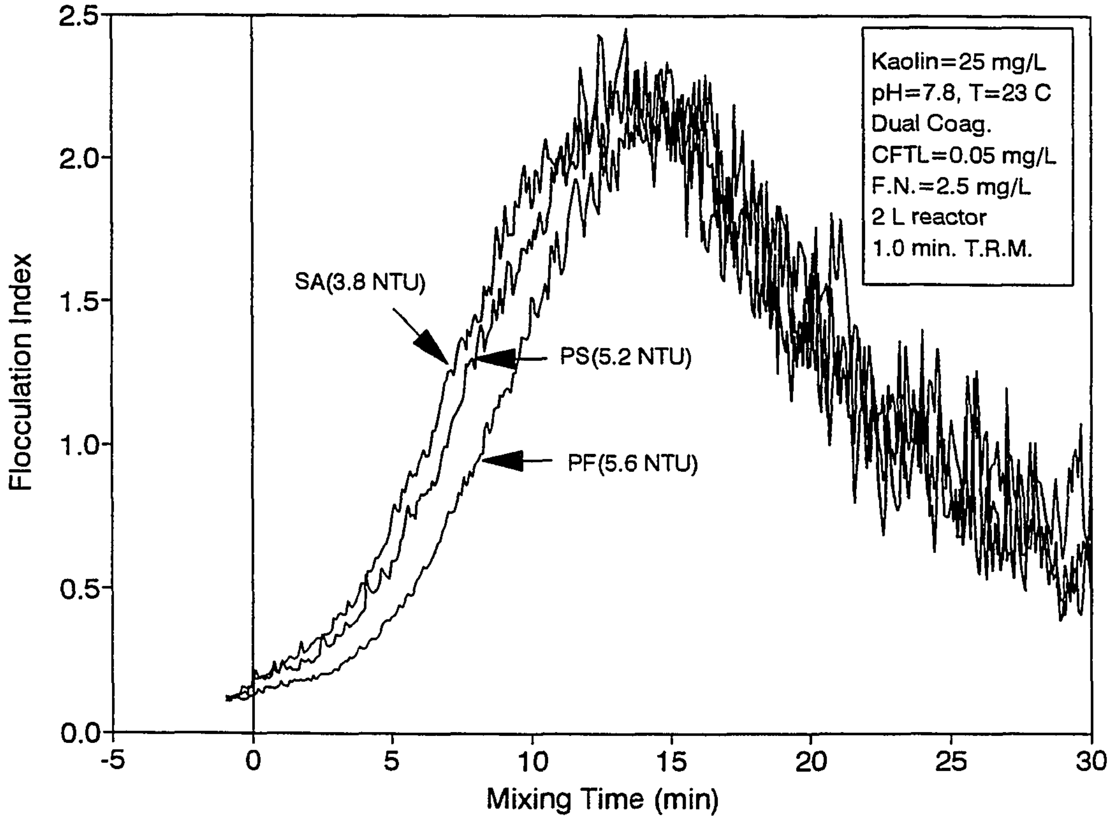


Figure 7.47: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics at pH 7.8 for 25 mg/L kaolin clay suspension at 23 °C using the 2 L reactor. Supernatant turbidities are shown after 10 min. of settling (total rapid mixing = 1.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 30 rpm).

rapid mixing time of 1.0 minute. Again, the simultaneous addition (SA) sequence was the best followed by the PS alternative as shown by the Flocculation Index and residual turbidity after 10.0 minutes of settling.

So, how can the addition sequence of the cationic polymer and ferric nitrate affect the flocculation kinetics? The answer to this question needs a closer look at the differences that these different addition sequences have on the rapid mixing durations, floc strength and collision efficiency.

First, it should be noted that the effect of rapid mixing duration on the inorganic coagulant (ferric nitrate in this case) is more dramatic than its effect on cationic polymers (see previous section). It should also be noted that although the total rapid mixing time was the same regardless of the addition sequence in the previous figures, the rapid mixing time for each coagulant depends on the addition sequence provided. For example, when the total rapid mixing period is 2.0 minutes, ferric nitrate coagulant gets 2.0 minutes of rapid mixing if it is added before or with the cationic polymer. It gets, however, only 1.0 minute when added 1.0 minute after the cationic polymer addition. A similar statement applies to the cationic polymer. As was found in the previous section, extended rapid mixing (2.0 minutes) was superior to shorter rapid mixing times for clay concentrations of 5, 25, and 50 mg/L at both room and 5 °C conditions when using ferric nitrate alone or when dual coagulants were used. For 100 mg/L clay concentration 1.0 minute of rapid mixing was optimum for ferric nitrate alone at both room and low temperatures.

If only rapid mixing duration is taken into account, one would expect the SA and PS alternatives to have similar effects on the flocculation kinetics because the inorganic coagulant gets the same rapid mixing duration. Furthermore, these alternatives would be expected to outperform the PF alternative for clay concentrations of 5, 25, and 50 mg/L where 2.0 minutes of rapid mixing was superior than shorter rapid mixing periods. On the other hand, the PF would be expected to outperform the other two alternatives when 100 mg/L clay concentration and is coagulated using 2.0 minutes of rapid mixing. This is because, the ferric nitrate coagulant gets only 1.0 minute of rapid mixing when PF is used compared to 2.0 minutes with the SA and PS alternatives. And at this clay concentration 1.0 minute of rapid mixing with ferric nitrate was optimum. However, there is more to it than only rapid mixing time for ferric nitrate as will be discussed below.

Second, the way the cationic polymer and the hydrolysis products of the inorganic coagulant are adsorbed on the clay particles depends on the addition sequence. When cationic polymers are added before inorganic coagulants, the particles with adsorbed "patches" of cationic polymer are subsequently covered by the much smaller inorganic hydrolysis species, thus reducing the collision efficiency and perhaps the floc strength. This does not occur when the cationic polymer is added after the inorganic coagulant addition. When the cationic polymer is added simultaneously with the inorganic coagulant, it is possible that the majority of the cationic polymer molecules will adsorb to the suspended particles after the inorganic coagulant molecules due to the much smaller number of cationic polymer molecules. The adsorption of both the cationic polymer molecules and ferric hydrolysis species depend on the frequency of collisions between the cationic polymer molecules and clay particles on one side and the collision of the ferric hydrolysis species and the clay particles on the other side. The larger size of the cationic polymer molecules reduces the value of the diffusion coefficient while increases the collision radius with the clay particles. With the high mixing intensity utilized in this study, the transport of the cationic polymer molecules as well as the metal hydrolysis species and clay particles is largely due to shear. The rate of collision between clay particles and either the cationic polymer molecules or the ferric hydrolysis products is a function of both the size and number of the coagulant species. With much smaller number of the cationic polymer species, it is expected that the majority of the cationic polymer molecules will adsorb on the clay particles after the metal hydrolysis species.

The third difference lies in the difference in the matrix of the first formed aggregates during rapid mixing which could affect the strength of the flocculi formed at the end of rapid mixing. As was shown earlier, the role of rapid mixing is not just to disperse the coagulant and its hydrolysis products uniformly throughout the suspension, but it is an intense mixing flocculation, through which the initial growth of dense and strong particulates takes place. When ferric nitrate is added before the cationic polymer addition, the initial stages of particles growth take place in the absence of the cationic polymer. This would lead to the formation of particulates that are not very strong and not very dense particles. When the cationic polymer is added before the inorganic coagulant, the initial stage of particle growth produce strong particulates. When ferric nitrate is added later, the cationic polymer has already been adsorbed on the clay particles and therefore does not fully participate in the aggregation of the newly formed ferric nitrate precipitate and the clay particles.

When the cationic polymer is added simultaneously with the ferric nitrate, it is fully available to participate in the formation of the combined ferric nitrate precipitate and the clay particles. The cationic polymer therefore becomes a part of the initial particulates matrix which are the building blocks of the bigger particles, making them stronger and denser than those obtained using the other two alternatives. This would therefore allow the particles to grow to a bigger size at the end of the rapid mixing period. This can be noticed on the figure since the ratio value at the end of the rapid mixing period was always higher for the simultaneous addition alternative than the other two sequences.

The combined effects of the above three factors determines the addition sequence effects on the flocculation kinetics. For cases where the rapid mixing period was below the detrimental limit, the rapid mixing period as well as the "patched" configuration favor the use of the PS alternative over the PF alternative as was the case with clay concentrations of 5, 25, and 50 mg/L. In the case where 100 mg/L clay concentration and 2.0 minutes of total rapid mixing time were used, the "patched" configuration is still favors the PS sequence while the rapid mixing time favors the PF sequence. In the present work **(Figures 7.44 to 7.46)** the combined effects of these effects were slightly in favor of using PF at these conditions.

In all the cases studied, the simultaneous addition was the best addition sequence. It seems that the third reason discussed earlier largely affects the strength of the flocculi and consequently the flocs formed. The production of larger and stronger flocculi when simultaneous addition is used compared with the other two alternatives can be seen by observing the higher Flocculation Index value at the end of rapid mixing. **Figure 7.48** shows the Flocculation Index values during 5.0 minutes of rapid mixing at 250 rpm. No flocculation period was given for these experiments. The SA sequence was compared with the case where PS sequence was used and to the use of ferric nitrate alone. In the PS experiment, the polymer was added after 2.5 minutes of ferric nitrate addition. For experiments with the same ferric nitrate dosage, particle growth started at a higher rate when SA sequence was used. The growth of particles to a higher diameter (as evidenced by the Flocculation Index) during such high mixing intensity period is a clear indication of the formation of stronger flocs (or flocculi) when SA was used compared to the PS case.

The stronger flocs formed when SA is used compared to PF and PS sequences can also be seen by comparing the Flocculation Index curves of **Figures 7.43 and 7.45**. The only difference between these two figures is that 1.0 minute rapid mixing was applied to the former, while 2.0 minutes to the latter. A comparison was performed in **Figures 7.49 to 7.51** to make it easier to notice the differences. These figures show that when total rapid mixing was increased from 1.0 minute to 2.0 minutes, the PF sequence and the PS sequence were largely influenced in the negative direction. On the other hand, in the SA case, 2.0 minutes of total rapid mixing time did not hurt the flocculation kinetics, and in fact was somewhat beneficial. This is a strong evidence regarding the strength of flocs formed when the cationic polymer and the inorganic coagulant were added simultaneously.

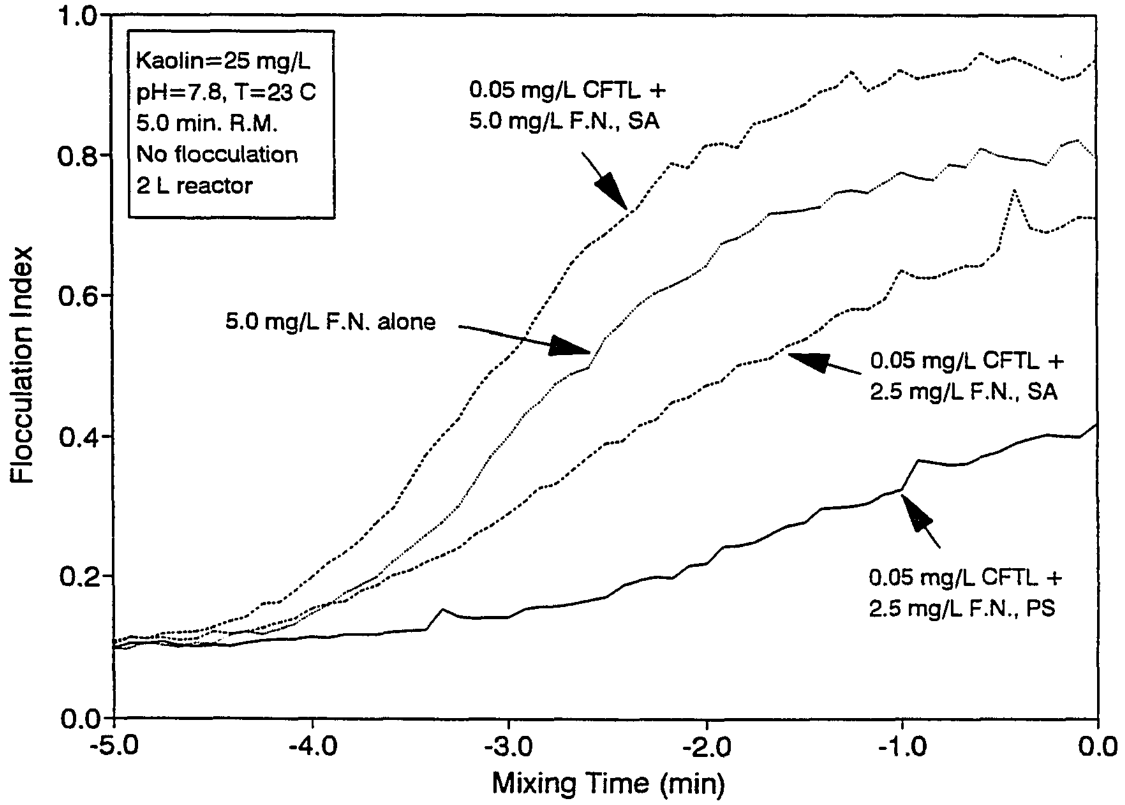


Figure 7.48: Effects of addition sequence of dual coagulants (CFTL + F.N.) on flocculation kinetics during rapid mixing at pH 7.8 for 25 mg/L kaolin clay suspension in the 2 L reactor. The polymer was added 2.5 min. after ferric nitrate addition in the PS experiment (total rapid mixing = 5.0 min. at 250 rpm; slow mixing = 0.0 min.).

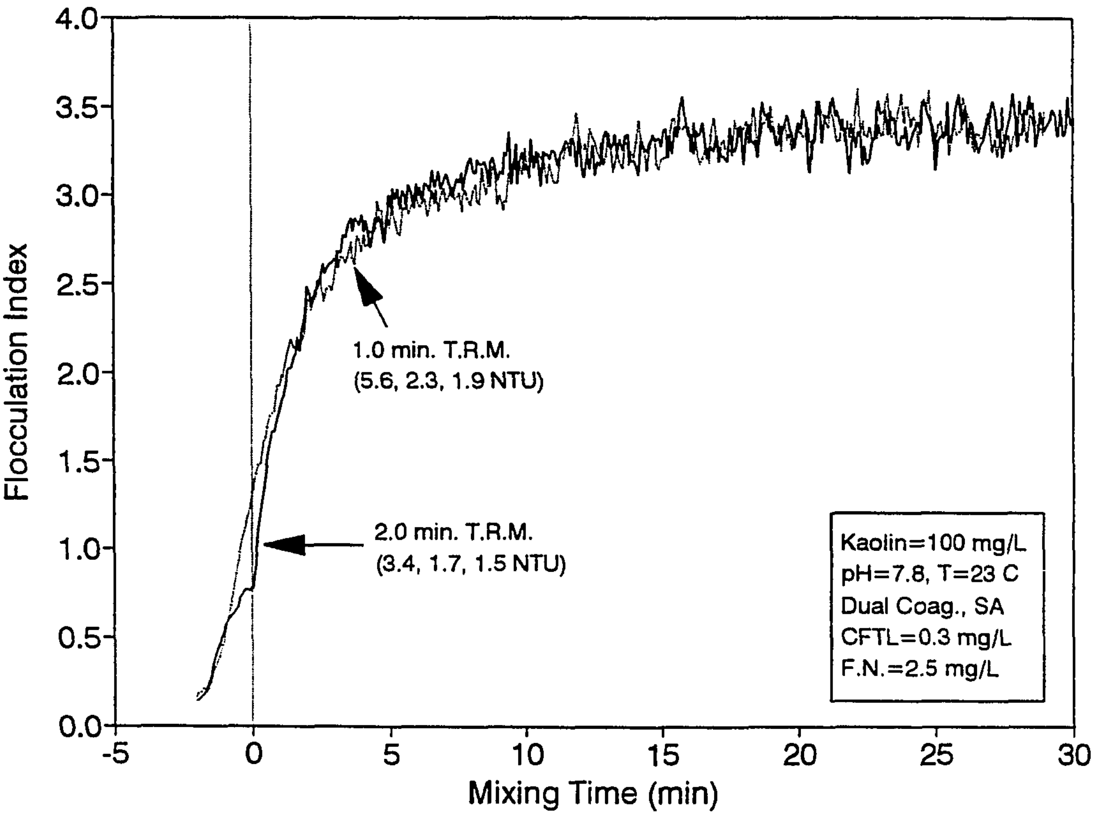


Figure 7.49: Effects of extended rapid mixing duration (2.0 min.) on flocculation kinetics when simultaneous addition (SA) sequence is used for 100 mg/L kaolin clay suspension at 23 °C. (rapid mixing at 250 rpm; slow mixing = 30 min. at 60 rpm).

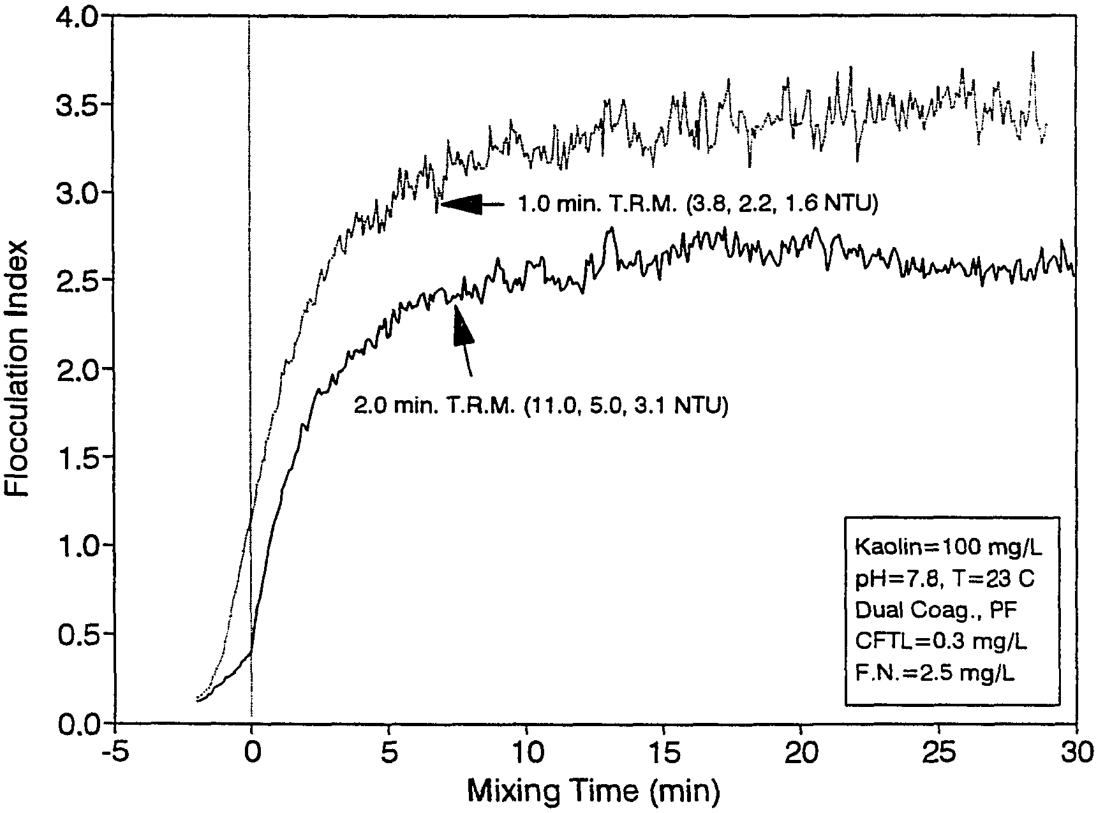


Figure 7.50: Effects of extended rapid mixing duration (2.0 min.) on flocculation kinetics when polymer first (PF) sequence is used for 100 mg/L kaolin clay suspension at 23 °C. (rapid mixing at 250 rpm; slow mixing = 30 min. at 60 rpm).

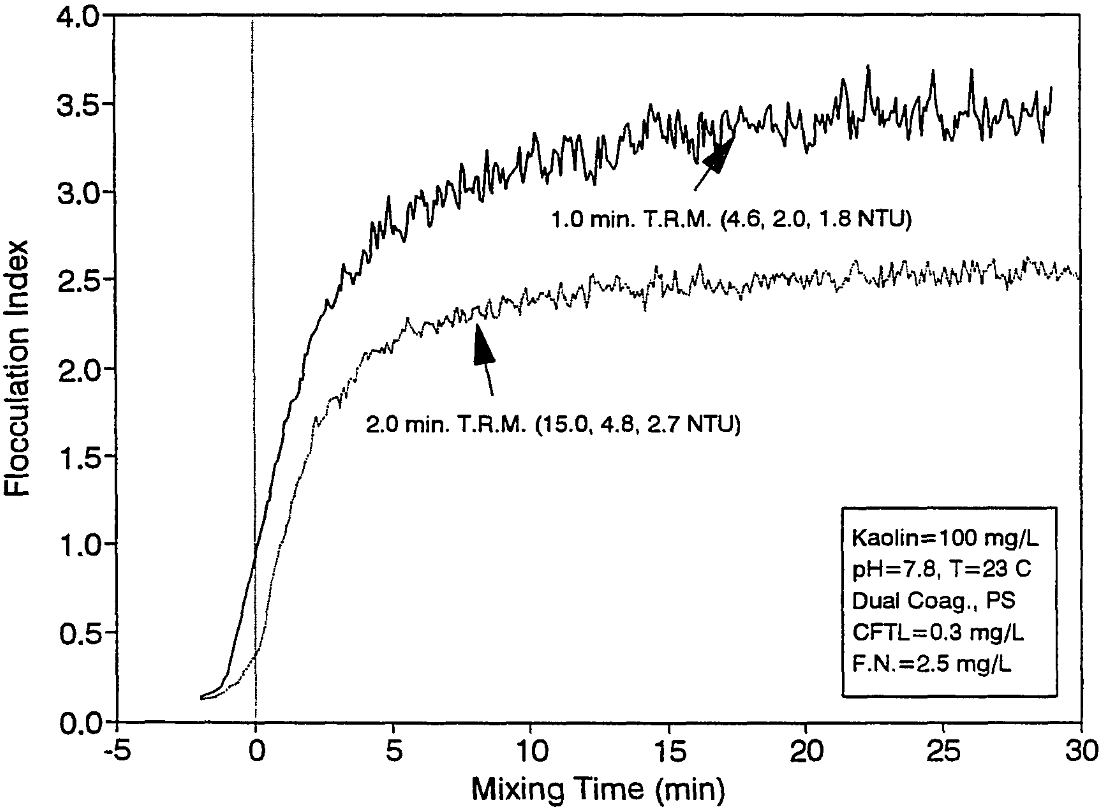


Figure 7.51: Effects of extended rapid mixing duration (2.0 min.) on flocculation kinetics when polymer second (PS) sequence is used for 100 mg/L kaolin clay suspension at 23 °C. (rapid mixing at 250 rpm; slow mixing = 30 min. at 60 rpm).

7.5 Temperature Effects

Temperature effects are presented herein in two steps. First, the effects of temperature on flocculation kinetics using ferric nitrate and the cationic polymer (Cat-Floc TL) each used alone are presented. After that, temperature effects on dual coagulants when added simultaneously are presented. The choice of simultaneous addition for this work was because this mode of addition was found to be the best addition sequence alternative, and produces stronger flocs than the other two alternatives (see section 7.4). Only a limited number of experiments will be presented here about the effects of low water temperature on flocculation kinetics using ferric nitrate alone. Kang (1994) and Kang and Cleasby (1994 a,b), using an identical system to the system used in this study, should be consulted for more details on temperature effects on flocculation kinetics using ferric salts.

Figure 7.52 presents the experiments conducted to find an optimum dose for ferric nitrate coagulant at 5 °C for the 25 mg/L clay suspension at pH 6.0 and zero sulfate concentration. It also compares the results of flocculation kinetics at room temperature with the results at 5 °C for 2.5 mg/L ferric nitrate dose at the same conditions. As can be seen from this figure, the flocculation kinetics at 5 °C were very poor at all the different ferric nitrate dosages as evidenced by both the Flocculation Index and the supernatant residual turbidity after 30 minutes of settling. It can also be seen that the flocculation kinetics at room temperature with 2.5 mg/L ferric nitrate dose were substantially better than those at low temperature.

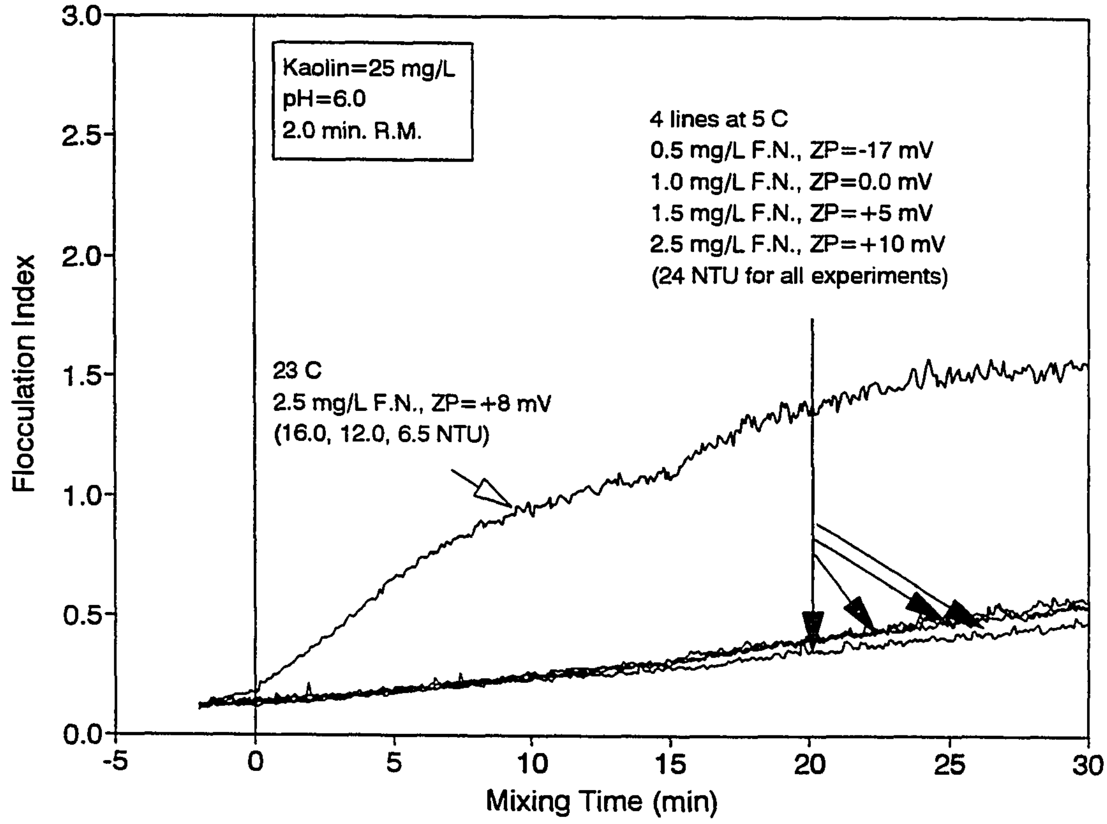


Figure 7.52: Effects of temperature on flocculation kinetics using ferric nitrate (F.N.) alone for 25 mg/L kaolin clay suspension at pH 6.0 and zero sulfate concentration (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

Figure 7.53 shows a similar comparison at similar experimental conditions to those in **Figure 7.52** (i.e. clay concentration = 25 mg/L, ferric nitrate dose = 2.5 mg/L used alone) but at pH 7.8. Again the poorer performance in the Flocculation Index values and supernatant turbidity at low water temperature compared to those parameters at room temperature is substantial.

The effects of temperature on the flocculation kinetics of high turbidity water (100 mg/L clay suspension) using higher ferric nitrate dose (5.0 mg/L) are presented in **Figure 7.54** at pH 7.8. The flocculation kinetics were also impaired by low water temperature at this high clay concentration suspension. The deleterious effects of low temperature, however, was less severe at this high clay concentration than at lower clay concentration (25 mg/L).

Figures 7.55 through 7.57 show the effects of temperature on flocculation kinetics using cationic polymers alone for three different kaolin clay concentration (25, 50, and 100 mg/L) at pH 6.0. The deleterious effect of cold temperature was substantial for 25 mg/L clay concentration (**Figure 7.55**). This deleterious effect diminished for the 50 mg/L clay concentration suspension (**Figure 7.56**) and was almost eliminated for the 100 mg/L clay concentration suspension (**Figure 7.57**). In **Figure 7.57**, the Flocculation Index curve for the 5 °C experiment became higher than the Flocculation Index for the room temperature experiment after about 10 minutes of flocculation. This is believed to be caused by the settling of large flocs during flocculation for room temperature experiments. Settling during flocculation in cold temperature experiments was substantially less. And as was mentioned earlier, the effect of these settled flocs on the Flocculation Index values is lost. It should be

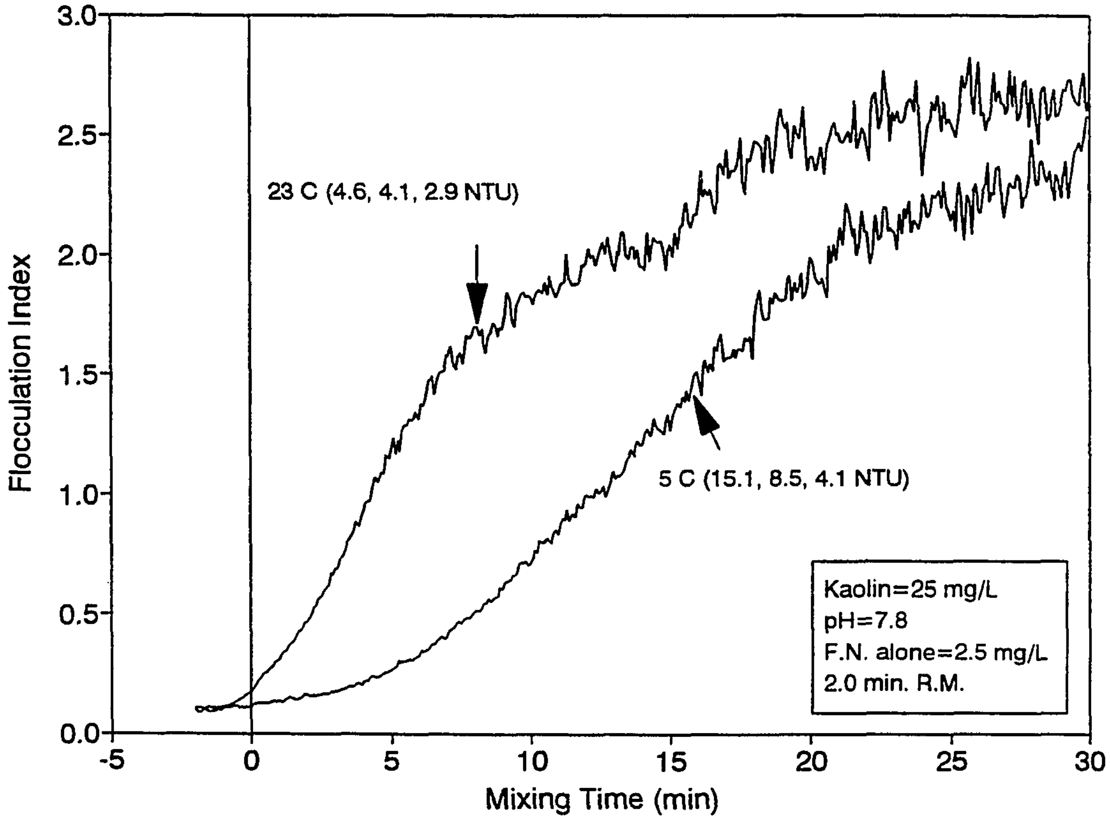


Figure 7.53: Effects of temperature on flocculation kinetics using ferric nitrate (F.N.) alone for 25 mg/L kaolin clay suspension at pH 7.8 (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

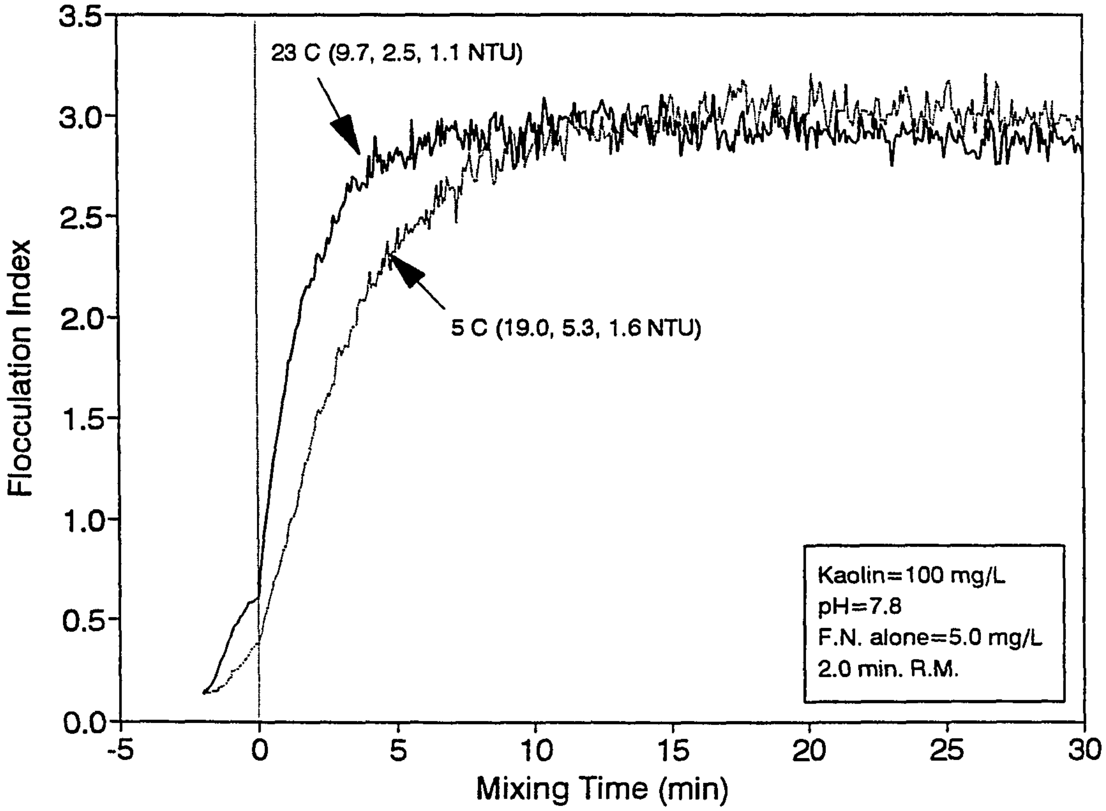


Figure 7.54: Effects of temperature on flocculation kinetics using ferric nitrate (F.N.) alone for 100 mg/L kaolin clay suspension at pH 7.8 (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

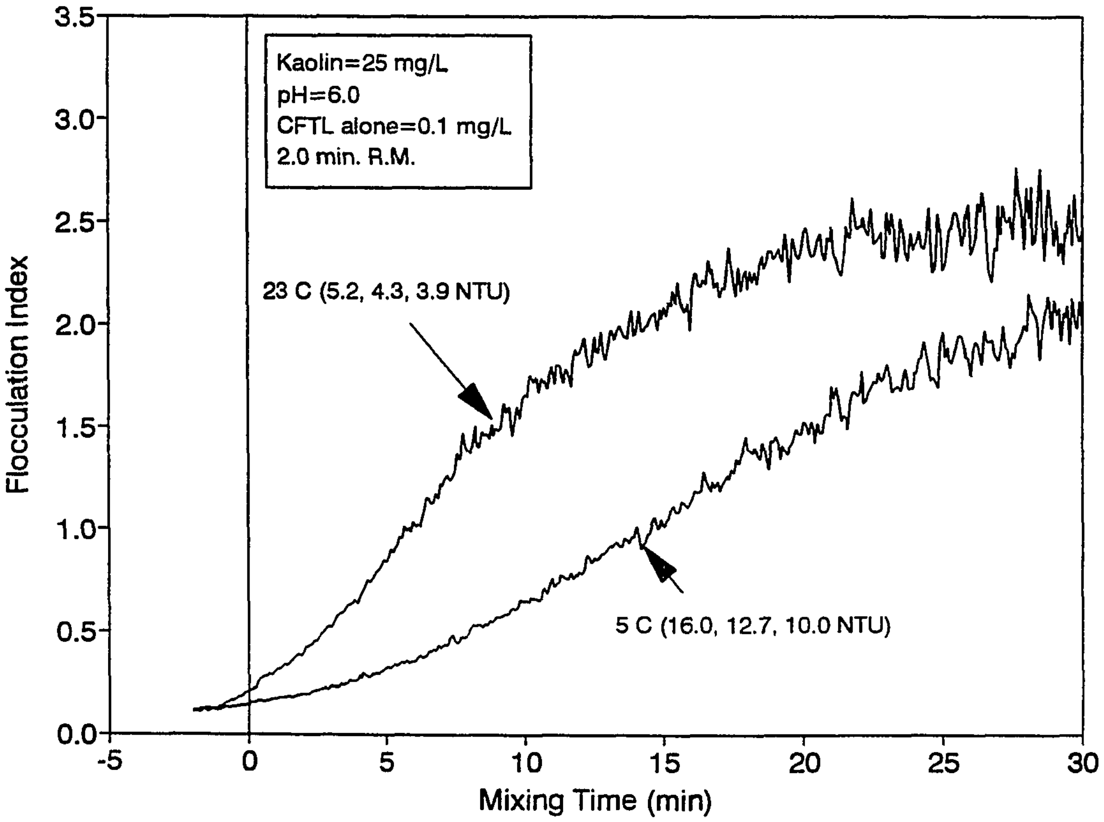


Figure 7.55: Effects of temperature on flocculation kinetics using a cationic polymer (CFTL) alone for 25 mg/L kaolin clay suspension at pH 6.0 (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

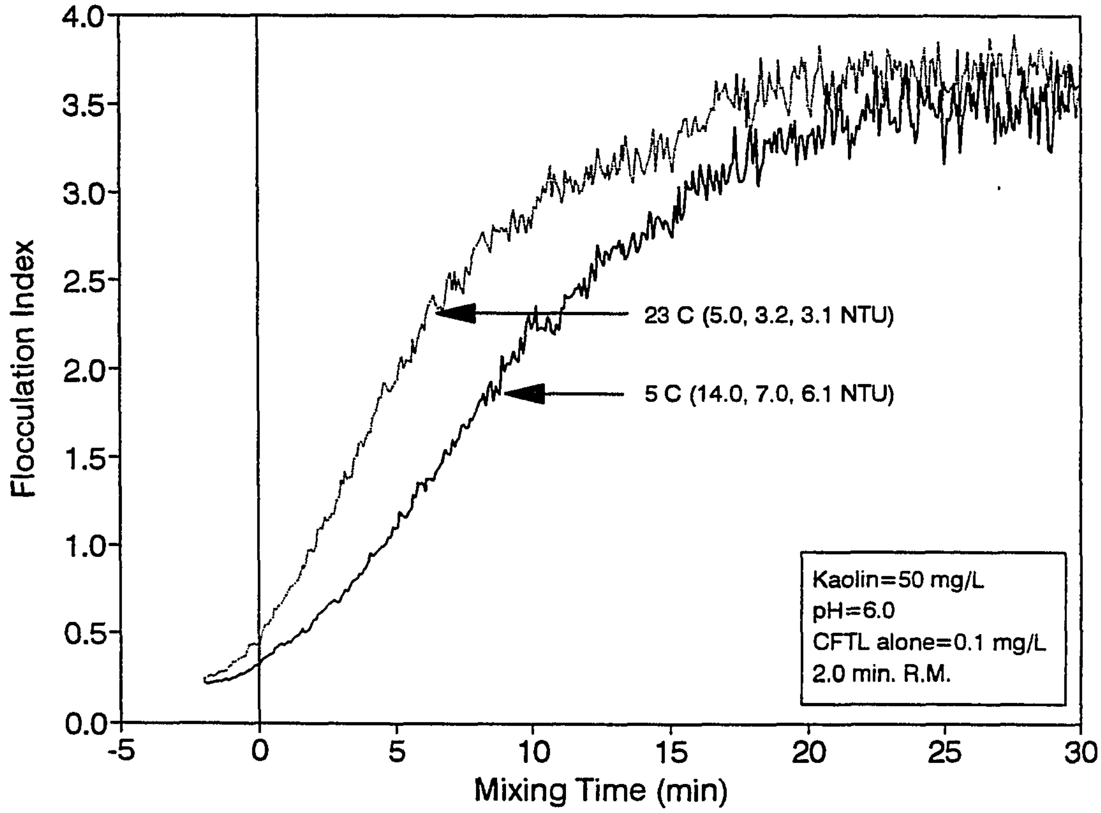


Figure 7.56: Effects of temperature on flocculation kinetics using a cationic polymer (CFTL) alone for 50 mg/L kaolin clay suspension at pH 6.0 (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

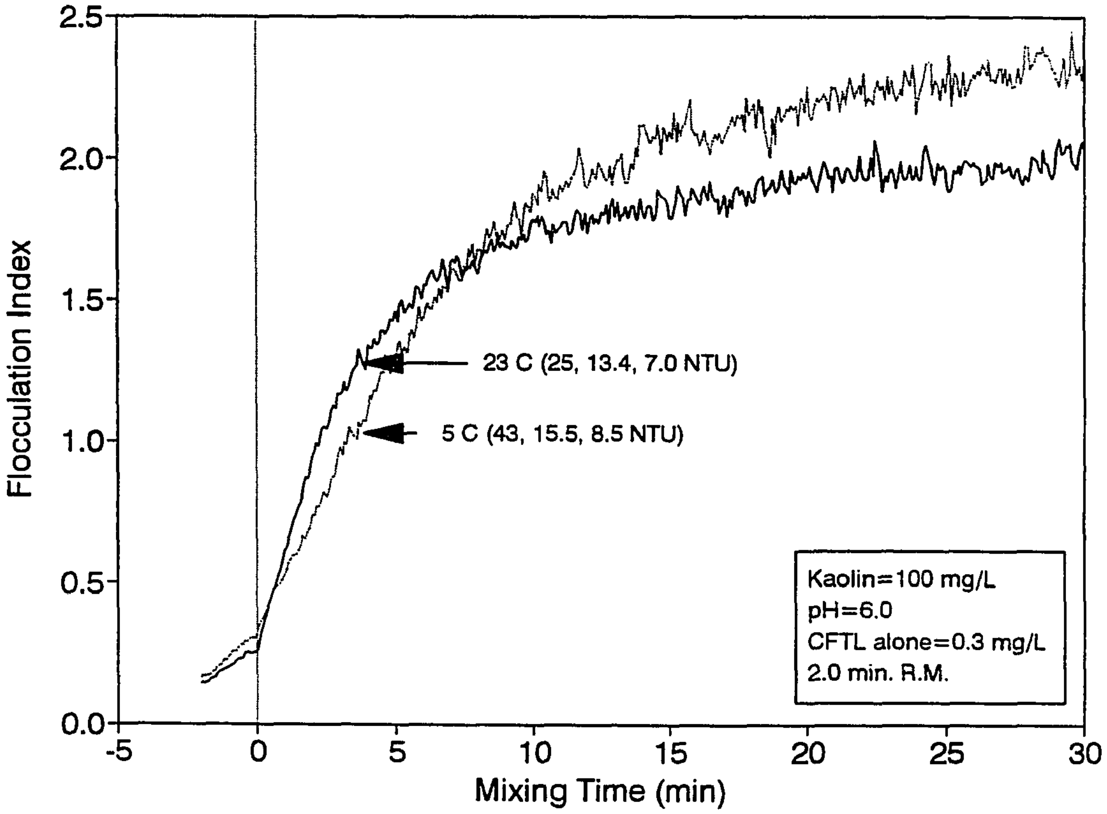


Figure 7.57: Effects of temperature on flocculation kinetics using a cationic polymer (CFTL) alone for 100 mg/L kaolin clay suspension at pH 6.0 (rapid mixing = 2.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

noted at this point that the ratio values for the 100 mg/L kaolin clay concentration experiments were obtained using a different magnification setting on the PDA instrument (RMS Gain was set at 500) than that of the 25 mg/L and 50 mg/L clay concentration. Therefore, the ratio value for 100 mg/L clay concentration should not be compared with those of 25 and 50 mg/L clay concentrations.

The results obtained above regarding the deleterious effect of cold water temperature on the flocculation kinetics when ferric nitrate alone was used are in agreement with the recent studies reported in the literature (Hanson and Cleasby 1990, Kang and Cleasby 1994, Morris and Knocke 1984). The reason for such an impairment was generally ascribed to the physical and chemical changes that low water temperature has on the suspension and the coagulant, respectively.

However, in case of cationic polymers, temperature has no chemical effect on the coagulant. Cationic polymers induce coagulation by adsorbing to the negatively charged particles, thus neutralizing their charge and/or producing patched particles (negatively charged particles with positive patches of adsorbed cationic polymer) that have a tendency to agglomerate. Since the cationic polymer dosing solution is obviously a solution of water and the cationic polymer, the ionization of the cationic polymer and the negatively charged element (the counterion) is already complete. Therefore, low temperature has no effect on the rate of ionization of cationic polymers. Moreover, cationic polymers do not have the polymerization and the precipitation steps (which could be affected by temperature) before adsorption as inorganic coagulants do.

From **Figures 7.55 and 7.56** one can then conclude that the negative impact that low temperature has on flocculation kinetics when cationic polymers are used is due to physical effects. Cold temperature could have an effect on the rate of adsorption of the cationic polymer on the clay particles. It also reduces the collision frequency between the suspended particles by reducing the G value at a given rotational speed of the impeller. Another possible effect is the reduction in the floc strength at low temperature. However, the impact of low water temperature on the rate of adsorption of cationic polymers on the suspended matter surface is minimal (see section 7.3). In the present study, increasing the rapid mixing intensity which should increase the rate of polymer adsorption was not beneficial to the flocculation kinetics at low temperatures. In addition, increasing the rapid mixing time at low temperature, should reduce the negative effects of low water temperature, since more time would be given for the cationic polymer to adsorb. However, this was not observed in the present study. These observations would, therefore, minimize or even eliminate rate of adsorption as a possible cause for the reduced flocculation kinetics at low temperatures. The reason why low temperature did not have a significant effect on the flocculation kinetics with cationic polymers with high suspended solids concentration (**Figure 7.57**) will be discussed later.

Let's now move to the effects of low temperature on flocculation kinetics using dual coagulants. **Figures 7.58 to 7.61** show the Flocculation Index value against mixing time for four different clay concentrations (5, 25, 50, and 100 mg/L, respectively) at pH=7.8. In all of these figures, the cationic polymer was added simultaneously with ferric nitrate.

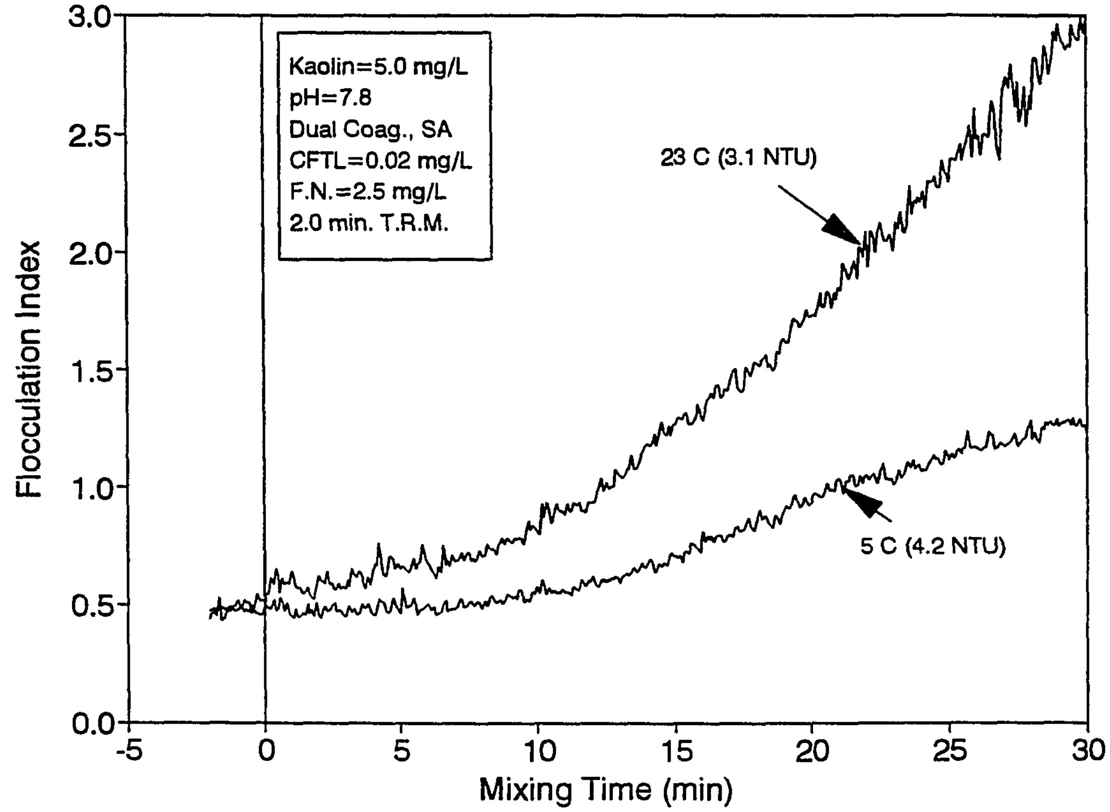


Figure 7.58: Effects of temperature on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 5.0 mg/L kaolin clay suspension at pH 7.8 (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

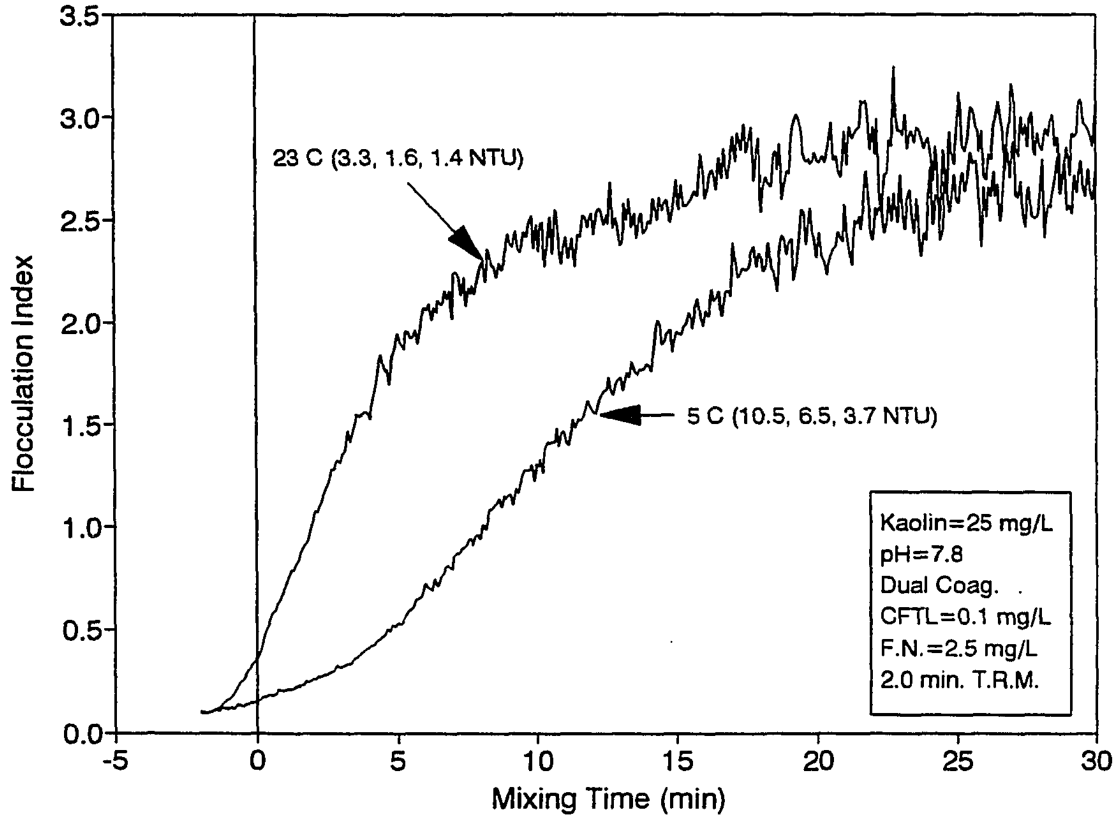


Figure 7.59: Effects of temperature on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 25 mg/L kaolin clay suspension at pH 7.8 (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

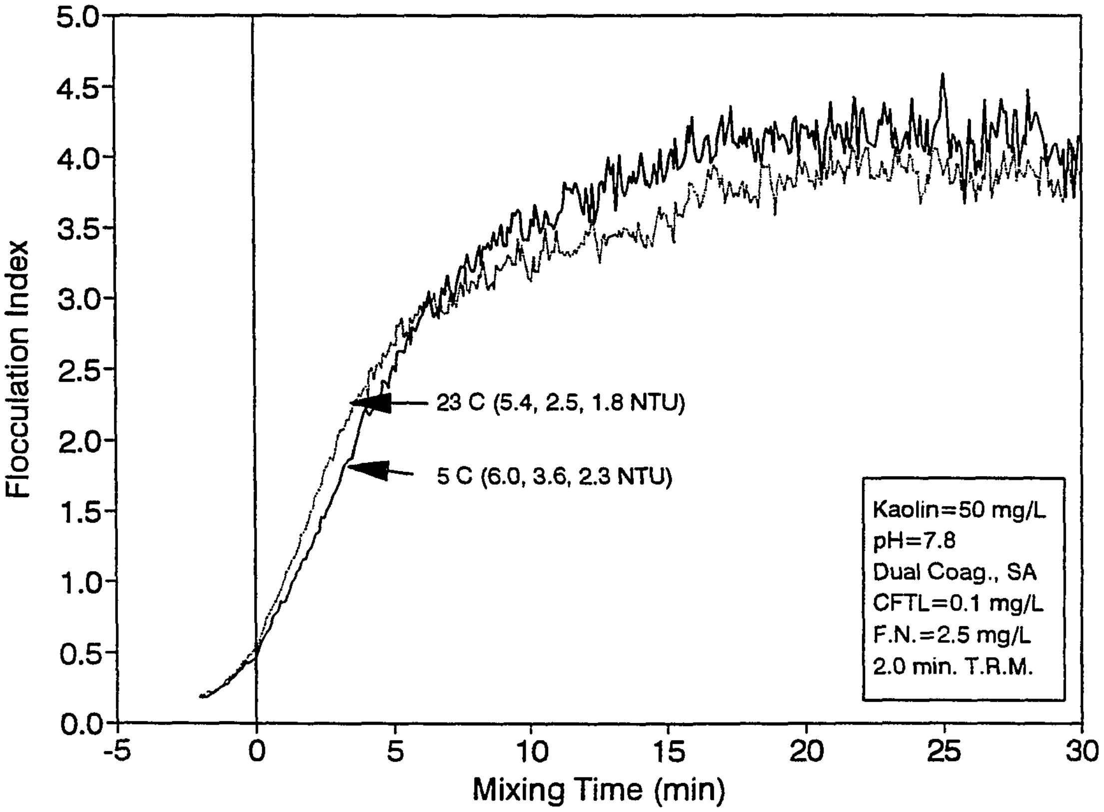


Figure 7.60: Effects of temperature on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 50 mg/L kaolin clay suspension at pH 7.8 (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 15 min. at 60 rpm followed by 15 min. at 45 rpm).

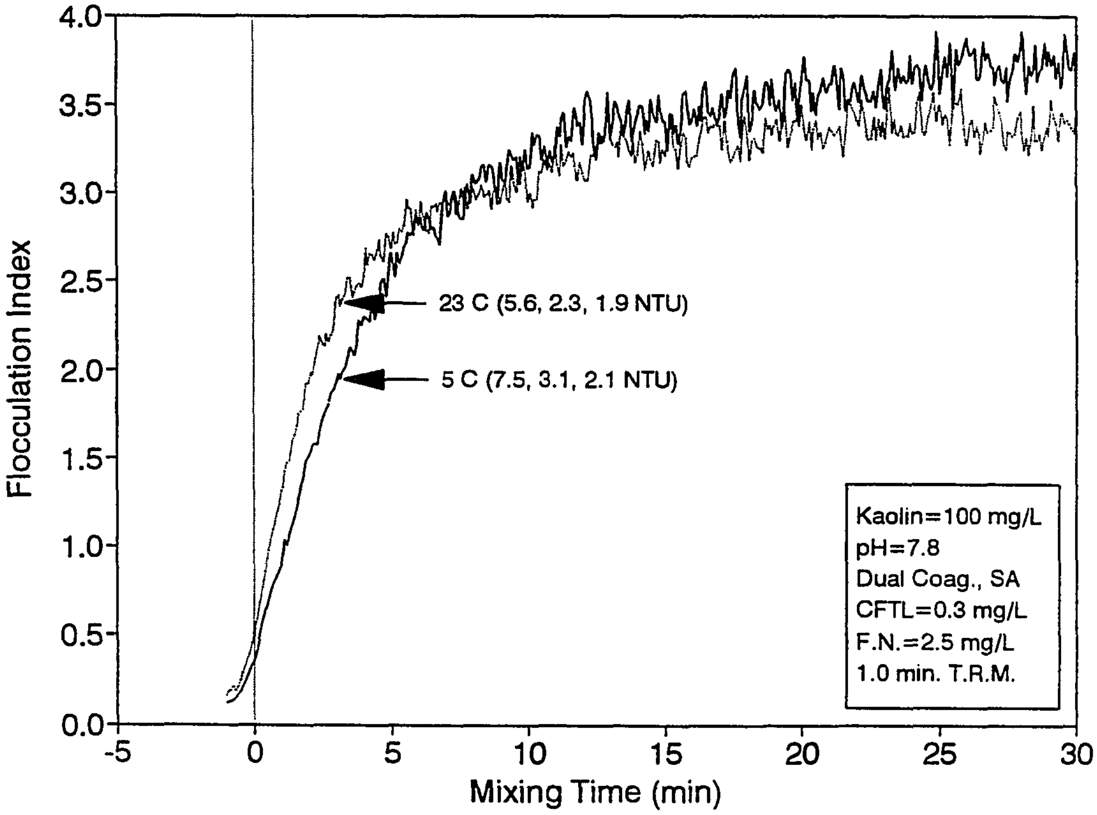


Figure 7.61: Effects of temperature on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 100 mg/L kaolin clay suspension at pH 7.8 (total rapid mixing = 1.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

Simultaneous addition has been found to be the best addition sequence at this pH as was shown earlier, especially for low water temperatures. **Figure 7.58** presents the low temperature effect on flocculation kinetics at low turbidity waters (5 mg/L clay suspension).The detrimental effect of low water temperature on the flocculation kinetics at this low turbidity is clear, as the Flocculation Index curve and residual turbidity values show. **Figure 7.59** shows that, for 25 mg/L clay concentration, there is a substantial decrease in flocculation kinetics at low water temperature compared to that at room temperature. On the other hand, **Figures 7.60 and 7.61** show almost similar results at low and room temperatures for clay concentration values of 50 and 100 mg/L. In other words, the effects of low water temperature diminishes as the suspended solids concentration increases, and is almost eliminated at high values. This behavior is similar to the case where cationic polymers alone are used, as was presented previously. It should be noted here that **Figure 7.61** was conducted using only 1.0 minute of total rapid mixing time. This was found to be the optimum period at 5 °C and 100 mg/L clay concentration. All the other experiments shown in this section were conducted using 2.0 minutes of total rapid mixing time.

So, why does low water temperature have a more dramatic effect at low suspended solids concentration than at high suspended solids concentration? And why was the detrimental effect of cold temperature eliminated at high clay concentration when the cationic polymer alone or dual coagulants were used but not when ferric nitrate alone was used? The following is an attempt to answer these questions.

The coagulation process consists first of particle destabilization and then the transport of these destabilized particles to each other to form aggregates (the flocculation process). In the case of cationic polymers alone, the destabilization step can be assumed to be independent of temperature. Therefore, any effect that low water temperature has on the coagulation process using cationic polymers alone is due to its effect on the flocculation step. The flocculation step by itself can be viewed as consisting of two steps. The first step is the aggregation of the individual particles to form aggregates. The second step is the partial breakup of these aggregates. The aggregation step is a function of both the rate by which the particles are transported to each other as well as the collision frequency factor. The breakup process, however, is a function of the floc strength and the applied shear rate, or G. It is well known that the maximum floc diameter or the average size of flocs is an inverse function of the applied velocity gradient, G. The balance between the floc growth and breakage determines the particle size distribution.

If the collision efficiency factor is assumed to be independent of the temperature value, then any differences in the flocculation kinetics at low and room temperatures would be due to differences in the particle collision rate and/or floc breakup.

Particles are transported by means of the applied shear and by differential settling, assuming that the perikinetic flocculation is negligible. Low water temperature can affect the rate of particle transport for a given power input. For a given rpm value, the mean velocity gradient, G, is less for low water temperature due to an increase in water viscosity. In addition the differential sedimentation, which is a transport process, is impaired by the low temperature. Temperature can also affect the breakup process. Hanson and Cleasby (1990) related the impaired flocculation kinetics at low temperature to the reduced floc strength. They also found that ferric salt coagulants produced stronger flocs than alum.

For low turbidity waters, the transport of particles, which determines the collision frequency of the particles, is the rate limiting step in the flocculation process. The collision frequency of particles is a function of both the particle concentration and the applied mean velocity gradient, G. If the same power input or rotational speed is applied for the same low turbidity water at low temperature, then the value of G becomes smaller. For a decrease in temperature between 23 °C to 5 °C, the value of G is reduced to 78 % of its value at 23 °C. The rate of collision between particles due to differential settling, assuming that the same particles are still present at both low and room temperature, is decreased to about 60 %. Therefore, a decrease in temperature of this low turbidity water would decrease the rate of collision of the particles, which is already a rate limiting step. Therefore, low water temperature would be expected to have its most detrimental effect on low turbidity waters.

One could argue that, if this is the case, then increasing the slow mixing intensity would compensate for the loss in G value, and returns the G value to its value at room temperature, thus eliminating low temperature effects. It should be noted, however, that the flocculation process is a two step process, and that the rate of growth of particles is a function of both the rate of collision and aggregation as well as the rate of floc breakup. Aggregates at low water temperature are weaker than those at room temperature. Therefore increasing the G value at cold temperature to that at room temperature would have an effect on the breakup step of the flocculation process because the flocs formed at low temperature are weaker. It should be noted that floc breakup can occur in two modes. The first is the stripping of the individual primary particles from the floc surface by turbulent drag while the second is large scale splitting of the flocs (Tambo and Francois 1991).

For high turbidity waters, the collision frequency between the suspended solids is high and therefore is not limiting. The breakup step which is dependent on the floc strength and mixing intensity now limits the size of the resulting flocs that form. For a specific energy input, the G value at low temperature becomes smaller. Therefore (for cases where collision frequency is not rate limiting) if floc strength were not affected by temperature, and if these flocs could still be kept in suspension at this lower G value, the flocs at cold temperature should be larger than those at room temperature. However, the reduction in floc strength at lower temperature seems to occur regardless of the coagulant type. The extent of the reduction is, however, dependent on the type of coagulant used.

Another purpose of slow mixing (other than increasing particle collision) is to keep the flocs in suspension in order for them to collide with other particles. At low temperature, the G value required to keep the flocs in suspension should be lower than room temperature due to the increased water viscosity at low temperature. Therefore, lower G could be used for low temperature water without risking the settling of the large flocs.

At low temperature, both G and the strength of flocs are reduced (for a specific power input). These two factors have a compensating role on the maximum floc size that can be achieved. Therefore, if the floc strength is not largely reduced (as in the case of cationic polymers or dual coagulants) it is possible that the floc size would not be reduced at low temperatures. This can be achieved at low water temperature because the lower G value does not result in the loss of flocs due to settling as was observed at room temperature. Because flocs formed with ferric nitrate are affected largely by low water temperature, the detrimental effect of low temperature was only reduced, but not eliminated at the high clay concentration suspension.

To test the hypothesis presented above about the floc strength, the rapid mixing time for the 100 mg/L clay concentration was increased to 2.0 minutes instead of 1.0 minute as in **Figure 7.61**. The 2.0 minute rapid mixing time at low temperature and at this clay concentration is detrimental. Therefore, the difference between flocculation kinetics at room and low temperature was substantial as **Figure 7.62** shows.

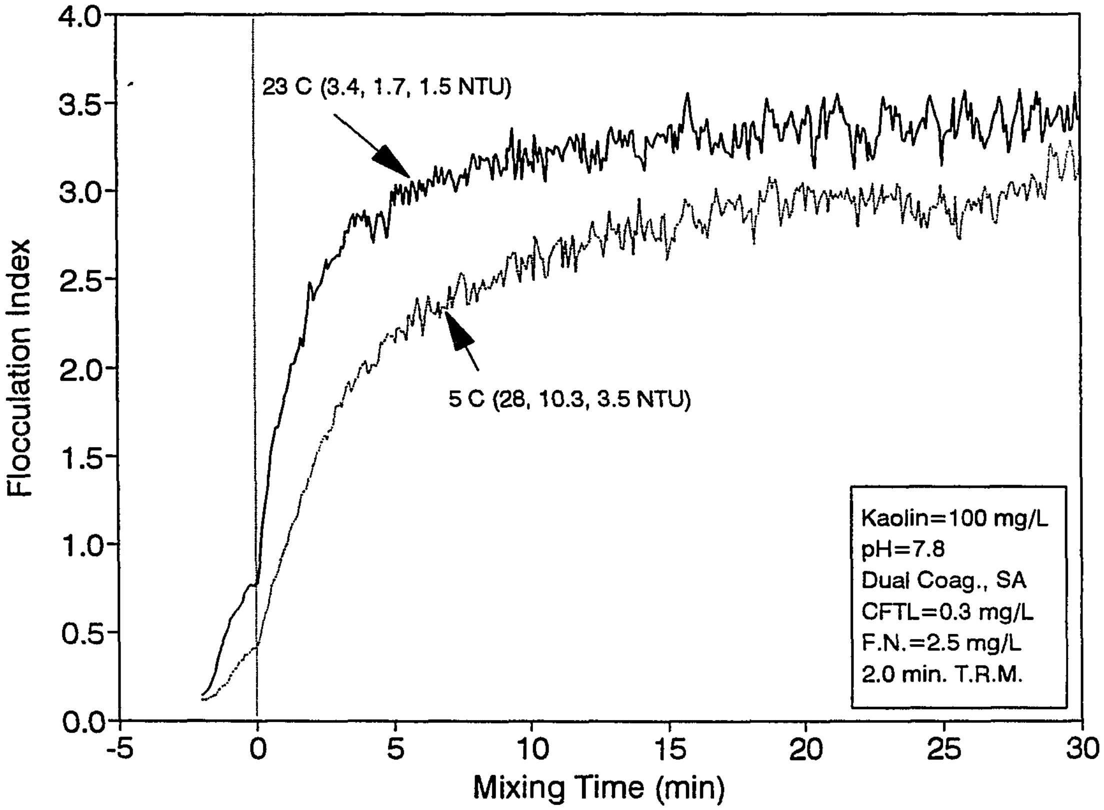


Figure 7.62: Effects of temperature on flocculation kinetics using dual coagulants (CFTL + F.N.) added simultaneously for 100 mg/L kaolin clay suspension at pH 7.8 (total rapid mixing = 2.0 min. at 250 rpm; slow mixing = 30 min. at 60 rpm).

8. CONCLUSIONS

The work reported here was designed to study the effects of temperature, rapid mixing time and intensity, sulfate, and coagulant addition sequence of dual coagulants using either ferric nitrate or a cationic polymer alone or in combination. Kaolinite clay (with four concentrations: 5, 25, 50, and 100 mg/L) suspended in distilled water with added salinity was used at two temperatures (5 or 23 °C) and two pH values (6.0 or 7.8) to simulate natural water. Sulfate effects were also studied using either zero concentration or 0.001 M concentration. Addition sequence of cationic polymers was studied by comparing three addition sequences: the addition of polymer before ferric nitrate addition, the addition of polymer after ferric nitrate addition, and simultaneous addition. The following conclusions were drawn from this work:

1- Extended rapid mixing proved to be an important step for particle growth when inorganic coagulants or dual coagulants were used. This growth of particles during rapid mixing affects (in a negative way if the rapid mixing period was excessive, and in a positive way if it was not excessive) the flocculation process as well as the sedimentation process. The production of flocs under high intensity mixing produces strong and dense flocculi (small flocs) that are the building blocks for bigger flocs.

For coagulation with cationic polymers alone, the rapid mixing duration had a minimal effect on the flocculation kinetics or the sedimentation process. This is probably due to the formation of stronger flocs when cationic polymers are used, and the production of flocculi under high intensity mixing is not critical.

2- Rapid mixing should continue until the flocculi formed during rapid mixing reach a certain diameter. The time needed to attain such diameter is a function of the suspended matter concentration. At high suspended matter concentration, the rate of particle collision is high and consequently the rapid mixing time needed for the flocculi to reach such a specific diameter is shorter.

3- Rapid mixing at a low mixing intensity ($G \cong 450\ s^{-1}$) and longer mixing times gave better flocculation kinetics than high mixing intensity ($G \cong 900\ s^{-1}$) with shorter mixing times for the same Gt product value. For the same rapid mixing duration, high intensity mixing gave almost similar flocculation kinetics to the lower mixing intensity, but with inferior residual turbidity values. This could be due to the breakage of flocs formed during rapid mixing at the higher mixing intensity. Particles resulting from the breakage of a bigger floc have a lower tendency to aggregate.

4- The use of a cationic polymer alone was superior to both the use of an inorganic coagulant alone or the combined use of these coagulants when the mechanism of coagulation of the inorganic coagulant was completely charge neutralization (i.e., the inorganic coagulant dosage was small enough that almost no precipitation occurred, as was the case at pH 6.0 and zero sulfate concentration at 25 or 50 mg/L clay concentration). For low turbidity waters (5 mg/L clay, in the present study), neither the use of inorganic or cationic polymer coagulants alone or in combination as dual coagulants was able to induce noticeable aggregation in the absence of a precipitate from the inorganic coagulant.

Under the above conditions, it is believed that the patchy configuration of adsorbed cationic polymer and the original negative charge on the particles surface can be used to explain the superiority of using cationic polymers alone. When the inorganic coagulant is used either alone or in dual coagulants, the patchy configuration is absent (when the inorganic coagulant is used alone) or is reduced (when dual coagulants are used) due to the much smaller and much numerous hydrolysis species of the inorganic coagulant. The presence of a patchy configuration produces a stronger attachment between the collided particles.

5- Dual coagulants outperformed the sole use of each coagulant alone when the inorganic coagulant dose was high enough to form metal hydroxide precipitate (as was the case when 2.5 mg/L ferric nitrate was used at pH 7.8 or, in the presence of 0.001 M sulfate at pH 6.0). The use of dual coagulants in this case reduced the inorganic coagulant dosage to half its required value when used alone without reducing the flocculation kinetics and the residual settled water turbidity. For low turbidity waters (5 mg/L clay concentration), the substitution of half of the inorganic coagulant dosage with a cationic polymer could not compensate for the loss of the metal hydroxide precipitate at this low turbidity where the collision rate of particles is the limiting factor in particle aggregation.

It is believed that (for dual coagulants) the contribution of the inorganic metal hydroxide precipitate to the total suspended solid concentration improves flocculation kinetics, while the cationic polymer produces larger and stronger flocs, thus improving the flocculation kinetics compared with the sole use of each coagulant alone.

6- When the use of dual coagulants shows an advantage over the use of the inorganic coagulant or the cationic polymer each used alone, the cationic polymer should be added simultaneously with the inorganic coagulant. Simultaneous addition was found to produce the strongest flocs as was evidenced by the higher rate of particle growth during rapid mixing, as well as the higher resistance to shear induced by extended rapid mixing periods.

It is hypothesized that the presence of the cationic polymer during the first stages of particle growth allows the cationic polymer to participate in the formation of the aggregates between the metal hydroxide precipitate and the clay particles. The cationic polymer, therefore, becomes a part of the initial particulates matrix which are the building blocks of the bigger particles, making them stronger and denser than those obtained using the other addition sequence alternatives. The addition of the cationic polymer before or after the inorganic coagulant addition does not allow for such participation.

For dual coagulant addition, the rapid mixing duration applied for the inorganic coagulant and the sequence of adsorption of the cationic polymer and the inorganic coagulant could also be used to explain the results obtained herein. When the total rapid mixing duration is below the detrimental rapid mixing duration for the inorganic coagulant alone, the addition of the inorganic coagulant at the beginning of the total rapid mixing period is beneficial. When the total rapid mixing period is longer than the detrimental rapid mixing period for the inorganic coagulant alone, the addition of the inorganic coagulant after the cationic polymer addition is preferred. The rapid mixing duration applied to the cationic polymer is not as critical or important as with the inorganic coagulants (see conclusion number 1 above).

The sequence of adsorption of the coagulants on the suspended matter particles also depends on the addition sequence. When cationic polymers are added before inorganic coagulants, the particles with adsorbed “patches” of cationic polymer are subsequently covered by the much smaller inorganic hydrolysis species, thus reducing the collision efficiency and floc strength. This does not occur when the cationic polymer is added after the inorganic coagulant addition. When the cationic polymer is added simultaneously with the inorganic coagulant, it is possible that the majority of the cationic polymer molecules adsorb to the suspended particles after the inorganic coagulant hydrolysis species adsorb, due to the much smaller number of cationic polymer molecules compared to the inorganic coagulant hydrolysis species. And, also, possibly due to the higher rate of diffusion of the smaller inorganic coagulant species.

7- Low temperature has a detrimental effect on the flocculation process for low turbidity waters whether a cationic polymer alone, an inorganic coagulant alone, or a combination thereof is used. This detrimental effect is reduced (for inorganic coagulants) and almost eliminated (for cationic polymers coagulants used alone or in dual coagulants) for higher turbidity waters.

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ACKNOWLEDGMENTS

I would like to thank my major professor Dr. John L. Cleasby for his guidance and suggestions throughout the course of this research. Thanks are also extended to the committee members: Dr. Richard Dague, Dr. Charles Glatz, Dr. LaDon Jones, and Dr. Thomas Wheelock.

I would also like to thank my parents for their encouragement and support. The help of Lim-Seok Kang and Md. Wahid Sajjad is also appreciated.

APPENDIX

THE AUTOMATIC IMAGE ANALYZER EXPERIMENTS

The second flocculation kinetics monitoring device was an Automatic Image Analyzer (AIA) (Lemont OASYS). The AIA provides the number of particles in various size ranges, depending on the magnification of the microscope. For the magnification used in the experiments reported here (~ 550 ×), the AIA measures the particle number in the size range from ~ 0.87 μm to less than 100 μm. A sample of the suspension was withdrawn slowly (to prevent floc breakage) from the reactor using a large opening needle (no. 13) at different flocculation times. These samples are transferred to counting cells especially constructed for this purpose. The AIA obtains the image of these samples through the use of a video camera mounted over a light microscope. The AIA identifies and measures objects based on the contrast between the object and the background, which is represented by the level of gray in the field of view.

The AIA was used to study the effects of rapid mixing time, addition sequence, and temperature on the flocculation kinetics using dual coagulants only for 25 mg/L clay suspension and pH 7.8. These results are shown in Figures A1 to A3. In these figures the number of particles counted at time t in all the particle size ranges obtained by the AIA are summed, and then divided by the original number of particles in the suspension before the addition of the coagulant. The size range of the particles measured by the AIA at the high magnification used in obtaining these figures, makes it indicative of the rate of disappearance of primary particles.

The results obtained by the AIA are consistent with the results obtained by the PDA and, therefore strengthen the validity of the conclusions that were drawn based on the PDA results.

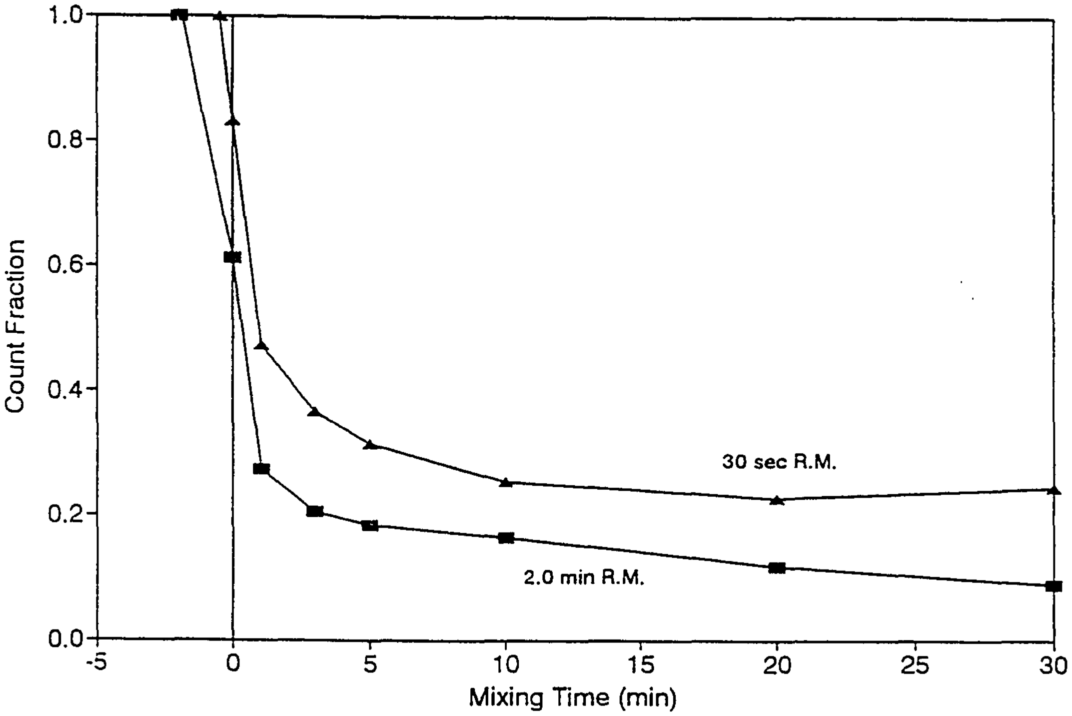

Figure A1: Effects of rapid mixing duration on flocculation kinetics using dual coagulants added simultaneously (2.5 mg/L ferric nitrate + 0.1 mg/L Cat-Floc TL) for 25 mg/L clay suspension at 23 oC and pH 7.8.

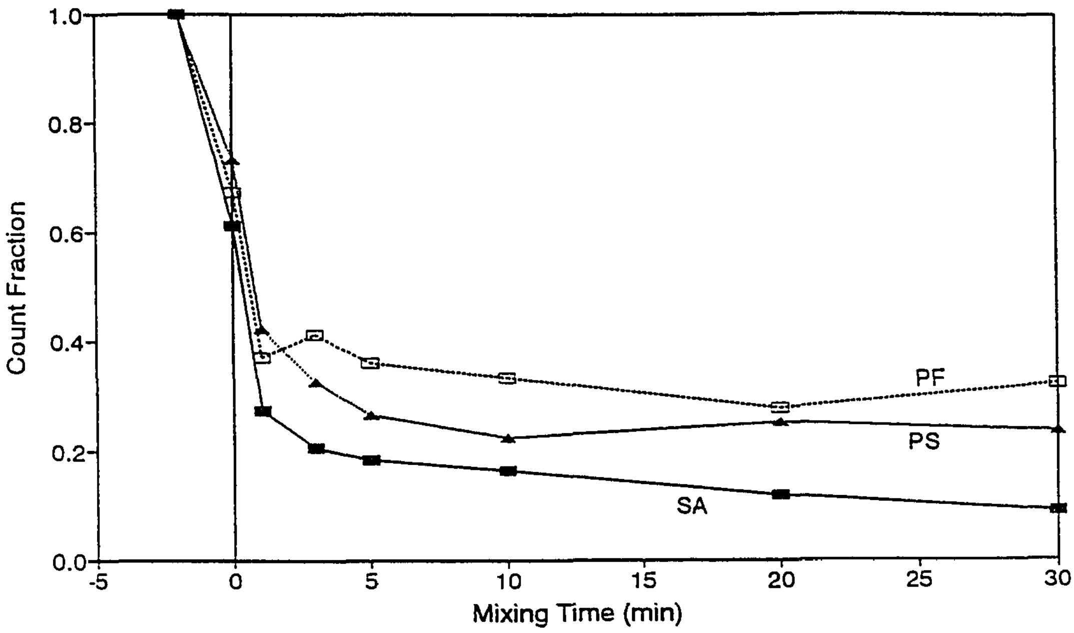

Figure A2: Effects of addition sequence on flocculation kinetics for 25 mg/L clay concentration at 23 oC and pH 7.8. Ferric nitrate dose = 2.5 mg/L and Cat-Floc TL dose = 0.1 mg/L.

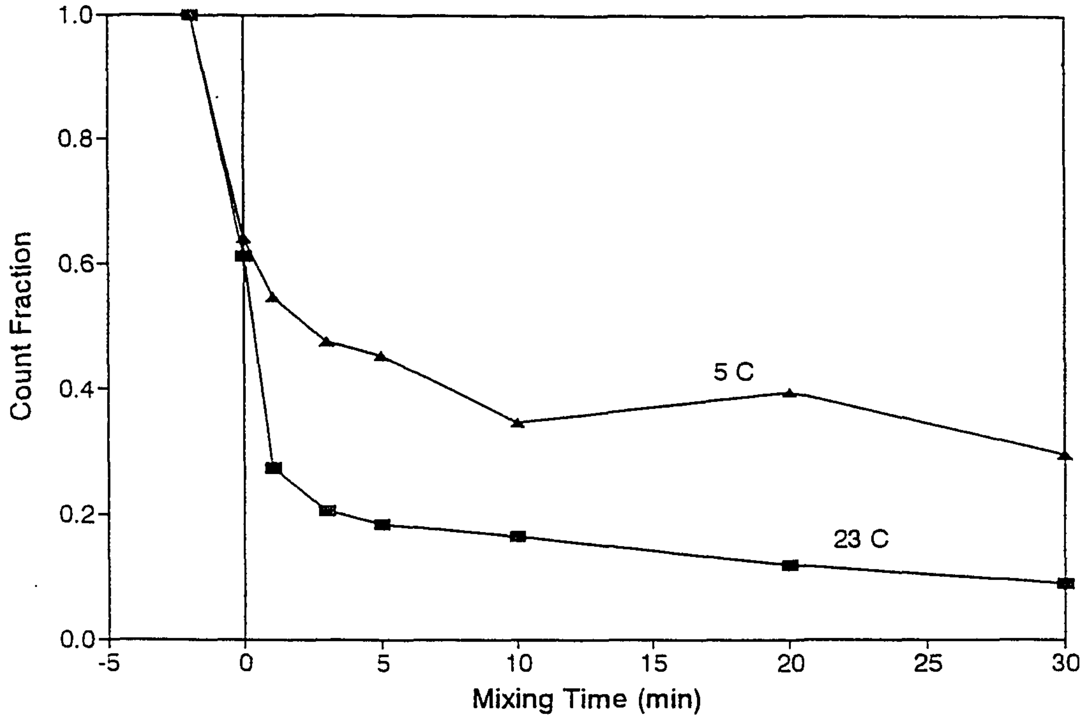

Figure A3: Effects of temperature on flocculation kinetics using dual coagulants added simultaneously for 25 mg/L clay suspension at pH 7.8. Ferric nitrate dose = 2.5 mg/L anf Cat-Floc TL dose = 0.1 mg/L.