UNIVERSITY COLLEGE LONDON

DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

Floc Properties in Stirred Suspensions

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Abstract

The present work was carried out in order to introduce a newly modified light transmission technique and to measure the properties of flocs in a test using this technique. The changes in solution and hydraulic conditions have been made in a systematic manner to show how these factors play a role in the flocculation process under typical water treatment conditions. The experimental results presented suggest that, following a pre-test routine under standard conditions, the procedure can characterise the flocculation behaviour and give information on floc density changes, depending on the solution or hydraulic conditions.

The principle of turbidity fluctuations, which is well known for simple experimental procedure, is employed for monitoring. Basically, it measures the intensity and fluctuations of light occurring when suspension flows through a light beam. The data obtained directly from the monitoring have been used to derive parameters representing the characteristics of flocculation and the floc properties. It allows a convenient means of real time determination of floc properties. Previously used commercial PDA (Photometric Dispersion Analyser) has been modified to reduce forward scattered light, by using a better collimated light beam. The tests have been carried out in stirred suspensions of latex, kaolin and two different kinds of silica particles with selected polymers and electrolytes.

To investigate the influence of solution conditions, the standardised pre-test routine has been performed to observe the basic flocculation characters shown in polymer concentration distribution. During the pre-tests, the relationship between polymer concentration and the flocculation rate has been shown. During the main tests, it is found that (1) cationic polymer with high molecular weight leads to extremely high degree of flocculation while the speed of the flocculation depends greatly on the concentration and charge density of polymers. (2) the charge density of polymer also plays a role in determining the optimum polymer dosage, although its effect on the floc structure, which corresponds to conformational changes during the adsorption/flocculation process under shear, has not been observed. (5) Adding electrolyte to flocculating suspension could change the effective polymer concentration range. The electrolyte concentration below the c.c.c. (critical coagulation concentration) could enhance latex flocculation in terms of flocculation rate. This trend becomes more significant in the case of polymer with low charge density.

As hydraulic condition is used as a variable, the following are observed. (1) Monitoring flocculation could assess the reversibility of flocculation process which depends on mode of action of the polymer. (2) Continuous aggregation and break-up in the later stage resulted in denser flocs and the limiting size which is related to the floc strength. (3) Shear rate plays an important role in governing the rate of the process.

Although the current monitoring method provides useful information on the rate of flocculation as well as the development of floc structure, the complementary use of other measurement techniques such as particle counting or image analysis will give information on more complicated floc properties.

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Nomenclature

- a particle radius
- a_i, a_j radii of particles i and j
- a_k radius of fractal k-fold aggregate

A Hamaker constant

- A_{12} Hamaker constant for media 1 and 2
- A_{123} Hamaker constant for the interaction of media 1 and 2 through medium 3
- α dimensionless particle size
- C light-scattering cross-section of the particles
- C_i molar concentration of ions of type i
- D_i, D_j diffusion coefficients of particles *i* and *j*
- d distance
- d_F mass fractal dimension
- δ thickness of Stern layer
- e elementary charge

 $[\eta]$ intrinsic viscosity

- f fraction of added polymer to particles
- f(k) distribution of aggregate sizes
- F(d) interaction energy per unit area between two thick parallel flat plates
- g acceleration due to gravity
- G velocity gradient or shear rate
- Gt Camp number
- \overline{G} mean velocity gradient

 γ_1, γ_2 dimensionless functions of the zeta potentials

 Γ gamma function

- I_0 incident intensity
- J_{ij} number of collisions in unit volume per unit time
- κ Boltzmann constant
- k aggregation number
- k_{ij} collision coefficient between particles *i* and *j*
- k_F flocculation rate constant
- \overline{k} mean aggregation number
- κ Debye-Hückel parameter
- L length
- La aggregate size
- λ wavelength
- m relative refractive index
- M viscosity-average molecular weights of the polymers
- M_a aggregate mass
- μ viscosity of the fluid
- n number concentration per unit volume
- N_i, N_j number concentrations of particles *i* and *j*
- N_0 initial concentration of primary particles
- N_T total number concentration
- ν kinematic viscosity of the fluid
- ϕ volume fraction of the suspended particles
- ϕ_S volume fraction of solid in the aggregate
- ψ_d electrical potential
- ψ_0 surface potential
- Q scattering coefficient
- R_{ij} collision radius
- ho density
- ρ_s density of the particles
- ρ function of the dimensionless size α
- ρ_E effective, buoyant density of an aggregate in a liquid

 $\rho_S, \ \rho_L \ \text{and} \ \rho_F$ densities of the solid particles, the liquid and the aggregate, respectively

- t time in seconds
- t_{Ads} the time required for adsorption
- t_F characteristic aggregation time or the half life of the aggregation
- T relative turbidity
- au turbidity
- ε permittivity of the medium
- z valency of the ions (assuming a symmetrical, z-z electrolyte)
- ζ zeta potential
- $\zeta_1, \, \zeta_2$ zeta potentials of particle 1 and 2
- Z_i valence of ions of type i

Chapter 1

Introduction

1.1 General background

In most water and wastewater processes including sedimentation, flotation and filtration, the efficiency of removal of fine particles in suspension can be improved by aggregation in a coagulation/flocculation sequence. Coagulation/flocculation can be defined as the destabilisation of colloidal suspension and particle collision followed by the aggregate formation respectively. Great improvement in solid/liquid separation can be achieved by this kind of operation.

Most particles in suspension have a surface electric charge when brought into contact with a polar medium such as water. This charge is usually negative in natural water. The kinetic stability in suspension is maintained by the existence of an electric charge on the surface of the colloidal particles which tends to attract opposite charge ions (counter-ion) and to repel like charge ions (co-ion). This ionic atmosphere which is developed around a charged colloid particle is called an electrical double layer. The charge on the particle is distributed over its surface and is balanced by the total charge in the double layer in which there is an excess of oppositely charged ions (counter-ions).

Destabilisation occurs when the repulsion forces between particles in suspension are removed or reduced so that particles stick together on collision. The colloidal particles in most processes are destabilised by adding salts and polymers to reduce the charge. Polymers adsorbing on a particle surface produce strong flocs as a result of either bridging or charge neutralisation. Cationic polymers, which are commonly used flocculants in water and wastewater treatment, can have different effects on aggregation depending on their properties such as molecular weight, charge density and the viscosity of the added solution. It is believed that long chain polymers with high molecular weight lead to strong flocs which can resist disruptive forces better than aggregates formed as a result of charge neutralisation.

A simple flow-through optical technique, developed by Gregory and Nelson (1984), based on measurements of fluctuations in light transmission through flowing suspensions is able to monitor flocculation continuously. The well-known advantages of this technique are simple set-up procedure and real-time investigation of flocculation characteristics (floc density, flocculation rate and relative turbidity and particle number concentration). Previous studies using this method were successful to demonstrate its adaptability to flocculation monitoring in certain condition.

The previous studies have highlighted the measurements in one or two solution and hydraulic conditions, giving a limitation to obtaining knowledge of aggregation in various circumstances. Therefore, it was suggested that systematic changes in conditions of suspension and the improved, modified monitoring technique are useful to understand the state of aggregation.

1.2 Purpose of the current work

In the water industry, it is generally accepted that the mechanism of orthokinetic flocculation in a given system is mainly due to the optimised shear conditions such as mixing intensity (or velocity gradient, G value) and retention time during flocculation, so that large separable flocs of suitable density are rapidly formed and leave few residual primary particles or small aggregates. Furthermore, the shear resistance and rheological behaviour of flocs formed by polymeric flocculants may play an important role in determining the optimum polymer dosage, which now can be defined as the minimum amount of polymer dosed under the best mixing conditions to achieve the maximum flocculation (Langer et al. 1994). Considering the elaborated relationship between the above factors which influence the actual separation process, the adaptability of the monitoring technique in certain circumstances should be examined through a range of pre-tests in various hydraulic and solution conditions, so that the best separation

1. Introduction

condition can be determined.

It is well known that aggregate density decreases appreciably as the floc size increases. Most aggregates have non-uniform structure, and the concept of fractal dimension has been employed to express floc structure. The structure of flocs is important not only as one of the experimental outcome, but as one of the factors which can affect further aggregation process. Considerable researches have been made by several methods which derive information on floc structure (Tambo and Watanabe 1979; Gregory 1989; Logan and Klips 1995) and understanding the structure has been recognised to be very important although much remains to be complex.

The objective of this study is therefore to suggest modified versions of a previously developed monitoring technique which measures the fluctuations in the intensity of light transmitted through flowing suspensions, and gives the intended changes in conditions such as materials, solution and shear to understand various behaviours while the flocculation of negatively charged particles occurs in the presence of assorted polyelectrolytes of different properties. The experimental results obtained through the systematic changes in condition will provide better picture of flocculation as well as the knowledge for further work.

The monitoring gives flocculation degree, relative turbidity and relative particle number concentration which are defined for this technique. Although subject to some limitation, the method also gives the fractal dimension of flocs and the structural changes of flocs in specific cases can be suggested using the obtained results.

To study various aspects of a specific flocculation, jar tests are carried out in different situations while the flocculation is monitored in real time. Although the obtained results gives simplified information on the properties and could not provide detailed information on, for instance, floc size distribution, the experimental results will show that monitoring flocculation by the current technique can provide useful information on floc properties.

Chapter 2

Literature Review

2.1 Aggregation

Raw water may contain suspended particles of colour, turbidity, and bacteria that are too small to settle in a reasonable time period, and cannot be removed by simple filtration. Aggregation of very small particles in the colloidal size range (1-1000 nm)is a common method of increasing their size and enhancing the efficiency of solid-liquid separation. The object of aggregation is to alter these particles in such a way as to allow them to adhere to each other, hence, they can grow to a size that will allow removal by sedimentation and filtration. The aggregation of particles is generally referred to as either coagulation or flocculation. Coagulation is generally defined as the process of destabilisation of colloidal suspensions. On the other hand, flocculation is considered to be a physical/chemical treatment process that forms larger particles (flocs) from destabilised colloidal particles by collisions between them, as opposed to the physical treatment operations of sedimentation and filtration that follow. However, these processes occur simultaneously in most cases and it is difficult to distinguish one from the other. In this work, flocculation will be used as a generic term; while if destabilisation of colloids is of more interest, the terms, coagulation and/or destabilisation will be used.

Most colloids of interest in water treatment remain suspended in solution because they have a net negative surface charge that causes the particles to repel each other. Therefore in many cases, it is very difficult to produce aggregates only by collisions which can be brought about by Brownian diffusion, induced fluid motion, or differential sedimentation (see 2.2 Charged Interface and 2.3 Aggregation Kinetics). Therefore, it is important to understand the way that flocculating agents work during the process (see 2.4 Polymeric Flocculants). Among the properties of aggregates of particles generated in water and wastewater treatment, the relationship between the size and structure of the flocs is possibly of most significance to the efficiency of operation of a number of unit processes including sedimentation, flotation, deep bed and membrane filtration and dewatering. The fact that most aggregates formed in coagulation/flocculation processes have fractal, self-similar structure is of great importance in current water treatment studies due to the consequence that the effective density of aggregates decreases as their size increases (see 2.5 Fractal Properties of Aggregates).

2.2 Charged interface

2.2.1 Colloid and surface charge

Colloidal stability is a central topic in surface and colloidal science, and many efforts have been devoted toward the development of suitable theories. Considerable experimental works have also been done, for many decades, using different systems, for instance, clays, silver iodide, polymer latexes, and metal oxides.

DLVO theory still holds a central position in this context, and it was quite successful in describing colloidal stability as the result of particle surface interactions due to van der Waals and to electrical interactions. However, the detailed analysis of different systems revealed the importance of other factors. Polymer-dependent colloidal stabilisation and destabilisation can only be understood by considering steric interactions, particle bridging, and depletion. A quantitative analysis of particle aggregation rates also requires the consideration of hydrodynamic interactions, which in turn are related to the nature of the surface hydration layer (Gregory 1989).

Colloidal particles are conventionally defined as particles less than 1 μ m in at least one important dimension. In general, they are aggregates of numerous atoms or molecules, but are too small to be seen with an ordinary optical microscope and they may pass through most filter papers. Colloidal particles in water are normally free from flocculation due to the inter-particle repulsive force caused by the electric double



FIG. 2.1. The structure of the electric double layer according to Stern theory; The electrical potential, ψ_d , is changed depending on the concentration of indifferent electrolyte. The value is higher in the case of the low concentration of electrolytes, giving the tension of diffuse layer. δ is thickness of Stern layer and ψ_0 is surface potential. At high ion concentration, ψ_d becomes lower and the diffuse layer is reduced as a result of the increased κ , adapted from the figure by Shaw (1992).

layer (Overbeek 1952).

Electric double layer can be regarded as consisting of two regions, an inner region which may include adsorbed ions and counter-ions (Stern layer) and a region in which the counter-ions are distributed according to the influence of electrical forces and random thermal motion (Diffuse layer). The structure of electric double layer is shown in Fig. 2.1. The extent of diffuse layer depends markedly on the ionic concentration of solution. The electric potential (ψ) in solution, which is usually expressed as a function of distance from Stern plane, cannot be measured directly but it can be estimated from electrokinetic or zeta potential (ζ) which affects electrokinetic behaviour at the surface of shear between the charged surface and the electrolyte solution. In most cases zeta potential is nearly equal to Stern potential and the zeta potential can be regarded as the potential that determines the electrical interaction between particles. More detailed explanation will be given in the following section.

2.2.2 Colloid interactions

Interactions between colloidal particles in suspension can be classified into a number of ways. The reason these interactions are very important in colloid studies is that they can easily outweigh other forces which become dominant for larger particles. The stability can be determined whether the overall effect is to give a repulsion (stable system) or an attraction (unstable system). DLVO theory was developed independently by Deryagin and Landau (1941) and Verwey and Overbeek (1948) is widely known as the basic theory of colloidal stability. Added electrolytes cause a compression of the diffuse parts of the double layers around particles and may exert a specific effect through ion adsorption into the Stern layer. The particles aggregate when the range of double layer repulsive interaction is sufficiently reduced to permit particles to approach close enough for van der Waals forces to predominate. There can be other interactions giving a rather short range interaction which can considerably modify colloid stability in case the ionic surface group is hydrated (Hydration effect), particle surfaces are hydrophobic (Hydrophobic interaction) or polymer adsorbs on the particle surface (Steric interaction, Polymer bridging and Charge neutralisation). Hydration effects are associated with polar groups at the particle surface or adsorbed counterions, which are hydrated to some extent. This effect shows a short-range repulsion due to the work which some water of hydration is displaced as the particles approach very close. Hydrophobic interaction arises when approaching surfaces have little affinity for water and can give an attraction which is stronger and of longer range than van der Waals attraction. Steric interaction, which is also called "steric stabilisation", gives a repulsion at close distance. It arises with the interpenetration of the hydrophilic chains of adsorbed polymer and when the adsorbed layer is not too thin. However, it is not usually possible to predict such effects in a satisfactory quantitative manner, especially in practical systems. Polymer bridging and charge neutralisation are the interactions between polymer and colloid surface rather than colloids, and will be reviewed later in 2.4 Polymeric Flocculants.

2.2.2.1 Van der Waals interaction

Van der Waals forces denote the universal attractive force between atoms and molecules (London 1930). These attractive contributions to those forces include the spontaneous electrical and magnetic polarisations, giving a fluctuating electromagnetic field within the media and in the gap between them. These forces also play an important role in the interaction of colloidal particles.

Hamaker (1937) derived a simple expression of interaction energy from the summation of all the relevant interactions between molecules in the bodies. The expressions obtained in this manner may be split into a purely geometrical part and a constant A. The constant A, called the Hamaker constant, is only related to the properties of the interacting macroscopic bodies and the medium. In many practical cases, the results are not too different from the more exact macroscopic computations. Therefore, this simple approach by Hamaker is still widely used though the assumption of pairwise additivity of intermolecular forces is open to doubt.

For the case of parallel flat plates separated by a distance d and the separation being a vacuum, the Hamaker result for the interaction energy per unit area is :

$$V_A = -\frac{A_{12}}{12\pi d^2} \tag{2.1}$$

where A_{12} is the Hamaker constant for media 1 and 2. The negative sign, by convention, implies an attractive energy.

For the case of two unequal spherical particles which is common in reality, the equation derived by Deryagin (1934) is widely used. He calculated the interaction force between bodies of similar material at close approach $(a \gg d)$ by integrating the interaction energy per unit area between two thick parallel flat plates, F(d) which is a function of the separation distance, d. The force of interaction between spherical particles can be expressed in terms of the energy of interaction between flat plates separated by the same distance, E(d),

$$F(d) = \frac{2\pi a_1 a_2}{a_1 + a_2} E(d) \tag{2.2}$$

This is valid only when the interacting bodies are very close.

Using equations (2.1) and (2.2), the interaction energy of two spherical particles, radii a_1 and a_2 , with separation distance d can be obtained :

$$V_A = -\frac{A_{12}}{6d} \cdot \frac{a_1 a_2}{a_1 + a_2} \tag{2.3}$$

For equal spheres, radius a_1 , the result follows from equation (2.2) :

$$V_A = -A_{11} \frac{a_1}{12d} \tag{2.4}$$

The expressions, equations (2.2) and (2.3), apply in many practical cases, though these become inaccurate at separations greater than 10% of the particle radius, but this is not a serious problem since in many cases the interaction energy is insignificant at larger distances. The inverse dependence of the interaction energy on the separation distance and the direct dependence on particle size are important features of equation (2.4).

A modified Hamaker constant where two spherical particles interact across a medium, not a vacuum, needs to be used. For the interaction of media 1 and 2 through medium 3, the appropriate constant can be written as :

$$A_{123} = A_{12} + A_{33} - A_{13} - A_{23} \tag{2.5}$$

Depending on the relative magnitudes of the individual constants, the presence of a third medium can significantly reduce the interaction.

A useful approximation for Hamaker constants of different media is the geometric mean assumption :

$$A_{12} \approx (A_{11}A_{22})^{\frac{1}{2}} \tag{2.6}$$

With this and the corresponding expressions for A_{13} and A_{23} , equation (2.5) becomes :

$$A_{132} \approx (A_{11}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})(A_{22}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})$$

$$(2.7)$$

For similar materials, media 1 interacting across medium 3 :

$$A_{131} \approx (A_{11}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})^2 \tag{2.8}$$

Equation (2.8) leads to the conclusion that the van der Waals interaction between similar materials in a liquid would always be attractive (positive Hamaker constant), whatever the values of A_{11} and A_{33} . However, for different materials, the possibility of negative Hamarker constants and van der Waals repulsion arises, for example when $A_{11} > A_{33} > A_{22}$ or $A_{22} > A_{33} > A_{11}$. For practically all aqueous dispersions, Hamaker constants of single materials lie in the range $0.3-10\times10^{-20}$ J. Some examples are given in Table 2.1.

		· · · · · ·
Material	A_{11} (microscopic) ^{<i>a</i>}	$A_{11} \ ({ m macroscopic})^b$
Water	$3.3-6.4 \times 10^{-20} \text{ J}$	$3.0-6.1 \times 10^{-20} \text{ J}$
Ionic crystals	$15.8 - 41.8 \times 10^{-20} \text{ J}$	$5.8 - 11.8 \times 10^{-20} \text{ J}$
Metals	$7.6 - 15.9 \times 10^{-20} \text{ J}$	$22.1 \times 10^{-20} \text{ J}$
Silica	$50 \times 10^{-20} \text{ J}$	$8.6 \times 10^{-20} \text{ J}$
Polystyrene	$6.2 - 16.8 \times 10^{-20} \text{ J}$	$5.6 - 6.4 \times 10^{-20} \text{ J}$
Hydrocarbons	$4.6 - 10 \times 10^{-20} \text{ J}$	$6.3 \times 10^{-20} \text{ J}$

TABLE 2.1. Values of Hamaker constants (Shaw 1992)

^aLondon-Hamaker approach; The individual atomic polarisabilities and the atomic densities of the materials involved in the interaction are used. The total interaction is assumed to be the sum of the interactions between all interparticle pairs.

^bLifshiftz approach; The interacting particles and the intervening medium are treated as continuous phases.

2.2.2.2 Electrical interaction

The nature of the electrical double layer can greatly influence the interaction between charged particles. The diffuse layer of counter ions around the particles extends to a considerable distance where ionic strength is low. Thus, particles approaching each other begin to experience electrical repulsion due to overlapping diffuse layer of like charges even at large separation. By contrast, at high ionic strength, particles can approach quite closely to each other before repulsion is felt since the diffuse layer is less extensive.

In the context of particle interaction, an important quantity is the electric potential at the inner boundary of the diffuse layer (see Fig. 2.1). This potential cannot be measured directly, but is believed to be close to the experimentally-accessible zeta potential.

For two spherical particles, radii a_1 and a_2 , with zeta potentials ζ_1 and ζ_2 , the electrical interaction energy, V_E , as a function of the separation distance, d, can be written in the approximate form :

$$V_E = \frac{64a_1a_2}{a_1 + a_2}\pi\varepsilon(\frac{kT}{ze})^2\gamma_1\gamma_2\exp(-\kappa d)$$
(2.9)

where ε is the permittivity of the medium, z is the valency of the ions (assuming a symmetrical, z-z electrolyte), and e is the elementary charge. The term γ_1 and γ_2 are dimensionless functions of the zeta potentials : $\gamma_1 = \tanh(ze\zeta_1/4kT)$ etc. The interaction decreases exponentially with a separation distance, with a decay length,

 $1/\kappa$, where κ is the Debye-Hückel parameter. This is a function of ionic strength and, for aqueous electrolytes at 25 °C, can be obtained from :

$$\kappa = 2.32 \times 10^9 \sqrt{\Sigma C_i Z_i^2} \ (m^{-1}) \tag{2.10}$$

where C_i is the molar concentration and Z_i is the valence of ions of type *i*. The sum is taken over all types of ion present in the solution (refer to Fig. 2.2).

The Debye-Hückel parameter is of crucial importance in determining the range of electrical interaction between particles. The corresponding length, $1/\kappa$, can range from values near to 1 μ m in deionized water, to less than 1 nm in concentrated salt solutions.



FIG. 2.2. Schematic representation of the ion concentration distribution in diffuse layer by the influence of electrical forces and random thermal motion; $1/\kappa$ is a decay length. Adapted from the figure by Shaw (1992).

The pre-exponential term in equation (2.9) depends on the zeta potentials of the particles and is always positive (repulsion) if the potentials are of the same sign and negative (attraction) for potentials of opposite sign.

For identical particles, equation (2.9) reduces to the simple result :

$$V_E = 32\pi\varepsilon a (\frac{kT}{ze})^2 \gamma^2 \exp(-\kappa d)$$
(2.11)

For small values of zeta potential, this simplifies still further to :

$$V_E = 2\pi\varepsilon a \zeta^2 \exp(-\kappa d) \tag{2.12}$$

As shown in the above equations, the increase in the Debye-Hückel parameter, κ , by increasing concentration of dissolved salts reduces range of repulsion, and the salts containing highly charged counter-ions are very effective in the destabilisation of particles in suspension.

2.2.2.3 Combined interaction

The general character of the total energy of interaction between the particles can be deduced from the properties of the two components. According to equations (2.4) and (2.12), van der Waals energy, which is attractive, decreases as an inverse power of the distance between the particles, and electric double layer energy, which is repulsive, is an approximately exponential function of the distance between the particles with a range of the order of the thickness of the double layer (κ). For the interaction between particles of same materials, attraction by van der Waals energy predominates at small and large interparticle distance, and repulsion by electrical double layer energy may predominate at intermediate distances, depending on the actual values of the two forces. Fig. 2.3 exhibits a typical potential energy diagram and two different potential energy curves depending on the gap between the interaction energies. In Fig. 2.3(a), the energy barrier exists at the short separation distance. It is believed that this energy barrier can be removed by a narrow range of electrolyte concentrations. The concentration, which leads to rapid aggregation due to no repulsive interaction energy, is called the critical coagulation concentration (c.c.c.). In Fig. 2.3(b), the total energy curve $V_T(i)$ has a repulsive energy maximum and if the maximum is large enough compared with the thermal energy, kT, of the particles, the system will be stable at a certain distance. However, although the double layer repulsion predominates over van der Waals attraction at any interparticle distance in curve $V_T(i)$ except at very close distance, small increase in electrolyte concentration causes compression of diffuse layer, and predomination of attraction possibly at all distances, eventually results in the unstable system as demonstrated in curve $V_T(ii)$.



FIG. 2.3. Potential energy diagrams obtained by summation of the van der Waals energies and the electric double layer energies: (a) Schematic diagrams of potential energy for the approach of equal spherical particles; (b) Examples of possible potential energy diagrams depending on the variables in equations (2.4) and (2.12): (i) Stable system. The repulsive energy maximum is positive at any distance (ii) Unstable system due to the compression of diffuse layer. Attraction is negative and repulsion is positive. Adapted from the figure by Hunter (1987)

2.3 Aggregation kinetics

2.3.1 General

Collisions by Brownian motion or by induced velocity gradients could lead to aggregation of particles destabilised in suspensions. Most discussions of aggregation kinetics usually start from the classic work of Smoluchowski (1916). It is convenient to assume that all the particles are identical initially then aggregates of various sizes and different concentrations are formed after a period of aggregation. The rate of change of k-fold aggregates, where k = i + j can be written as :

$$\frac{dN_k}{dt} = \frac{1}{2} \sum k_{ij} N_i N_j - N_k \sum k_{ik} N_i \tag{2.13}$$

where k_{ij} and k_{ik} are coefficients in second order rate expression for i - j and i - k collisions, giving the collision rate, the number of collisions in unit volume per unit time which is expressed :

$$J_{ij} = k_{ij} N_i N_j \tag{2.14}$$

The first term of equation (2.13) represents the formation of k-fold aggregates by collision of any pair of aggregates, and the loss of k-fold aggregates by collision, and aggregation, with any other aggregates is expressed as the second term. For further discussions, it should be noted that irreversible aggregation in which no break-up of aggregates occurs is assumed for equation (2.13).

In the following sections, the discussion will be placed on the collision mechanisms : perikinetic aggregation by Brownian motion, orthokinetic aggregation by applied fluid motion and differential settling by different settling rates between aggregates.

2.3.2 Perikinetic flocculation

In a dispersion, the thermal energy of the system leads to continuous random displacement of small particles, which is observable as Brownian motion. Smoluchowski (1916) calculated collision frequency between i and j particles, where the frequency of collisions was obtained from the diffusional flux of particles towards a single stationary particles. First order of perikinetic flocculation is given as :

$$J_{ij} = 4\pi R_{ij} (D_i + D_j) N_i N_j \tag{2.15}$$

where J_{ij} is the number of contacts per unit time between particles of radii a_i and a_j , R_{ij} is collision radius (assume $R_{ij} = a_i + a_j$), D_i and D_j are diffusion coefficients, and N_i and N_j are number concentration. Hence, the rate constant is defined as $k_{ij} = 4\pi R_{ij}(D_i + D_j)$. Collision radius, R_{ij} , can be considered to become larger where there is significant long-range attraction between particles *i* and *j*. For single spherical particles, the diffusion coefficients are given by the Stokes-Einstein equation :

$$D_i = \frac{kT}{6\pi a_i \mu} \tag{2.16}$$

where k is Boltzmann constant, T is absolute temperature, a_i is radius of particles, and μ is viscosity of the fluid. Equation now can be written again as :

$$J_{ij} = \frac{2kT}{3\mu} N_i N_j \frac{(a_i + a_j)^2}{a_i a_j}$$
(2.17)

The rate constant now becomes as :

$$k_{ij} = \frac{2kT}{3\mu} \cdot \frac{(a_i + a_j)^2}{a_i a_j}$$
(2.18)

The important feature in equation (2.17) is that k_{ij} is approximately constant for particles about the same size. $(k_{ij} = 1.23 \times 10^{-17} \text{ m}^3/\text{s} \text{ for aqueous dispersions at} 25 ^{\circ}\text{C})$

The rate constants, giving the rate of change of aggregate concentration, can be acquired by inserting the appropriate values into equation (2.13). It is assumed that the aggregation is at the very early stage and initial particles are mono-disperse for convenience. The rate of change in the concentration of primary particles, N_1 , is expressed as follows :

$$\left(\frac{dN_1}{dt}\right)_{t\to 0} = -k_{11}N_1^2 \tag{2.19}$$

where k_{11} is the rate constant of primary particle collisions.

Therefore, the initial rate of decrease of the total particle concentration, N_T , can be written as :

$$(\frac{dN_T}{dt})_{t\to 0} = -\frac{k_{11}}{2}N_1^2 \tag{2.20}$$

where $k_{11}/2$ is often called the flocculation rate constant and has a value of 6.13×10^{-18} m³ s⁻¹ for aqueous dispersions at 25 °C.

2.3.3 Orthokinetic flocculation

The aggregation process under conditions where the suspension is subjected to some form of shear, either by stirring or by flow is called orthokinetic flocculation. Orthokinetic flocculation leads to higher collision frequency than perikinetic flocculation for large particles and large flocs so that most real flocculation processes are carried out in this condition. All the experiments performed in this work are also concentrated on this collision mechanism.

Smoluchowski (1916) assumed the collision in a uniform laminar shear to derive the collision frequency. Rough feature of the orthokinetic collision is given in Fig. 2.4.

The collision frequency is :

$$J_{ij} = \frac{4}{3} N_i N_j G(a_i + a_j)^3 = k_{ij} N_i N_j$$
(2.21)

Where the collision constant is defined as k_{ij} (=4 $G(a_i + a_j)^3/3$), equation (2.21) shows that the collision frequency depends on the sizes of the particles and the velocity gradient or shear rate, G. The size effect is very important and differs greatly from the perikinetic case, where the collision rate constant is nearly independent of particle size.



FIG. 2.4. Schematic representation of orthokinetic collision of spheres in a uniform shear field, adapted from the figure by Elimelech et al. (1995)

The fluid velocity varies linearly in only one direction, perpendicular to the direction of flow. It is assumed that particle j is a fixed central sphere and particle i is one which flows on a straight streamline and hence the particles within a distance $a_i + a_j$ collide each other accordingly.

For equal spheres, radius a_1 , the orthokinetic rate for the very early stage of aggregation is, by analogy with equation (2.20), written as:

$$-\frac{dN_T}{dt} = \frac{16}{3}N_0^2 G a_1^3 \tag{2.22}$$

Equation (2.22) can be transformed to a simple form by using the term, volume fraction, ϕ , of the suspended particles $(=\frac{4}{3}\pi a_1^3 N_T)$:

$$\frac{dN_T}{dt} = -\frac{4G\phi N_T}{\pi} \tag{2.23}$$

Then equation (2.23) can be integrated suggesting a simple first-order rate law if the constant volume fraction is assumed.

$$\frac{N_T}{N_0} = \exp(\frac{-4G\phi t}{\pi}) \tag{2.24}$$

However, this equation should be modified in reality since most flocs are fractal objects. More detail on the orthokinetic rate of aggregation will be discussed later in Section 2.5.3.2. Back to the equation (2.24), it is shown that the particle concentration decease exponentially with shear rate, time and the volume fraction. If a fixed solids concentration is assumed, equation (2.24) depends on the dimensionless number, Gt, Camp number defined by Camp and Stein (1943). In the principle, the same relative degree of aggregation can be achieved in the cases

- high shear applied to solid of a fixed concentration in a short period
- low shear applied to solid of a fixed concentration in a long period

or where

- high volume fraction is maintained with small Gt value
- low volume fraction is maintained with large Gt value.

However, the case a uniform laminar shear field always applies is unrealistic in practice. Using the power input per unit mass of fluid, P, Camp and Stein (1943) replaced G by a mean velocity gradient, \overline{G} , defined by Camp (1946) :

$$\overline{G} = \sqrt{\frac{P}{\nu}} \tag{2.25}$$

where ν is the kinematic viscosity of the fluid ($=\mu/\rho$, where ρ is the density).

By inserting this equation into equation (2.21), the modified collision frequency for turbulent flow conditions can be written as:

$$J_{ij} = \frac{4}{3} N_i N_j \sqrt{\frac{P}{\nu}} (a_i + a_j)^3$$
(2.26)

Though the turbulent flow is much too complicated to be treated as above, the result from equation (2.26) is very close to that from a more rigorous treatment by Saffman and Turner (1956) for particle collisions in isotropic turbulence.

2.3.4 Differential settling

In the later stages of a flocculation process, where aggregates are large and dense enough to settle down, the aggregates tend to collide with each other due to the relative motion by their different sizes and densities. The appropriate rate can be easily calculated, assuming spherical particles and using Stokes law for their sedimentation rate. The resulting collision frequency, for particles of equal density, is :

$$J_{ij} = \frac{2\pi g}{9\mu} (\rho_s - \rho) N_i N_j (a_i + a_j)^3 (a_i - a_j)$$
(2.27)

where g is the acceleration due to gravity, ρ_s is the density of the particles and ρ is the density of the fluid.

Again, as seen in equation (2.27), differential sedimentation plays an important role on promoting aggregation when the particles are large and dense and the sizes of each particle are very different.

2.3.5 Comparison of rates

Collision brought about by perikinetic collision does not generally lead to the rapid formation of very large aggregates, especially in dilute suspension whereas aggregation carried out by fluid motion usually shows the high rate of interparticle collision, and the rapid aggregate formation. It is expected that orthokinetic aggregation predominates perikinetic aggregation for the later stage of process where large aggregates exist.

While equation (2.24) cannot be adapted well to real flocculation processes since the laminar shear and aggregation only between particles of the same size which are found in the early stage of aggregation are assumed, it is the case where flocs are formed and thus the different settling rates are expected to be dominant. Fig. 2.5 shows that perikinetic aggregation is dominant for the particle size range below 0.5 μ m whereas it becomes insignificant where the particle size is above 1 μ m hence fluid shear and differential settling predominate Brownian motion.



FIG. 2.5. Comparison of collision rate constants; One particle is taken to have a diameter of 1 μ m and the shear rate is assumed to be 50 s⁻¹ and the density of the particles 2 g/cm³. All other values are appropriate for aqueous dispersions at 25 °C. Adapted from the figure by Elimelech et al. (1995)
2.4 Polymeric flocculants

2.4.1 General

Polymeric flocculants have been widely used in solid-liquid separation for the reason that they have outstanding abilities to flocculate particles with a very small amount. They became very popular in practice because of the possibility of controlling properties such as the number and type of charged units, molecular weight and their effect on flocculation of particles in suspension at low polymer doses. Most flocculants in practical processes are of synthetic origin with polyacrylamide and its derivatives being the more widely used than natural materials. Aqueous polymerisation of acrylamide can give products of varying molecular weight, up to very high values (about 20 million). Though polyacrylamide is nominally nonionic, some hydrolysis of amide group occurs, giving carboxylate groups and hence a degree of anionic character. A range of charge densities of polyacrylamide can be obtained by controlling the degree of hydrolysis. Cationic polyelectrolytes based on polyacrylamide can also be prepared by copolymerisation of acrylamide with a suitable cationic monomer, very often dimethylaminoethyl acrylate or methacrylate, which are quanternised after polymerisation to produce strongly cationic characteristic. Charge density depends on the proportion of cationic monomer involved. Effective flocculants are usually linear polymers, often of high molecular weight, which may be nonionic, anionic or cationic in character.

2.4.2 Polymer adsorption

2.4.2.1 General

Adsorption of polymer on the surface of particles is essential to give the adequate destabilisation of particles and hence to allow the flocculation. It is usually believed to happen in the early stage of flocculation. Polymeric flocculants can adsorb on the surface of the particle by variety of interactions. The following section will give the discussion on these interactions. The usual result is that the polymer sticks to certain points on the surfaces, but for much of its length it is able to trail out into the solvent. Some segments are attached to the surface (as trains) separated from one another by loops which extend into the solution and ending in a tail at either end of the polymer chain as shown in Fig. 2.6.



FIG. 2.6. Schematic diagram of polymer adsorbed on a particle surface (Hogg 1999)

It is usually necessary for a substantial fraction of the added polymer to be adsorbed before particles are adequately destabilised. It is thought that polymers should not cover all the surfaces of particles since complete surface coverage would lead to a serious drop in the rate of adsorption. The amount of added polymeric flocculants should be controlled to be much less than at complete surface coverage to achieve the optimum flocculation.

Polymer adsorption, particularly in the context of flocculation, generally occurs through relatively weak segment-surface binding (Hogg 1999). The sum of a large number of such linkages leads to a relatively strong attachment of the molecule as a whole to the surface. As molecular weight (i.e. the number of segments per molecule) increases, the strength of the individual segment-surface linkages becomes less and less important. It follows that charge interactions are probably more important for low molecular weight than for high molecular polymer. It is certainly true that cationic polymers of low molecular weight are quite ineffective for the flocculation of positively charged particles. High molecular weight anionics, on the other hand, can cause substantial flocculation of negatively charged particles.

It is clear that polymer adsorption, in the context of flocculation, is a non-equilibrium process. Because of the multiple segment-surface interactions involved, the attachment process is effectively irreversible. However, as shown in Fig. 2.6, the polymer chain may attach to the surface at many points and not be able to desorb simultaneously from all sites. The presence of looser interparicle bridges gives a larger freedom of particle movement, and then more mechanical energy can dissipate within it, giving a chance to become more compact (Otsubo 1994).

It has been demonstrated that the effectiveness of flocculation is highly dependent

on the physical process of mixing the polymer with fine particle suspension. These observations clearly attest to the importance of adsorption kinetics in flocculation.

2.4.2.2 Types of adsorbing interactions

- Hydrogen bonding : This can occur when the particle surface and the polymer have suitable H-bonding sites.
- Hydrophobic interaction : When polymers are adsorbed on the surface of particles with hydrophobic character, it could cause the hydrophobic property to the tails of polymers. If the particle surface and segments of the polymer chain have hydrophobic character, then adsorption may occur as a result of hydrophobic interaction.
- Electrostatic interaction : Electrostatic attraction gives a dominant contribution to the interaction energy when polyelectrolytes adsorb on surfaces of opposite charge (i.e. usually cationic polymers on negative surface). When electrostatic interaction is the only significant affinity, then dissolved salts in solution can affect the adsorption of polymers. Adsorption of polyelectrolytes deceases with increasing salt concentration, either because of screening effects or competition for charged surface sites between ionic segments of the polymer chain and dissolved ions.
- Ion bonding : Although it is clear that there is a repulsion between polyelectrolytes and the particle surface of like sign (i.e. usually anionic polyelectrolyte and negative surface), adsorption can be achieved in the presence of certain ions, giving attraction to both sides (e.g. Ca²⁺ bridging between polyacrylamide chain and anionic surface sites).

2.4.2.3 Adsorption rate

The adsorption rate depends on the rate of arrival of polymer molecules at a particle surface and it can be written as equation (2.14) assuming that i and j are for particles and polymer molecules respectively. Normally, there will be far more polymer molecules than particles $(N_i \ll N_j)$ and it might be assumed that adsorption would be very rapid compared to the flocculation rate. According to equation (2.14), adsorption rate should increase with polymer concentration in the mixture. Gregory (1982) calculated the time required for adsorption, assuming that the particle number concentration remains constant and the rate constant, k_{ij} , is independent of surface charge.

$$t_{Ads} = -\frac{ln(1-f)}{k_{ij}N_i} \tag{2.28}$$

where f is a fraction of added polymer to particles. The inverse dependence on particle number concentration suggests that adsorption can be quite slow for dilute suspension due to low particle number concentration. It is important to note that the same fraction of added polymer should remain in this case although the required time is independent of polymer concentration. The amount of adsorbed polymer needed to destabilise particles is proportional to particle concentration. The process of polymer adsorption and particle aggregation proceed simultaneously and this might lead to difficulty in deriving the actual adsorption rate in practice.

2.4.3 Flocculation by polymer

In this study, suspensions are flocculated by using cationic polyelectrolytes since the majority of particles found in nature mainly bears negative charges. It has been well documented in the literature that the adsorbing polymers can affect the particle flocculation through two postulated mechanisms; polymer bridging and electrostatic patch. Polymeric flocculants used in practical processes can be separated by their properties, molecular weight and charge density. Depending on the properties, polymeric flocculants show different ways to promote particles to stick together.

2.4.3.1 Polymer bridging

The concept of bridging between two or more particles by an adsorbed polymer, first proposed by Ruehrwein and Ward (1952) is that long chain polymers, which have molecular dimensions comparable to the size of colloidal particles, generally adsorb on particles and with small amounts, an individual chain can get attached or two or more particles, so bridging together, overcoming the repelling tendency of likely charged particles. Linear polymer of high molecular weight which can form extended loops and tails on the particle surface, is thought to be very effective by the high possibility of attachment to other particles. Especially, at low ionic strength, where double layer repulsion reaches long range, polymer of high molecular weight is more effective, having polymer bridges long enough to span the gap. It is expected that polymers are insufficient to form adequate bridging links between particles at low dosages and particles can get restabilised at excess dosage, since there is no longer bare particle surface for attachment of segments. Therefore, appropriate amount of polymer, the optimum dosage, should be added to suspensions for the best result.

In some cases, when the tails of polymers attached on particle surface have the hydrophobic property, these layers would lead to an attraction between the particles since the presence of the layers could restrict the natural structuring tendency of water, resulting in water molecules migrating from the gap between particles.

Aggregates produced by polymer bridging are usually very strong and resistant to shear. However, in case very high shear applies and hence they are broken, they may not easily reform (Pelton 1981) due to the scission of polymer chains (Horn and Merril 1984).

2.4.3.2 Charge neutralisation

In many practical applications, it is found that the only effective polymeric flocculants are polyelectrolytes with a charge opposite to that of the particle surface though, in some cases (e.g. polymer bridging), polymers of the like sign of charge are also found effective for the flocculation of negatively charged particles. The adsorption of a cationic polyelectrolyte on a negatively charged particle would play an important role on neutralising the surface charge and forming a rather thin layer on the particle surface, where low molecular weight, high charge density polymer is involved (Kasper 1971). This may well be detected experimentally by the reduction of the measured electrophoretic mobility of the particles to zero (Hunter et al. 1983). Due to a strong interaction between the ionic group on the polymer and charged sites on the particle surface, adsorption can continue beyond the point of neutrality and hence charge reversal, giving a positively charged surface and the restabilisation of the particles can arise. It is usually thought that the optimum polymer concentration to achieve the best flocculation result corresponds to about half surface coverage.

However, in case adsorbed polyelectrolytes cover the surfaces of opposite charge completely and the adsorbed polyelectrolyte layer is thick enough, steric interaction occurs. When two particles coated with a layer of polymer approach, the interaction between the adsorbed chains causes a repulsion that can be sufficient to induce stability. Depending on the thickness of the layer, weak flocculation can occur. It produces flocs of rather open structure although mild shear may lead to re-dispersion of flocs.



FIG. 2.7. Interactions of negatively charged particles adsorbed by cationic polymers, adapted from the figure by Elimelech et al. (1995)

2.4.3.3 Electrostatic patch

An important refinement to the simple charge neutralisation, electrostatic patch model, assuming particle charge is not neutralised uniformly by adsorbed polyelectrolyte of high charge density though overall charge neutralisation may occur, was given by Kasper (1971) and Gregory (1973). They suggested that a charge mosaic or electrostatic patch arrangement on the particle surface are formed by this local heterogeneity of charge when the charge density of the polyelectrolyte is high and that of the particle surface is low. The most important consequence of patchwise adsorption is that particles with no net charge can still show strong electrical attraction between regions of opposite charge on different particles, giving quite strong attachment. This extra attraction shows measurable increase in flocculation rate (Gregory 1976). It is found that increasing the charge density of polymers will increase their electrostatic patch attraction to particles of the opposite charge, and that more extended adsorbed polymer configurations will favour flocculation (Mabire et al. 1983; Tiravanti et al. 1985). On the contrary, Gill and Herrington (1987) and Smith-Palmer et al. (1994) investigated the flocculation of kaolin suspensions using cationic polyacrylamides of similar high molecular mass (about 10^6) but of different charge densities. They found that the settling rates decreased as the charge density increased. It is reported that charge neutralisation is less likely to affect flocculation behaviour and that polymer bridging is the only predominant mechanism of suspension destabilisation.

Even though electrostatic patch interaction may lead to stronger binding than simple charge neutralisation, flocs are generally not as strong as those produced by polymer bridging. However, an advantage of flocs by charge neutralisation or electrostatic patch effects is that flocs can readily re-form after the breakage as flocs which have broken tails to catch another particle.

Lindquist and Stratton (1976) have studied the role of charge density and molecular weight on the adsorption and flocculation of silica particles with polyethylenimine and proposed both polymer bridging and charge neutralisation may function simultaneously, and the relative importance between them is pH dependent. They found that polymer bridging should dominate flocculation due to the low cationic charge of basic polymers at high pH (> 9) and, at low pH (< 9), strong electrostatic attraction between polycations and negative particles is the dominant mechanism.

2.4.3.4 Kinetics of polymer flocculation

When a polymeric flocculants is added to a stirred suspension, several processes are initiated, the relative rates of which may significantly affect the flocculation. The following steps, which are not easy to separate and may occur simultaneously, should be considered (refer to Fig. 2.8 for graphical illustration).

- (i) Mixing of polymer solution throughout the suspension
- (ii) Adsorption of polymer molecules on the particles, to give some degree of destabilisation, either by charge neutralisation or by giving opportunity for bridging between particles; Rate of adsorption process is expressed as given in equation (2.28).

- (iii) Re-arrangement of adsorbed polymer molecules from an initially extended state to a flatter, equilibrium conformation
- (iv) Collisions between destabilised particles to give aggregates
- (v) Break-up of flocs under the influence of applied shear
- (vi) Floc re-formation either by charge neutralisation or electrostatic patch



FIG. 2.8. Diagrams of kinetics of polymeric flocculation, adapted from the figure by Spicer et al. (1996)

2.5 Fractal properties of aggregates

It is possible that various shapes of aggregates occur in the earliest stages. There is no doubt about the shape of a doublet in the simplest case of equal spheres. However, aggregates formed after a second contact with a single particle can be shaped in several ways and, with higher aggregates, the number of possible structures rapidly increases. Fig. 2.9 exhibits some examples of possible shapes of triplets. This is why it is impossible to describe the structure of aggregates in complete detail. A considerable advance in characterising aggregate structure has been made by the concept of fractals, which was introduced by Mandelbrot (1983). The concept of the fractals has permitted a quantitative analysis of complicated floc structure. Simple theoretical models to explain building fractal structures and the computer simulation followed by the study of model aggregates have come out after the introduction of the concept (Witten and Sander 1981; Meakin 1983; Vicsek 1983; Jullien and Botet 1985; Brown and Ball 1985). In recent years, particular progresses (Eriksson et al. 1993; Huang 1994; Gregory and Chung 1995; Bower et al. 1997; Waite 1999) have been made with regard to characterisation of the structure of aggregates from various materials with the observation that such particle assemblages often appear to exhibit mass fractal properties.



FIG. 2.9. Possible shapes of aggregates consisting of 3 spherical particles

2.5.1 Basic concept

Fractal dimension, strictly mass fractal dimension, is defined as the slope of the logarithmic plot of mass against size of the object, as shown in Fig. 2.10. Fractal dimension can be seen to measure the degree of occupation of the embedding space by the particles of aggregate. Aggregates, which have irregular shapes, usually have a non-integer slope and their dimensions are less than those of regular, 3-dimensional objects whose value of the slope is 3. The relationship between aggregate mass, M_a , and size, L_a , is just :

$$M_a \propto L_a^{d_F} \tag{2.29}$$

where d_F is the fractal dimension. The lower the fractal dimension, the more open is the aggregate structure. Another main feature on fractal objects is a self-similar structure, which remains invariant under a change of scale.

Computer modeling of aggregation has given very useful insight into the progress. With a great progress in computer simulation, many attempts to characterise the structure of aggregates have been made even before the concept of fractals was introduced.

Particle-cluster or diffusion-limited aggregation model, considering no inter-particle interaction, was attempted as the starting point of modeling. It was based only on the random addition of single particles to growing clusters (Vold 1963) and leads to compact aggregates having higher d_F . The cluster-cluster model, which is more realistic as aggregate growth occurs, shows lower fractal dimension, hence more open structure since, in contrast to the particle-cluster case, it is unlikely that a particle will penetrate some way into a cluster before encountering another particle and sticking. Reaction-limited aggregation model, considering repulsion between particles, thus low collision efficiency, shows more compact structure than that by diffusion-limited aggregation (Lin et al. 1989). It is thought that particles approaching on aggregate have more opportunity to explore other configurations and to achieve some degree of inter-penetration while particles collide many times before sticking occurs due to low collision efficiency. Experimental results on practical systems have usually shown good agreement with computer simulations and model studies. However, it is found that flocs reformed after breakage by agitation or high shear rate in a stirred vessel have more compact structures (Clark and Flora 1991; Oles 1992).



FIG. 2.10. Linear relationships between log (mass) and log (size) of fractal aggregates in the cases of particle-cluster and cluster-cluster aggregation, adapted from the figure by Gregory (1997)

2.5.2 Size-density relation

The fact that aggregate density decreases appreciably as the size increases had been empirically observed well before the concept of fractals was introduced (Tambo and Watanabe 1979). This behaviour is one of the most important practical implications of the fractal structure of aggregates.

The effective, buoyant density of an aggregate in a liquid, ρ_E is simply :

$$\rho_E = \rho_F - \rho_L = \phi_S(\rho_S - \rho_L) \tag{2.30}$$

where ρ_S , ρ_L and ρ_F are the densities of the solid particles, the liquid and the aggregate, respectively, and is ϕ_S is the volume fraction of solid in the aggregate.

Since most measurements of aggregate density involve some form of sedimentation procedure, the buoyant density, ρ_E is the relevant property. When ρ_E is plotted against the floc size, a, logarithmically, a linear decrease is often found, implying a relationship of the form :

$$\rho_E = Ba^{-y} \tag{2.31}$$

where B and y are constants.

Because of the proportionality between ρ_E and ϕ_S , it follows that the exponent y is related to the fractal dimension :

$$d_F = 3 - y \tag{2.32}$$

Computational and experimental studies so far have shown that particle-cluster mechanism and re-arrangement of aggregate structure by applying shear lead to more compact structure which has high density and thus is preferable in most solid-liquid separation processes.

2.5.2.1 Strength and break-up of aggregates

In practice, the break-up of aggregates always occurs in turbulent flow and the reflocculation can be followed depending on the properties of the used materials in the process. There has been experimental attempts to demonstrate aggregation dissociation, which is absent from Smoluchowski's equation (2.13) (Cornell et al. 1979; Reynolds and Goodwin 1987; Jeffrey and Ottewill 1988). However, more detailed information on the structure of flocs and the aggregation kinetics was achieved more recently by newly developed monitoring techniques. The break-up process varies, depending on the strength of aggregates and the applied shear. As discussed in Section 2.3.3, the latter is usually expressed in the term, \overline{G} , in orthokinetic aggregation and, in spite of the complicated nature of turbulent flow, the value can be well applicable to the practical cases according to the previous researches by Camp (1946) and Saffman and Turner (1956). However, the aggregate strength have been studied quite recently and often judged by a limiting size of aggregates, which is related to mass through the fractal dimension (Mühle and Domasch 1991; Tambo and François 1991). A collision between two aggregates under the condition of constant shear rate leads to attachment until the shear force tending to separate them is greater than the binding force, where the sum of their hydrodynamic radii exceeds a certain critical value.

However, the above approach using a limiting size is not entirely true to obtain the aggregate strength in every case because of the nature of aggregate. It was stated at the beginning of this section that the size of an aggregate is inversely proportional to density. Also the density depends greatly on the number of particle-particle contacts which influences the strength of an aggregate.

There is no widely-accepted definition of aggregate strength and information is usually based on the size and the break-up of flocs under different shear conditions.

2.5.3 Collision rates of fractal aggregates

It was already reviewed that Smoluchowski suggested the model of aggregation kinetics, assuming spherical particles of same size initially (see Section 2.3). However, the fact that aggregates formed after several contacts with primary particles or other aggregates have unpredictable irregular shapes was ignored in the theory. Assumption for the above fact should be included to derive the more exact collision rate of the fractal aggregates

2.5.3.1 Perikinetic collision of fractal aggregates

The growth of aggregates by perikinetic (diffusion-controlled) aggregation gives an increasing collision radius and a reduced diffusion coefficient. These effects tend to cancel out and it results in a collision rate coefficient, which is not greatly dependent on aggregate size. For fractal aggregates, the hydrodynamic radius, which determines the drag and hence the diffusion coefficient, is likely to be somewhat less than the outer capture radius corresponding to the physical extent of the aggregate (Gregory 1997). This means that real perikinetic collisions will occur rather more rapidly than predicted from Smoluchowski theory. Torres et al. (1991) calculated the ratio of these two radii to be about 0.6 for high degrees of aggregation. However, for aggregates greater than a few μ m in size which are realistic in the high degree of aggregation, perikinetic aggregation is negligible and collisions induced by shear become far more significant.

2.5.3.2 Orthokinetic model of fractal aggregates

As given in equation (2.21) in Section 2.3.3, the collision rate of orthokinetic aggregation is greatly dependent on the size of aggregates but aggregates are assumed as spheres here. The orthokinetic collision rate for fractal aggregates in a uniform shear field can be derived where the primary particles are assumed to be uniform spheres of radius a_0 and the radius of an *i*-fold aggregate, with fractal dimension, d_F , is $a_i = a_0 i^{1/d_F}$

$$J_{ij} = \frac{4}{3}Ga_0^3(i^{\frac{1}{d_F}} + j^{\frac{1}{d_F}})^3 N_i N_j$$
(2.33)

The *i* and *j* are the number of primary particles *i* and *j* which are contained in aggregates. When $d_F = 3$, i.e. for coalesced, non-fractal aggregates, equation (2.33) becomes



FIG. 2.11. Collision rate coefficients for aggregates with different fractal dimension, calculated by equation (2.33); It is assumed that the size of primary particles is 0.1 μ m and their aggregates collide with a particle with a diameter of 10 μ m in a shear field with shear rate, G, 50 s⁻¹.

identical to the Smoluchowski result for orthokinetic collisions, equation (2.21).

Fig. 2.11 shows that fractal dimensions less than 2 leads to very much faster growth of aggregates than the Smoluchowski result, equation (2.21). Fractal aggregates grow more rapidly in terms of their mass (or aggregation number) since the aggregates with open structure have more chance to collide with particles and the effective size grows even more rapidly due to the relationship between mass and size in equation (2.29)

2.6 Experimental techniques

One flocculation process can have many complicated aspects such as floc structure, floc size distribution and flocculation rate. Therefore, the investigation of such aspects in the process in order to understand a particular flocculation is vital. There have been several experimental techniques such as microscopy (Clark and Flora 1991; Bower et al. 1997), particle counting (Pandya and Spielman 1983; Tambo 1991), light scattering (Oles 1992; Jung et al. 1996) and turbidity fluctuation (Gregory and Nelson 1984; Gregory and Chung 1995) in experimental studies. Recent developments in these techniques have given useful insight required to understand flocculation. However, it is believed that an understanding of all features in flocculation can not be achieved by using only one of these techniques.

In this section, turbidity fluctuation and particle counting will be introduced since the techniques are mostly involved in the current work. Turbidity fluctuation technique has mainly been used. This technique is more concerned with the properties of aggregates produced under different conditions and with the determination of the optimum dosage of additives needed to give effective flocculation. In spite of many advantages in the use of turbidity fluctuation, the method offers indirect investigation and does not give the actual properties of flocs.

Particle counting and electrophoretic mobility measurement are also performed to determine the particle size and to derive the value close to zeta potential. In research using these techniques, the main interest is usually placed on the absolute rate of aggregation of model suspensions in order to compare the theory of aggregation kinetics or to derive information on colloidal interactions, respectively. However, particle counting does not make a contribution further than determining the size range of initial particles and determining the mean size of the particles due to instrumental problems found during the tests (see the following section).

2.6.1 Particle counting

As mentioned in Section 2.1, the removal of particles from water and wastewater is essential and requires understanding of particle hetero-dispersity, especially with respect to size. A joint mathematical and experimental approach to studying changes in size distributions in these processes has proven quite insightful. Previous approaches (Vigil and Ziff 1989; Tambo 1991; Spicer and Pratsinis 1996a; Serra and Casamitjana 1998a) to describe the floc size distribution using this technique have been made and given improvement on this area. Recommendations for analysts and manufacturers of particle size distributors based on mathematical principles are elucidated. Flocculation modeling is quite advanced but can be used predictively only under certain, well defined conditions. Insights from flocculation modeling in the last ten years might make significant design and operational differences in the near future (Lawler 1997).

Particle size distributions are usually measured with particle counters. Among two commonly used detection techniques in particle counting, electrical and optical methods, giving electrical sensing zone (electrozone) and optical sensing zone (lightscattering) counters, respectively.

The basic electrozone concept made by Coulter is that the number of particles in a known volume of electrolyte solution is countable by drawing the suspension through a very small hole that has an electrode on either side of it. The passage of a nonconducting particle through the orifice causes a momentary increase in the electric resistance between electrodes placed either side of the orifice. The resulting change in current can be amplified as a voltage pulse, and the number of pulses generated by the sample can be counted and the height of the voltage can be analysed to get particle volume. With a hole of a accurately known diameter, a stable current supply and a known amplification factor, the height of each current pulse becomes proportional to the volume of particles travelling through the hole. The distribution, the numbers of counts in each range of signal sizes, is interpreted as the particle size distribution, when the relationship between signal size and particle size is known.

In comparison with optical techniques, the electrozone technique is independent of the shape or composition of the particles since the voltage pulse produced is proportional to the particle volume, not the actual size, assuming particles have infinite resistance in comparison to the electrolyte solution. A particle passing through the orifice gives a pulse which depends only on the volume of electrolyte displaced and hence on the volume of the particle. For an aggregate, the pulse height is proportional to the total volume of the constituent particles, without the included fluid.

One of the main disadvantage of the technique is known as the coincidence effect which occurs when two or more particles produce just one pulse and are counted as one larger particle by passing simultaneously through the sensing zone. Although statistical correction for this effect is possible, it is best to ensure that the sample is sufficiently dilute to avoid the problem. The dilution process, which is sometimes needed to be in high degree, may cause some change in the particle size distribution, especially for aggregating particles.

Another disadvantage is that the electrozone technique cannot conveniently be used over a very wide range of aggregate size. An orifice should be changed to maintain a diameter of the orifice not to be more than about 50 times the primary particle size. As aggregates grow larger, they can reach a size where orifice blockage becomes a problem. Liang and Kendall (1998) found that this occurs more often as particle volume fraction increases.

The light scattering behaviour of a colloidal dispersion offers another way of particle counting and sizing. In the light-scattering technique, particles are made to pass singly through a focused light beam (i.e. usually a coherent laser beam) and either the transmitted light or scattered light intensity is measured. Each particle passing through the beam causes a reduction in transmitted light or an increase in the scattered light. The scattering technique is the very sensitive but the presence of very small impurities in suspension can cause a problem.

2.6.2 Electrophoretic mobility

In electrostatic stabilisation, the magnitude of the surface charges determines the magnitude of the repulsion between the particles and, hence, the stability of the suspension. Information about the magnitude and sign of the surface charge can be obtained from electrokinetic measurements in which the motion of the charged particles in an electric field is measured. In practice, the electrical potential near the surface of the particle (called the *zeta potential*, ζ) is measured and used as an indication of the repulsion. The corresponding surface charge can be determined from the ζ -potential using theoretical equations and the properties of the suspension.

Colloidal particles develop a surface charge when dispersed in a polar solvent (e.g. water). The particles acquire a surface charge usually by adsorption of ions from solution and the surface normally hydrated in water. The charge of the surface is dependent on the pH of the solution. At low pH values, adsorption of H^+ ions produces

a positively charged surface while at high pH, the adsorption of OH^- ions leads to a negatively charged surface. At some intermediate pH, the adsorption of H^+ ions will balance that of the OH^- ions, and the surface will be effectively neutral; this pH value is known as the point of zero charge (PZC).

It is more practical to measure the zeta potential (i.e. the electrostatic potential at a small distance from the particle surface). The pH value where the zeta potential is zero is called the isoelectric point (IEP).

Theoretical analysis gives the following relationship between the surface charge density, σ_0 , of a particle dispersed in a liquid:

$$\sigma_0 = 2.83(\varepsilon \varepsilon_0 R_G T c)^{1/2} \sinh(\frac{zF\psi_0}{2R_G T})$$
(2.34)

where ε is the dielectric constant of the liquid, ε_0 is the permittivity of vacuum, R_G is the gas constant, T is the absolute temperature, c is the concentration of the electrolyte ions in the solution, z is the valence of the electrolyte ions, and F is the Faraday constant. For low potential (the Debye-Hückel limit), valid for when the surface potential, ψ_0 is less than 50mV, equation (2.34) becomes:

$$\sigma_0 = \varepsilon \varepsilon_0 \kappa \psi_0 \tag{2.35}$$

By knowing the concentration of the electrolyte added to the suspension, the valence of the electrolyte ions, the dielectric constant of the liquid medium (78 for water) and the absolute temperature of the experiment and the physical constants, the surface charge can be determined from the surface potential (or vice versa).

When an electric field is applied to a suspension of charged colloidal particles, the particles move with a velocity that is proportional to the applied field strength. The motion is referred to as electrophoresis. It can provide valuable information on the sign and magnitude of the surface charge and surface potential. The measured potential is called zeta potential and the value of the zeta potential is not the potential at the surface of the particle. It is the potential at the shear plane between the moving particle (with its bound water layer) and liquid. It corresponds to the potential of a surface removed from the particle surface by at least one hydrated radius of the counter-ion.

In a particle electrophoresis apparatus, a dilute suspension is placed in a cell and a voltage V is applied to two electrodes at a fixed distance l apart. The sign of the surface



FIG. 2.12. Schematic diagram of particle electrophoresis cell, adapted from the figure by Shaw (1992)

charge is obtained directly because it is opposite to that of the electrode toward which the particle is migrating. The electronic magnitude (EM) is obtained by measuring the particle velocity. The velocity is measured by viewing the particles in the suspension (by using a microscope) and timing the motion of a given particle between a fixed graduation scale in the microscope. The velocity of more than 20 different particles is commonly measured to provide an average value and a standard deviation. In many cases, the zeta potential ζ is given approximately by:

$$\zeta = \frac{\mu u}{\varepsilon} \tag{2.36}$$

In this equation, μ is the viscosity of the liquid, ε is the dielectric constant of the liquid, and u is the electrophoretic mobility equal to the particle velocity v, divided by the electric-field strength equal to V/l. It only applies to when the diffuse layer is thin relative to particle size ($\kappa a \gg 1$).

2.6.3 Light scattering methods

A suspension of particles illuminated by a light beam causes some of the light to be scattered. In general, scattering by particles depends on their size, shape and refractive index, the light wavelength and the angle of observation. A complete theory (Mie theory) is available for spherical particles (Kerker 1969) and there are several approximate approaches possible. For studies of particle aggregation, it is usually necessary to make simplifying assumptions and even so it may not be possible to derive a detailed aggregate size distribution. Often, some forms of the size distribution are assumed and appropriate parameters (e.g. moments of the distribution) are derived from light-scattering measurements.

A consequence of light scattering by particles is that there is a reduction in the intensity of light transmitted through the suspension. Measurement of extinction or turbidity can be a very simple method of deriving information on particle size or the state of aggregation of suspensions. More detailed information can be obtained by measuring the angular distribution of scattered light, although the technique is more elaborate. Static light scattering involves measurement of average scattered light intensities and can give information over a wide range of particle sizes. Dynamic light scattering gives values of the diffusion coefficients of particles, from which size information can be derived. This method is only applicable to rather small particles (below about 2 μ m) and so is of limited use in aggregation studies.

2.6.3.1 Turbidity

The observed turbidity (extinction) of a suspension is due to the scattering of the incident light away from the forward direction. If the incident intensity is I_0 , then the intensity that survives after passing through a solution of length L is

$$I = I_0 \exp(-\tau L) \tag{2.37}$$

where τ is the turbidity, which depends on the number concentration and light scattering properties of the particles.

The intensities I_0 and I in the above equation can be substituted by the initial voltage V_0 and V obtained after light passes through a suspension.

$$V = V_0 \exp(-\tau L) \tag{2.38}$$

If the suspension is of uniform particles, with a number concentration per unit volume n, then the turbidity is defined simply as:

$$\tau = nC \tag{2.39}$$

where C is the light-scattering cross-section of the particles. C represents the effective cross-sectional area of the beam from which light is removed as a result of scattering by the particle. It is related to the geometrical cross-sectional area of the particle by a scattering coefficient, Q, which, for spherical particles, is simply

$$Q = \frac{C}{\pi a^2} \tag{2.40}$$

where a is the particle radius.

The scattering coefficient depends greatly on the light wavelength and on the size and refractive index of the particles. For very small particles of the size less than about 10% of the wavelength λ , Rayleigh theory applies and for very much larger particles of the size of many times the wavelength, Q approaches 2. For intermediate sizes more elaborate computations based on Mie theory have to be carried out. The scattering coefficient from Rayleigh theory is given by

$$Q = \frac{8}{3}\alpha^4 \left(\frac{m^2 - 1}{m^2 + 1}\right)^2 \tag{2.41}$$

where m is the refractive index of the particles relative to that of the suspending medium and α is a dimensionless particle size given by

$$\alpha = \frac{2\pi a}{\lambda} \tag{2.42}$$

For a typical value of relative refractive index (say 1.2, corresponding to polystyrene particles in water) and bearing in mind that α cannot exceed about 0.3 for Rayleigh theory to apply, equation (2.41) is only valid up to Q values of about 10^{-3} , i.e. for particles which scatter less than 1/1000 of the light incident upon them.

For larger particles, Q can be computed exactly from Mie theory (Kerker 1969). For very large particles, the scattering coefficient approaches a limiting value of 2, i.e. the amount of light scattered by a large particle is twice the light incident upon it due to the diffraction of light at the edge of the particle. The particle size at which Q becomes effectively constant depends on the wavelength and the refractive index of particles. For latex particles in water, the limiting value is not reached until the particle diameter is about 30 times the light wavelength.

When the particle refractive index is not greatly different from that of the suspension medium, and the particles are quite large, a very convenient approximate form for Q may be used. This is the anomalous diffraction approximation (van de Hulst 1957) :

$$Q = 2 - (\frac{4}{\rho})\sin\rho + (\frac{4}{\rho^2})(1 - \cos\rho)$$
(2.43)

where ρ is a function of the dimensionless size, α , and the relative refractive index, m:

$$\rho = 2\alpha(m-1) \tag{2.44}$$



FIG. 2.13. Scattering coefficient calculated as a function of dimensionless size, α ; Dotted line by actual calculated result from equation (2.43) when m=1.2. Full line by exact computations based on Mie theory (Gregory 1985)

This expression may be applied when α is large and m small. Some results from the anomalous diffraction approximation are given in Fig. 2.13, together with the corresponding exact results from Mie theory. When the scattering coefficient is plotted against a size, it exhibits a regular series of maxima and minima as shown in Fig. 2.13. It can be seen that the approximate result follows very well the form of the exact computations, especially with regard to the positions of the maxima and minima. The approximate value of the scattering coefficient is, at worst, about 14%, too low when m = 1.2. For smaller values of refractive index, the agreement between Mie theory and the anomalous diffraction approximation becomes even better.

For a suspension of uniform spherical particles, with radius a and number concentration n, the volume fraction, ϕ is simply $4\pi na^3/3$. The specific turbidity, τ/ϕ , then follows from equations (2.39) and (2.40) :

$$\frac{\tau}{\phi} = \frac{3Q}{4a} \tag{2.45}$$

Since the scattering coefficient depends on particle size, it is possible, in principle, to derive particle size information from turbidity measurements on a suspension of known concentration. In an aggregating suspension, the volume fraction should remain constant and the change in turbidity might be a useful measure of the degree of aggregation.



FIG. 2.14. Specific turbidity as a function of particle diameter derived from equation (2.45) with Q calculated from equation (2.43) (Gregory 1985)

When plotted against particle size, for mono-sized particles, there is a sharp rise in specific turbidity with particle size up to a maximum value at about 1.5 μ m, above which the turbidity falls rapidly and goes through a series of maxima and minima which are less pronounced than those in scattering coefficient (refer to Fig. 2.14). For very large particles, where the scattering coefficient becomes nearly constant, the specific turbidity varies inversely with particle size.

2.6.3.2 Turbidity fluctuations

Monitoring aggregation by turbidity fluctuation technique has been modified and thus improved since Gregory and Nelson (1984) introduced a simple flow-through optical technique and Gregory (1985) gave the theoretical basis.

Basically, the intensity of a narrow beam of light transmitted through a flowing suspension is monitored by a photodetector and its output consists of a steady component (dc, the mean value) which depends on turbidity of the suspension and a fluctuating part (ac, the root mean square value) which arises due to random variation in the number of particles in the light beam. Since the number fluctuations follow the Poisson distribution, the variance about the mean is equal to the mean number of particles in the light beam thus the standard deviation of the voltage about the mean value, rms, depends on the square root of the particle concentration.



(a) Turbidity fluctuation technique



(b) Fluctuation signal in stable condition

(c) Fluctuation signal in unstable condition

FIG. 2.15. Principle of turbidity fluctuation technique

For a mono-disperse suspension of particles with light-scattering cross-section Cand number concentration n, it can be shown that

$$V_{rms} = \overline{V} \sqrt{\frac{nL}{A}} C \tag{2.46}$$

where L is the optical path length and A is the cross-sectional area of the light beam.

In this equation, V_{rms}/\overline{V} is defined as R, the ratio value. This is also called "flocculation rate" or "flocculation degree" since it contains useful information as stated above. If the concentration is expressed as a volume fraction and the scattering coefficient, equation (2.40) is introduced, we obtain

$$\frac{R}{\sqrt{\phi}} = \sqrt{\frac{3\pi L a_0}{4A}} Q_0 \tag{2.47}$$

where the radius and scattering coefficient of the primary particles are designated a_0 and Q_0 , to distinguish them from the corresponding values for aggregates. As aggregation occurs, it can be shown that the ratio value increases. Use of the ratio value is very convenient since it is not affected by contamination of optical surfaces and electronic drift. The dc (\overline{V}) and rms (V_{rms}) values are changed in the same relative way by these effects.

This expression shows that, for constant values of scattering coefficient and volume fraction, ratio should increase as the square root of particle size. For similar conditions, the turbidity, given by equation (2.45), decreases as the particle size increases.

In an aggregating suspension, there will be a distribution of aggregate sizes, f(k), where k is the aggregation number. For a fractal k-fold aggregate, the aggregate radius, a_k , can be written in terms of the primary particle radius and the appropriate fractal dimension, d_F :

$$a_k = a_0 k^{\frac{1}{d_F}} \tag{2.48}$$

The corresponding scattering cross-section is then

$$C_k = \pi a_0^2 k^{\frac{2}{d_F}} Q_k \tag{2.49}$$

where Q_k is the scattering coefficient for the aggregate.

For a distribution of aggregate sizes f(k) and a mean aggregation number $\overline{k}(=n_0/n_T)$, it can be shown (Gregory and Chung 1994)

$$\frac{R^2}{\phi} = \left(\frac{3\pi L a_0}{4A}\right) \frac{1}{\bar{k}} \int k^{\frac{4}{d_F}} Q_k^2 f(k) dk \tag{2.50}$$

The corresponding expression for specific turbidity is

$$\frac{\tau}{\phi} = \frac{3}{4\overline{k}a_0} \int k^{\frac{2}{d_F}} Q_k f(k) dk \tag{2.51}$$

It was shown (Rosen 1984) that aggregate size distributions may adopt a selfpreserving form and that a very simple exponential form may be appropriate in some cases. In terms of aggregation number this can be written

$$f(k) = \frac{1}{\overline{k}} \exp(-\frac{k}{\overline{k}}) \tag{2.52}$$

For fairly large aggregates, it may be acceptable to treat the scattering coefficient as constant, although this assumption may not hold for aggregates of rather open structure (low d_F). With the assumptions of an exponential size distribution and a constant Q_k , the integrals in equations (2.50) and (2.51) can be evaluated analytically, giving

$$\frac{R^2}{\phi} = \frac{3\pi L a_0 Q_k^2}{4A} (\bar{k})^{2m-1} \Gamma(m+1)$$
(2.53)

and

$$\frac{\tau}{\phi} = \frac{3Q_k}{4a_0} (\bar{k})^{m-1} \Gamma(m+1)$$
(2.54)

where $m = 2/d_F$ and Γ is the gamma function.

Combining equations (2.53) and (2.54) gives :

$$\left(\frac{R}{\tau}\right)^2 = \frac{4\pi L a_0^3}{3A\phi} \cdot \frac{\Gamma(2m+1)}{[\Gamma(m+1)]^2}$$
(2.55)

The assumption of constant Q_k is no longer a serious limitation since the scattering coefficient has been cancelled out in deriving equation (2.55).

If the solid volume fraction, ϕ , is fixed and the scattering coefficient is also assumed constant, then equation (2.53) will be rearranged to give

$$R = (constant) \cdot (\overline{k})^{\frac{4-d_F}{2d_F}}$$
(2.56)

If the fixed volume fraction and the constant scattering coefficient and fractal dimension of the aggregates are assumed, equation (2.55) will be rearranged.

$$(\frac{R}{\tau})^2 \propto \overline{k} \tag{2.57}$$

where \overline{k} is the mean aggregation number which can be derived from dc and the ratio value and d_F is the fractal dimension. The fractal dimension cannot exceed 3 in a three-dimensional world and thus the exponent in equation (2.56) must always be positive. This results in the ratio value increasing with aggregation number. As seen in equations (2.55) and (2.56), the measurement using turbidity fluctuation technique is very useful to understand the degree of aggregation and the structure of aggregates without detailed quantitative analysis of the data in terms of aggregate size. With the same assumption as above, a simple means of continuously determining the average degree of aggregation and the fractal dimension can be achieved.

By substituting for k from equation (2.54), we obtain

$$\log \tau = (constant) + \frac{2(2-d_F)}{d_F} \log \frac{R}{\tau}$$
(2.58)

Turbidity, τ , will be substituted by $T(=\ln \frac{V_0}{V})$ for convenience in this work. According to equation (2.58), for an aggregating suspension, the logarithmic plot of R/τ against τ should give a straight line with a slope of $2(2 - d_F)/d_F$. While $(R/\tau)^2$ in equation (2.57) is a good indication for aggregation number with time, equation (2.58) is still questionable since the scattering coefficient in equation (2.54) is not cancelled out and should be assumed as a constant value during test although it provides a convenient means of "real time" determination of the fractal dimension subject to the assumption mentioned above.

Chapter 3

Experimental Procedures

3.1 Materials and preparation

This section presents a description of the main materials used and the preparation procedures prior to carrying out the experiments.

3.1.1 Suspensions

The selection of suspensions was made by investigating how the properties of particles such as their initial size and shape affect the density and the structure of aggregates. The particles chosen can be categorised by the following factors; (1) the size of primary particles, (2) the shape of the particles, and (3) the type of dispersion (mono-disperse or poly-disperse). Deionized water to be mixed with the selected particles was prepared by ELGASTAT OPTION 3. The specific conductivity of the water was maintained below 1.5 μ S/cm. The pH of the water was not adjusted to any particular value. The charge density of the type of polymers used in this work is not influenced by the pH of the solution (Dentel 1991). The following sections describe the particles used and procedures to prepare the suspensions.

3.1.1.1 Latex

Suspension of spherical latex particles which are mono-disperse and have a mean diameter of 1.7 μ m has been used. The suspension was made up as described below. Deionised water and sodium chloride were placed in a 1 L flask and immersed in a water bath at 70 °C. The flask was fitted with a stirrer with a variable speed control. Materials taken for the preparation of latex suspension is given in Table 3.1. The contents were stirred at 350 rpm until they are at a temperature of 70 °C. At this stage styrene was added and a few minutes were allowed for temperature equilibrium. Then sodium persulphate was added as an initiator and stirring continued for 20 hours. The reaction mixture had a distinct milky-white latex appearance due to polymerisation. Prior to use the suspension was purified by cross-flow filter unit (SATORIUS) using a filter with 0.2 μ m pores. Sub-micron particles were found when diluted suspension was investigated microscopically and were removed by decanting the top part of the diluted suspension after it was allowed to settle in a bottle for a few days.

TABLE 3.1. Mixture contents for suspension of latex with a diameter of 1.7 μ m

Material	Amount
Styrene	25 ml
Deionised water	210 ml
Sodium Nitrate (2 % solution)	15 ml
Sodium Persulphate	3 mg

By choosing appropriate level of the initiator, particles with a diameter of 1.7 μ m were obtained. A standard deviation less than 5% is measured by a Coulter particle counter (ELZONE PC280). The concentration of stock suspension is 10 g/L and is diluted to 100 mg/L for flocculation test. The measured pH of the suspension is 6.21.

3.1.1.2 Kaolin

Kaolin particles used in the test have a plate-like shape and an equivalent diameter of up to about 1.5 μ m. A suspension was prepared by kaolin powder (BDH Ltd.) as follows.

Kaolin powder (about 200 grams) was dispersed in deionised water by a high speed laboratory blender for 20 minutes. This suspension was made up to 1 litre with deionised water and allowed to stand overnight in a 1 L measuring cylinder. The top 500 ml was carefully decanted, retained and further diluted to 1 L as a stock solution. The suspension was found to contain 52.45 g/L, most of the particles being below 2 μ m in size when measured by a particle counter (Elzone 280PC). The pH of the suspension is 6.40. The stock suspension is diluted to 200 mg/L for tests.

The used latex and kaolin particles have almost the same refractive index, and latex suspension is found to be more turbid at the same concentration than kaolin. High scattering coefficient, caused by the size of latex particles at about 1.7 μ m may result in this higher turbidity as described in Fig. 2.13 (see page 41).

3.1.1.3 Silica

Two kinds of silica suspensions, which contain amorphous spherical, mono-disperse particles for the experiments in Chapter 4 and poly-disperse particles for Chapter 5, have been used in the test. The amorphous silica particles have the diameter of 1.5 μ m, given by the manufacturer (Geltech) while the latter were found to be mainly smaller than 5 μ m when measured by a particle counter.

For both silica samples, silica suspension of high concentration (about 50 g/L) was placed on a ultrasonic agitator for 30 minutes and was diluted to make up a stock suspension of 10 g/L. The measured pHs of the mono-disperse silica suspension and the poly-disperse silica suspension are 5.54 and 5.96, respectively. For the main tests, the stock suspensions were diluted to be 150 mg/L for mono-disperse particles and 400 mg/L for poly-disperse particles.

3.1.1.4 Measurements of electrophoretic mobility

The following figures exhibit the electrophoretic mobilities of the flocs of the particles which are used in this work. Section 2.6.2 discussed how to derive the zeta potential using electrophoretic mobility. In current experimental conditions such as average particle diameter between $1-4 \mu m$ and dissolved salt concentration less than 5 mMol of 1-1 electrolyte are used, equation (2.36) could be substituted by the following equation for convenience.

$$\zeta \simeq 12.8u \tag{3.1}$$

where the units of zeta potential and mobility are expressed conventionally as mV and $\mu m \cdot s^{-1} / V cm^{-1}$, respectively. Average zeta potential for wastewater colloids is from -16 to -22 mV.

It is observed in the results that the surface of the used particles are all negatively charged, and the polymer with higher charge density leads to zero mobility with smaller amount. The type and density of the charges charge which polymer and particle surface contain are important factors in determining a degree of flocculation. However, note that this only shows the mobility of particles/flocs and zeta-potential of the surface but not the highest flocculation rate since polymers of high molecular weight could lead to aggregation by bridging as mentioned in Section 2.4.3. Therefore, during the main tests using the light transmission technique, the highest degree of flocculation may not be achieved with the corresponding polymer concentrations.

The results shown in Fig. 3.1 exhibits the mobilities of silica flocs produced under the similar conditions to the actual flocculation tests which are shown in Chapter 5. Various amounts of Percol 63, 326 and 1697 were dosed into the poly-disperse silica suspension stirred for 600 seconds at 60 rpm. Flocculation was performed in the vessel and stirrer in the Set-up A in the presence of 5 mMol NaNO₃. After the flocculation tests, 20 ml was sampled for electrophoresis measurement.



FIG. 3.1. Electrophoretic mobility of poly-disperse silica particles/flocs in Percol solutions; the concentration of the suspension is 400 mg/L and the particles were flocculated by Percol 63, 326 and 1697 in the vessel used in the Set-up A

The results shown in Figs. 3.2 and 3.3(a) and (b) are obtained from the condition that the particles of latex, kaolin and silica are flocculated for 600 seconds by one of the polymers (Percol and Zetag series). The polymer of different amount to give various concentration was added into a stirred suspension at 60 seconds and the shear rate of 60 rpm for latex, mono-disperse silica and kaolin flocculation was applied constantly for 540 seconds. The flocculation tests were planned to occur in the vessel and stirrer used in the Set-up B in the presence of 5 mMol NaNO₃ (refer to Fig. 4.3(a) for a test schedule).



(b) Latex and Zetag series

FIG. 3.2. Electrophoretic mobility of latex particles/flocs in Percol/Zetag solutions; the concentration of latex suspension is 100 mg/L and the particles were flocculated by Percol 63, 326 and 1697 and Zetag 64, 89 and 92 in the vessel used in the Set-up B



FIG. 3.3. Electrophoretic mobility of mono-disperse silica and kaolin particles/flocs in Percol 63 solution; the concentration of the suspensions is 150 and 200 mg/L, respectively and the particles were flocculated by Percol 63 in the vessel used in the Set-up B

3.1.2 Polymeric flocculants

Copolymers of acrylamide and dimethylaminoethyl acrylate (DMAEA) quaternised with methyl chloride are widely used in the water industry. As described in Section 2.4.1, flocculants are broadly classified according to the nature of the charge they possess, that is, whether they are cationic, anionic and non-ionic. Other crucial parameters are molecular weight and charge density which are well known to affect mostly the adsorption of polymer on particle surfaces. The latter is generally expressed as a percentage of ionogenic group relative to all groups of every type for industrial products, but sometimes the exact information is not accessible for the commercially available materials. The polymeric flocculants used in the experiments were cationic polymers, named Percol 63, 326 and 1697 and Zetag 64, 89 and 92 supplied by Allied Colloids Limited, Bradford, England. Their molecular weights and charge densities are listed in Table 3.2.

Percol 63 is based on the copolymerization of acrylamide and dimethylaminoethyl acrylate (DMAEA) and is fully quaternised. It has a high molecular weight of 3 million and 30% charged. Percol 326 is a lower molecular weight (4.5×10^5) cationic polymer also based on the copolymerization of acrylamide and DMAEA which had been quaternised with methylchloride and is 15% charged. Percol 1697 is a low molecular weight polymer, and is polydiallyldimethylammonium chloride (PolyDADMAC). It has a molecular weight of $3 - 4 \times 10^4$ and is 100% charged.

The Zetag series used in this study, have about the same molecular weight, which is higher than the selected Percols. The Percol series are originally produced for paper making process although, with the same product number (i.e. Percol 63 and Zetag 63), both Percol and Zetag would lead to the same results in the present experiments.

TABLE 3.2. Properties of polymer (I.V.=intrinsic viscosity)

Polymer	Туре	Charge	I.V. (Approximate M.W.)
Percol 63	Cationic	30 %	I.V. 7 (3×10^{6})
Percol 326	Cationic	15 %	I.V. 2 (4.5×10^{5})
Percol 1697	Cationic	100 %	I.V. < 1 $(3-4 \times 10^{4})$
Zetag 64	Cationic	40 %	I.V. 12 (6.8×10 ⁶)
Zetag 89	Cationic	80 %	I.V. 12 (6.8×10 ⁶)
Zetag 92	Cationic	25 %	I.V. 12 (6.8×10 ⁶)

Houwink equation (Somasundaran et al. 1984):

In Table 3.2, molecular weights for intrinsic viscosity were calculated by Mark-

$$[\eta] = KM^a \tag{3.2}$$

where $[\eta]$ is the intrinsic viscosity in dL/g of the polymers, M is the viscosity-average molecular weights of the polymers, $K = 3.73 \times 10^{-4}$ dL/g, and a = 0.66 at 25 °C for cationic polyacrylamide with charge densities up to 30%.

To make up a flocculant of 0.1% (w/w), deionised water was added to 150 ml volumetric flask containing 0.1 g of Percol 63 (or Percol 326, Zetag 64, 89 and 92) and 3 ml of methanol to give a total mass of 100 g. The prepared solution was mixed by rotating the flask at 20 rpm for about 3 hours to ensure uniform and complete dissolution. Most polymers are supplied as solid, while Percol 1697 is supplied as a 40% aqueous solution. Therefore, the solutions of 0.1% (w/w) were prepared by dilution with deionised water.

Sections 4.3.1 and 4.3.2 discuss the influence of the properties stated above using various polymer concentrations. While Section 4.3.1 present the results using the selected Percol series which have different molecular weight and charge density, the effect of charge density in the case of using high molecular weight will be shown in Section 4.3.2 using the Zetag series.

3.1.3 Other chemicals

Calcium nitrate and sodium nitrate $(Ca(NO_3)_2 \cdot 4H_2O, MW 236.15 \text{ and } NaNO_3 \cdot H_2O, MW 84.99)$ were obtained from BDH Ltd. and prepared as stock solutions of 0.4 M and 1 M (e.g 33.996 g and 94.46 g added to deionised water of volume 1 L) concentration respectively. The stock solution of sodium nitrate was added to give ionic strength in suspensions before polymeric flocculants were introduced into suspension. The amount of the effect by added sodium nitrate (e.g. 5 mMol) is too small to be detected by the current monitoring technique since the concentration does not lead to significant destabilisation or screening effect between the sodium ions and cationic segments of the used polymers. Calcium nitrate solution which is more effective coagulant than sodium nitrate due to its higher charge number, has been used to investigate how dissolved salts in suspensions affect polymeric flocculation and how well they solely

perform as coagulating agents. The difference in their effectiveness as coagulants will be given in Section 4.2.1.

3.2 Experimental methods

The principle of the monitoring technique has been presented in Section 2.6.3.2. So far, a commercial instrument, PDA 2000 (Rank Brothers Ltd., Cambridge, UK), has been widely used to measure the fluctuations of light that occur when fluid containing particles flows through a light beam. The instrument consists of a high intensity light emitting diode and a sensitive photodiode that is matched to the LED and placed after the light beam has passed the measuring cell. The photodiode yields a voltage as a measure of light intensity. The principle of the monitoring technique in PDA 2000 has been used after some modification on the instrumental set-up, expecting improvement on the measurement. The detailed account will be described in the following sections.

In this research, two different instrumental set-ups have been used. One, which is previously modified from the conventional PDA set-up, uses a solid-state laser which has a high-intensity parallel beam instead of a light source of PDA 2000 (Gregory and Chung 1995). In the other set-up, a light emitting diode (LED) and a photodetector are placed in a small monitoring cell connected to its own circuit board for more convenient arrangement. Both set-ups are used in a similar manner to measure fluctuations in the intensity of light transmitted through a flocculating suspension.

3.2.1 Monitoring aggregation by modified PDA (Set-up A)

• Instrumental set-up

The set-up described below has been used for monitoring of flocculation of polydisperse silica particles described in Chapter 5. In this set-up, flocculation tests were carried out in a baffled vessel equipped with a stirrer at variable speed. The stirrer has two cross-shaped glass paddles on a glass rod and each cross has four blades of about 1.75 cm \times 1 cm. The illustration of the system is shown in Fig. 3.4. The sample was withdrawn and re-circulated by a peristaltic pump at a rate of 20 ml/min. The flocculating sample was conveyed through a plastic tube with 3 mm internal diameter and 5 mm external diameter, which passed through the monitoring cell. The illuminated section of the tube is slightly compressed
between perspex plates to give an effective optical path length of about 1 mm. Therefore the light passes through a parallel-sided section of the tube. The transmitted light is received by a 1 mm diameter optical fibre set well back (about 10 cm) from the tube to reduce the amount of forward scattered light received. The distance which is relatively longer than the conventional set-up is the reason a solid-state laser was chosen as a light source in this set-up since it has some advantages such as a high intensity and can be collinated to give a parallel beam. The other end of the optical fibre is coupled to a photodiode in PDA 2000. The transmitted light was conveyed to PDA 2000 through the optical fibre, and the dc and rms values were converted from the light intensity and the fluctuating data occurred while the light transmitted the suspension or flocs for monitoring purposes (refer to Fig. 2.15). These values were stored in PC via Acquire (PC-Lab 812) for later analysis. Instrumental settings (e.g. time interval and amplification) have been changed between sets of experiments but this affects only the monitoring sensitivity, not the actual measurements.

• Flocculation test procedure

800 ml of poly-disperse silica suspension were prepared in a baffled vessel in each test. Turbidity reduction by various suspension concentrations was monitored in the preliminary tests to determine the appropriate silica concentration (refer to Section 3.2.3 for more discussion). The concentration of 400 mg/L was found to present a reasonable change in dc while monitoring flocculation (see Section 3.2.3). Suspensions were introduced initially and were well mixed at a stirring rate of high speed (240 rpm) for 30 seconds. Polymeric flocculants were added to a stirred suspension at 120 or 180 seconds, while a small amount of sodium nitrate (5 mMol) was inserted into deionised water initially, resulting in extra ionic strength in suspension initially. Each test is continued for 1000–1200 seconds, and the shear rate is maintained to be changed between the scheduled time interval. Test schedules will be shown in each section in Chapter 5.



(a) Set-up



FIG. 3.4. Schematic diagram of modified PDA set-up, Set-up A $\,$

3.2.2 Monitoring aggregation by a new arrangement (Set-up B)

• Instrumental set-up

Instead of using the monitoring cell of PDA 2000, a new light emitting diode and a photodetector were placed on a small monitor housing. The intensity of a narrow beam of light transmitted through the flowing suspension is monitored by the photodetector. Placing a LED set back in the pin-hole of the cell as shown in Fig. 3.5 is expected to give a light beam more parallel than that in the conventional set-up. Also, this set-up has been improved to reduce the influence of the ambient light by using a small housing.



(a) Monitoring cell in newly arranged setup

(b) Monitoring cell in conventional PDA



(c) External shape of the separate housing cell

FIG. 3.5. Graphical illustrations of the monitoring cells

Some more benefit can be found since placing a small, separate purpose-built

monitoring cell close to the stirred vessel gives the shorter distance between a monitoring cell and a stirred suspension in a vessel (2-3 seconds for conveying) the suspension sample from vessel to the cell) than the conventional PDA set-up. In the conventional set-up which includes the whole tubing over 1 m long, the problem may be arisen as follows:

- (i) Floc breakage (or re-structuring) in the tube may occur while the sample is moving at high flow rates (low flow rate).
- (ii) Flocs formed by low molecular weight polymer result in a contamination of optical area by sticking to the wall inside the tube.

The signal from the photodetector are separate into dc, converted from the average transmitted light intensity, and a smaller ac component, which arises from the random variation in sample composition, by the signal processing in a circuit board (refer to Fig. 2.15 on page 43). The outputs, dc and ratio, are obtained from the processing in the circuit board which functions equally as PDA 2000. More discussion of analysis of these raw data will be followed in Section 4.1.1.

Suspensions were flocculated in a plastic square-shaped vessel. The vessel is equipped with a stirrer, which has a speed controller and two metal paddle on a metal rod. The size of blade is $2 \text{ cm} \times 1.5 \text{ cm}$. The sample was withdrawn and recirculated by a peristaltic pump at a rate of 17.5 ml/min. The jar was thoroughly washed before each series, paying attention to rinsing any detergent off, to avoid the possibility of flocs sticking on the wall of the vessel. The flocculating sample was conveyed through a plastic tube with 3 mm internal diameter and 5 mm external diameter, which passed through the monitoring cell. In the cell, the plastic tube fits into a slot, such that light from a light emitting diode passes through the centre of the tube. The effective beam diameter defined by pin-hole is about 1 mm. The overall diagram of this system is shown in Fig. 3.6.

• Flocculation test procedure

Suspensions of latex, kaolin and mono-disperse silica were aggregated using this experimental set-up. Stock suspensions were diluted with deionised water and 100 ml was placed in a square-shaped plastic vessel in each test. The concentrations of suspension were determined to be 100 mg/L for latex, 150 mg/L for



(a) Set-up



stirrer

FIG. 3.6. Schematic diagram of new arrangement of turbidity fluctuation technique, Set-up B

mono-disperse silica and 200 mg/L for kaolin in preliminary tests (see the following section) and they were well mixed at a high stirring rate (240 rpm) for the first 20 seconds. The test schedules are demonstrated in each section when the changes are made. The simple salt solution (NaNO₃) was prepared to give ionic strength. Percol series were prepared to be 0.1% (w/w) originally while Zetag series were further diluted 10 times to make up a flocculant of 0.01% (w/w) to prevent the mixing problem due to their high viscosity.

Polymeric flocculants were added to a stirred suspension at 90 seconds. In the case where a large amount of salt solution was used to investigate aggregation

solely by dissolved salts, they were inserted into deionised water 10 seconds before the actual monitoring begins. However, dissolved salts were mixed with suspension initially in the tests to observe the influence of electrolyte on polymeric flocculation. In each test, depending on the purpose, the concentration of each kind of suspension and flocculant were changed.

3.2.3 Turbidity measurement for determining the concentration of suspension

It was mentioned in Section 2.6 that during flocculation monitoring, the current light transmission technique uses two components, the decreased led current (dc) and the increased rms values which are useful indicators of floc growth. However, if the suspension is fairly concentrated beyond the applicability of the Beer-Lambert Law as stated in equation (2.37), the light transmitted through the suspension is greater than predicted on the basis of the simple exponential law due to effects such as multiple scattering. Therefore, the present study uses the suspension concentrations which are set to be applicable to the Beer-Lambert Law but high enough to lead to the changes in ratio value during flocculation.

Turbidity reduction by various suspension concentrations was monitored in the preliminary tests to determine the appropriate suspension concentration for the experimental set-up. The difference between the concentrations or suspensions in these tests arise from the different nature of the particles (e.g. primary mean size, shape, and scattering coefficient).

When the light intensity passed through suspension of a certain concentration other than deionised water, the measured turbidity should be reduced to a certain extent for monitoring reason. Turbidity is proportional to particle number concentration according to equation (2.39), and the turbidity can have a great effect on the monitoring sensitivity. It was told in Section 2.6.3.2 that the light transmission technique employed in this study uses mainly the fluctuating signals during the monitoring. Therefore, if the turbidity is too low, indicating low particle number concentration (n), the changes in the corresponding ratio also be very small (see equation (2.46)). In the case of very high turbidity which is a sign of high particle number concentration, (1) optical path length (L, see Fig. 2.15) should be reduced significantly to let the light beam pass



FIG. 3.7. Turbidity obtained from tests using various particle concentration; (a), (b) and (c) measured in the Set-up B, (d) in the Set-up A

through the turbid path, or (2) very large flocs are formed due to the higher collision rate as described in collision rate coefficient, k_{ij} in equation (2.21). As a result, the fluctuating component (*ac*) becomes too high and the ratio overload is caused when these flocs are detected and the analysis of the results becomes problematical by the unwanted scatters in the derived data.

For the experimental set-up in this study, the $dc \ (\overline{V})$ reduction range of 30-40%is found to be a boundary (see equation (2.38) for the relationship between turbidity and dc). The concentration of suspension has been set to be in this region. However, in Fig. 3.7(c), the concentration of 200 mg/L for kaolin suspension leads to only 11.8% reduction in dc rather than 30-40%. The aggregation of kaolin particles is relatively a very fast process, compared to the others such as latex and silica aggregations and aggregation at higher concentration usually ends just in 50 seconds with a similar amount of flocculant. Therefore, the lower suspension concentration has been used in order to maintain the monitoring sensitivity and avoid the problems mentioned above.

Chapter 4

Aggregation under constant shear and various solution conditions

4.1 Introduction

During a flocculation process, flocs are generated with various sizes and densities under different solution and hydraulic conditions. Those factors are important in solid-liquid separation, especially where flocculation and flotation are the main processes in charge. Inorganic hydrolysing salts such as aluminium sulphate and ferric chloride have commonly been used to enhance particle separation in primary treatment (O'Melia and Stumm 1968; Jung et al. 1996) and the mechanism has been thoroughly investigated (Bottero et al. 1993). Hydrolysis of metal ions is the removal of protons from the hydration shell of the ions by addition of OH^- . Polymeric flocculants have been proved to be more effective than dissolved salts in solid-liquid separation and have become the well-known and widely used additives in flocculation process (Budd 1989). Their high effectiveness at low doses and the possibility of adaptation to various circumstances by controlling the properties of polymers have made them very popular.

There have been many experimental works first by Ruehrwein and Ward (1952) and Adachi and Kamiko (1994) and Hogg (1999) recently using polymeric flocculants to investigate various aspects of flocculation. Though progress in some aspects of flocculation has been made, the interpretation of the results in detail has been difficult due to the nature of various floc structures. In fact, various factors can have an influence on flocculation, such as types of suspension and flocculant, the ionic strength of solution and the nature of fluid motion. Therefore, this chapter begins with investigations on the effect of each factor mentioned above. Then, the influence of various particles and flocculants on the characterisation of flocculation, including floc properties, will be introduced, where the emphasis is on the physicochemical reaction between particles or particle and flocculant. Orthokinetic reaction is another main factor that affects floc properties, and the related results will presented in Section 4.4 using various constant shear and Chapter 5 using shears variable during a test.

The experimental results in this chapter were obtained by the newly arranged setup (Set-up B) described in Section 3.2.2. During preliminary studies, the range of flocculant doses and the particle concentrations were tested. Including the pre-tests described in Section 3.2.3, preliminary tests have been carried out to evaluate the suspension concentration as well as the polymer concentrations which result in the changes detectable by the employed monitoring set-up.

During preliminary tests, various amounts of the stock suspensions were injected into the stirred water to give a range of suspension concentrations. On the basis of the measurable changes in dc (usually 30–40% reduction with the injection of stock suspension into deionised water), the concentrations for each particles were determined and these are 100 mg/L for latex, 150 mg/L for silica and 200 mg/L for kaolin particles (refer to Figs. 3.7(a), (b) and (c)). At a given constant stirring rate (60 rpm in Set-up B), the current experimental procedure leads to steady state of flocculation (plateau region of ratio curve) usually within 500 seconds. Therefore, monitoring has been performed for 600 seconds for most tests in this chapter (refer to Fig 4.3). In order to determine the optimum concentration of coagulant/flocculant, another set of preliminary tests has been performed by taking the following steps;

- (i) Various amounts of additives such as dissolved salts or polymers were added to give the required concentration while moderate constant fluid shear (60 rpm in Set-up B) is applied by a stirrer, and
- (ii) the obtained results were examined, regarding the maximum ratio values in given

test time. The optimum concentration is defined by the highest maximum ratio value, regardless of time taken to reach the maximum ratio.

4.1.1 Interpretation of experimental results

The fundamental principles of the experimental techniques have been discussed in Section 2.6 and the monitoring methods have also been described in Section 3.2.1. While suspension is being flocculated, ratio and dc (or V) are obtained directly from the monitoring measurement. According to equation (2.56), the ratio value contains both aggregation number (\bar{k}) and the floc density (d_F) and indicates the degree of flocculation. The dc is the voltage that survives after light passes through a suspension and turbidity can be derived with the obtained dc using equation (2.38). These two different values are usually increased or decreased to a certain limiting value which is very much environment-dependent.

The changes of ratio and dc values are normally dependent on physical and chemical conditions in the flocculated suspension. In the case of the dc reading, an increase usually takes place, since an aggregate has a smaller light scattering cross-section than the total value for all the individual particles and more light is transmitted through the flowing suspension. However, this does not apply to every case; depending on the way they stick together, dc is often found to be decreasing. The ratio value shows a greater increase than the dc does as flocs grow. This provides a very useful empirical guide to the degrees of flocculation under different solution and hydraulic conditions and it is believed that the ratio value is a more sensitive measure of flocculation rate than turbidity (Gregory 1985).

The followings describe how to derive the supplementary values the from the raw data, dc and ratio obtained directly from monitoring. For convenience, the ratio and dc value are now expressed as R and V.

- Using the voltage V_0 obtained in the condition that the light beam passes through deionised water, T values are derived using the definition $T=\ln(V_0/V)$. The derived values should be proportional to the actual turbidity, τ . These two series of values (R and T) are plotted against time and the presented the charts exhibit the changes in ratio and turbidity with time.
- According to equation (2.57), $(R/\tau)^2$ indicates aggregation number, \overline{k} which



FIG. 4.1. Flow chart for the data shown in this study

is inversely proportional to particle number in the suspension and, hence, the values of $(T/R)^2$ should increase or decrease proportionally to particle number concentration. The value before adding flocculants is multiplied to give 100 (usually before 60–90 seconds). The values in the row are multiplied by the same factor. The converted values in the row are *RPNC* and are plotted against time.

• The values of log R/T and log T are plotted against each other, the log R/T values are located on the x-axis and the log T values on the y-axis, and the the curve generally contains straight regions for certain periods indicating constant fractal dimension of the growing flocs. The slope of the curve is converted to d_F using equation (2.58) which corresponds to $d_F = 4/(2 + s)$ where s is a slope of a linear region of the curve. If the obtained slope is negative (or positive), $d_F > 2$ (or < 2). Fractal dimensions infer a measure of compactness in a certain time period, but with the changes of d_F , the inference of the cohesion/break-up mechanism of flocs can be supported.

Note that T and RPNC do not represent the actual value or number for turbidity and particle number concentration but the values should be proportional to the real values. Therefore, they can be compared each other if initial turbidity and particle concentration are the same.

Although interpreting the variation in the ratio value has been found to be a good method to evaluate the degree of flocculation, it does not directly provide the properties of flocs, such as the floc size and density. However, the relative particle number concentration (RPNC) and the calculated fractal dimension (d_F) of the generated flocs together could yield information on the average floc size with the knowledge of the primary particle size and at least, the idea on the behaviour of the average floc size change can be given. With RPNC, it will be shown how much particle number in suspension has been reduced during flocculation (or increased during break-up) and d_F indicates how dense the flocs are generated during the certain period of flocculation.

The increasing ratio curves eventually saturate and converge to a certain limiting value. Previous studies have shown that, as flocs grow large enough to be vulnerable to breakage by fluid shear, a steady state is reached where the floc growth and the breakage rate are equal and at a balance. When a same constant shear is applied, the floc-size distribution no longer changes with time (Reich and Vold 1959). However, this does not imply that floc growth and breakage no longer occur in this period, but simultaneous aggregation and fragmentation by fluid shear are encountered in processes involving flocculation (Lu and Spielman 1985).

4.1.2 Verification of the measurement stability of the Set-up B

In order to verify whether the reliable measurements are made in the new set-up, this section represents the results obtained from the repeated measurements using both Set-up A and B under the same experimental condition and these will be compared.

The newly arranged set-up (Set-up B) shown in Fig. 3.6 has been developed for the current study, and in order to verify whether the new set-up (Set-up B) is able to produce the reliable measurements, series of test under the exactly same experimental condition have been performed in both set-ups. Note that the monitoring devices contained in the Set-up A were employed in the previous study as mentioned in Section 3.2 and hence the comparison of two results obtained from both set-ups should be sufficient for evaluation of the new set-up (Set-up B). Latex suspension of 100 mg/L concentration and 100 ml volume is placed in the 200 ml-square shaped plastic vessel used in the Set-up B. The selected Percol series were added into the latex suspension stirred at 60 rpm by a paddle of the Set-up B. After latex flocculations were monitored using Set-up B, the exact same flocculation tests were repeated to be monitored by the measuring instruments used in Set-up A such as laser light source, optical fibre and detector attached to the conventional PDA as shown in Fig. 3.4. The results shown in Figs. 4.2(a) and (b) were acquired using Set-up A while the results obtained under the same condition but using Set-up B are represented later in Fig. 4.27 (see page 105) in Section 4.3.1.

Considering the differences in flocculation rate, particle number concentration reduction and floc density (d_F) between both set-ups, it is verified that the results obtained from the same test using both Set-ups A and B can be considered to be equivalent.

TABLE 4.1. Calculated d_F and reductions in *RPNC* and *T* for 600 seconds during latex flocculation by Percol series; flocculation was performed by 100 μ g/L Percol 63, 180 μ g/L Percol 326 and 300 μ g/L Percol 1697 in the Set-up A

Stirring rate (conc.)	Calculated d_F		Particle number reduction	T reduction
Percol 63 (100 μg/L)	2.462 (90-400 sec)	about 3 (-600 sec)	11250-fold	92%
Percol 326 (180 μg/L)	2.471 (90-400 sec)	about 3 (-600 sec)	795-fold	72%
Percol 1697 (300 μg/L)	2.432 (90-400 sec)	about 3 (-600 sec)	62-fold	54%



FIG. 4.2. Latex flocculation by Percol series; 100 mg/L latex suspension flocculated by 100 μ g/L Percol 63, 180 μ g/L Percol 326 and 300 μ g/L Percol 1697 in the Set-up A

4.2 Effect of concentrations of single salt and polymers on flocculation of various suspension

4.2.1 Effect of single salts on various suspensions

It is known that the specific nature of the added salts can also affect the stability of colloids, apart from the valency of the counter ions (Overbeek 1952). In the Gouy-Chapman treatment of the diffuse double layer, ions are regarded as point charges. The Stern theory takes the finite size of the ions into account and hence specific effects can be explained.

The Stern layer is not dependent on electrolyte concentration except in the case that the permittivity of the Stern layer is affected. The adsorption of counter-ions brings down the potential across the Stern plane. When the counter-ions are strongly adsorbed, a sharp reduction in potential will be obtained across the Stern layer which leads to a lower stability. The adsorption of counter-ions will be more prominent, the higher the charge number of the ion. In fact, it is always shown that the critical coagulation concentration (c.c.c.) of an electrolyte is strongly dependent upon the charge number of its counter-ions. The electrostatic attraction between the charged particles and the oppositely charged ions is usually stronger with ions of higher charge number. For a series of ions, the greater polarisability of the larger ion will usually increase their adsorbability and hence it leads to a lower stability. The following sections discuss the influence of the valency of ions and the electrolyte concentration on coagulation using three chosen particles (latex, silica and kaolin). During the main tests in this and Section 4.2.2,

- (i) the stock suspension of high concentration is mixed with deionised water in a stirred jar to give the required concentration and high shear speed (240 rpm) is applied for 20 seconds,
- (ii) then the suspension begins to circulate at 30 seconds by peristaltic pump.
- (iii) Dissolved salts were added to the stirred suspension at 20 seconds and in some cases, this caused aggregation before the actual monitoring.
- (iv) Polymers were inserted at 90 seconds. Refer to Fig. 4.3 for graphical illustration of test procedure.



(a) Experimental procedure



FIG. 4.3. Schematic diagram of an experimental result in Sections 4.2-4.3

• Influence of the valency of the ions on aggregation

The tests has been performed using the Set-up B with latex suspension of 100 mg/L concentration. Sodium nitrate and calcium nitrate were chosen to examine the influence of the ions used to aggregate latex particles and each dissolved salt has been applied separately. These indifferent electrolytes are not used in practice as flocculating agents since they do not generally allow the formation of strong aggregates, which can withstand the shear forces encountered in most practical flocculation units. However, they can still reduce the electrical repulsion between the particles at high concentration as well as their presence in water can modify the behaviour of other additives (see Section 4.5 for experimental results).

Fig. 4.4 presents typical forms of ratio increase by the selected electrolytes. These curves exhibit an immediate increase in ratio, indicating the instantaneous formation of aggregates as soon as the monitoring begins. The immediate ratio increase occurs since the added salt results in an increased ionic strength and a decreased colloidal stability (refer to Section 2.2.2.2).

This figure also demonstrates that the presence of the cation, Ca^{2+} , of low concentration (50 mMol), results in an almost same amount of increase in ratio, compared to the case of NaNO₃ of much higher concentration (1 M) although more efficient aggregation in terms of ratio increase in the early stage is observed in calcium nitrate case. The reduction in turbidity (T) and the particle number concentration (*RPNC*) during 600 seconds test time are also observed (see the following section for more detailed information).

Note that the represented salt concentrations, 50 mMol for $Ca(NO_3)_2$ and 1 Mol for NaNO₃, were selected among several salt doses since these resulted in the highest maximum value of ratio for given test time of 600 seconds, where the peak ratio implies the highest degree of aggregation (refer to equation (2.56)). According to the definition of the optimum aggregation described in Section 4.1, these can be called the optimum concentrations. With concentrations over this value, the ratio value monitored at 600 seconds will not be higher than these values. (see Figs. 4.8-4.11 for more evidence)

When only the dissolved salt is used as an aggregating agent, the optimum con-



FIG. 4.4. Aggregation of latex particles by sodium nitrate and calcium nitrate

centration of dissolved salts may be equal to the critical coagulation concentration (c.c.c.) described in Section 2.2.2.2. In definition, the potential energy barrier just disappears and aggregation should then occur at a transport-limited rate, determined by the collision frequency at a critical concentration. In other words, collision efficiency increases with electrolyte concentration but it remains constant when the concentration reaches a certain value (c.c.c.).

The dependence of the c.c.c. on the charge number of counter ions in this case deviates from $1/z^6$ dependence ("Schülze-Hardy rule"). The observed ratio is about 20×, rather than 64×. However, the $1/z^6$ dependence is not theoretically expected at small zeta potential ($ze\zeta/4kT < 1$) so the discrepancy is of little significance.

• Optimum concentration of dissolved salts for aggregation

The stock solutions of sodium nitrate and calcium nitrate which were prepared in 1 Mol solution, were added to stirred deionised water to form salt solutions of various concentrations from 0.4 to 1.4 M (NaNO₃) and 10 to 70 mMol (Ca(NO₃)₂) for latex, from 40 to 100 mMol (Ca(NO₃)₂) for silica and from 0.5 to 30 mMol (Ca(NO₃)₂) for kaolin aggregation. The stirring rate was kept constant at 60 rpm for latex, silica and kaolin suspensions respectively.

As explained in the previous section (refer to Fig. 4.4), it was found that adding salts to suspension lead to an instant ratio increase. It should be noted that the stock solution of calcium nitrate has been added at about 20 seconds, and the aggregated sample was released from a vessel to the monitoring cell at 30 seconds. This procedure encouraged aggregation 10 seconds before the actual monitoring of the sample. This resulted in higher ratio values measured at 30-40 seconds for 30, 50 and 70 mMol than for the other concentrations in Fig. 4.9 though this behaviour is not clearly observed in Figs. 4.8, 4.10 and 4.11 in this section.

Figs. 4.5(a), (b), and (c) are presented to display the examples of changes in T during aggregation. It is generally observed that the turbidity of suspension usually decreases as aggregates begin to form, reflecting the reduced sum of individual scattering cross-sections. Figs. 4.5(a) and (b) also demonstrate that the turbidity (T) of aggregated latex and silica suspensions decrease as aggregation occurs. The salt concentration which leads to the high ratio increase also leads to high turbidity reduction and this trend applies vice versa for the salt concentration with the low ratio increase. The latex aggregation by 50 mMol Ca²⁺ concentration results in the highest decrease in turbidity, and the highest peak ratio is shown with this concentration, while the calcium concentration of 80 mMol leads to the largest ratio increase and T reduction for silica aggregation as shown in Figs. 4.5(b) and 4.10(c).

However, the turbidity results acquired by kaolin aggregation in Figs. 4.5(c) and 4.11(c) represent that turbidity (T) increases initially with increasing ratios although overall reduction in T is observed. An immediate increase in turbidity observed in Fig. 4.5(c) is possibly attributed to (1) a high degree of aggregation by a high particle concentration or (2) a highly variable nature of scattering coefficient in the size range of a doublet or a triplet containing primary kaolin particles of up to 1.5 μ m diameter. According to equation (2.42), the dimensionless aggregate size of a doublet should be about 8, which corresponds to the maximum scattering coefficient. Fig. 2.14 (see page 42) has shown that the scattering coefficient is approximately 3 when the dimensionless size is 8, and will increase or decrease extensively by small changes in the dimensionless size. Eventually, the sensitive nature of scattering coefficient causes a larger scattering cross-section area to be induced for a doublet or a triplet than expected from its actual size. However, noting that the scattering coefficient converges to 2 as aggregates grow larger, this complication in the kaolin case applies only in



the early stage and disappears in the later stage. Actually, the decease in T is observed from 180 seconds.

FIG. 4.5. Examples of change in T and RPNC during aggregation of latex, silica and kaolin particles by calcium nitrate

Figs. 4.5 derived from equation (2.57) also show the changes in the relative particle number concentration (*RPNC*). The shape of the curves appears almost opposite to the ratio curves. The *RPNC* reduction measured at 600 seconds are shown in Figs. 4.9(b), 4.10(b) and 4.11(b) for the corresponding concentrations. When deriving equation (2.57) for aggregation number, \overline{k} and equation (2.58) for fractal dimension, d_F , it was told in Section 2.6.3.2 that the scattering coefficient Q is cancelled out as equation (2.53) is deployed to equation (2.57) while Qremains in equation (2.58) as transformed from equation (2.54) and, hence, some uncertainty in the derived fractal dimension can be arisen in the early stage where primary particle/small flocs exist and the scattering coefficient is very inconsistent as shown in Fig. 2.13. However, the scattering coefficient diverges to

Suspension	$Ca(NO_3)_2$ conc.		Calculated d_F	
Latex	10 mMol	2.317 (80-600 sec)		
(100 mg/L)	20 mMol	2.480 (80-600 sec)		
	30 mMol	2.509 (80-400 sec)	2.682 (-600 sec)	
	50 mMol	2.469 (80-400 sec)	about 3 (-600 sec)	
	70 mMol	2.479 (80-400 sec)	about 3 (-600 sec)	
Silica	40 mMol	2.349 (80-480 sec)	$2.810 \ (-600 \ sec)$	
(150 mg/L)	60 mMol	2.206 (80-200 sec)	$2.501 \ (-400 \ sec)$	2.515 (-600 sec)
	80 mMol	2.326 (80-400 sec)	2.865 (-600 sec)	
	100 mMol	2.215 (80-200 sec)	2.385 (-400 sec)	about 3 (-600 sec)
Kaolin	0.5 mMol	1.622 (80-400 sec)	2.056 (-600 sec)	
(200 mg/L)	1 mMol	1.609 (80-200 sec)	1.928 (-600 sec)	
	5 mMol	1.686 (80-140 sec)	-(-600 sec)	
	10 mMol	1.723 (80-140 sec)	-(-600 sec)	
	30 mMol	1.567 (80 - 130 sec)	-(-600 sec)	
	50 mMol	1.841 (80-80 sec)	-(-600 sec)	

TABLE 4.2. Calculated d_F for latex, kaolin and silica coagulation

2 as flocs grow and the comparison of the differences between fractal dimensions can provide valuable information on their structures.

Relatively low fractal dimensions listed in Table 4.2 indicates the low density of kaolin flocs and the loose structure of the kaolin aggregates is responsible for the very high turbidity while relatively high fractal dimensions are observed in the cases of latex and silica aggregations (refer to Figs. 4.6 for the relationship between floc density and turbidity). Some of the calculated fractal dimensions in the later stage are omitted in the table or indicated as "about 3" since very high standard deviation has been caused by largely formed flocs passing through the monitoring cell (see Fig. 4.11(b) for variation in the log R/T-log T curve in the later stage and Fig. 4.7(b) for largely formed kaolin flocs). Raper and Amal (1993) also obtained d_F (also defined as scattering exponent) over 3 as a result of objects containing pores which are bounded by surfaces with a fractal structure. Flocs produced by latex and silica particles have fractal dimensions of 2.3-2.5

and 2.2-2.35 in the early stage respectively, which indicate dense structure, while for kaolin flocs, the fractal dimensions are lower (less than 1.85), and hence a loose structure is envisaged. In microscopic observation, there are many large loose flocs as well as small compact flocs produced by kaolin aggregation (see Figs. 4.7



(b) Loose flocs

FIG. 4.6. Schematic figures of flocs consisting of 20 particles but with different density

for photos of flocs). The presence of loose, larger flocs result in a heavy blockage of transmitted light than the dense flocs of smaller size, and as a result, lower dc values (high turbidity) are monitored as illustrated in Fig. 4.6. According to Table 4.2, the flocs generated in the early stage become more compact as aggregation continues. Although the high fractal dimensions are achieved with high salt concentrations, there is no significant dependence of floc density on the concentration of dissolved salt (or the ratio, degree of aggregation).

Amal et al. (1990), Lin et al. (1990) and Logan and Wilkinson (1990) have reported the typical fractal dimension values in the range 1.7–2.5 (or higher if re-structuring occurs). Among the obtained values, fractal dimensions of 1.7–1.8 are widely reported for the floc formed under diffusion limited aggregation (DLA) conditions while fractal dimensions in the range 2.2–2.3 are typical for reaction limited aggregation (RLA) (Waite 1999). When considering particlecluster/cluster-cluster aggregation rather than DLA/RLA, it is reported that cluster-cluster mechanism becomes dominant in the sheared condition (Potanin



(c) Kaolin flocs using 30 mMol $Ca(NO_3)_2$

FIG. 4.7. Flocs taken after 600 second aggregation by calcium nitrate

1990) and significant cluster-cluster aggregation leads to the markedly decreased fractal dimension (Amal et al. 1990) (refer to Fig. 2.10 on page 30). However, the re-collision between small flocs/particles and large flocs following surface erosion is encouraged in the later stage and aggregation in a similar manner to the particle-cluster collision is expected to occur and it is thought that this promotes the increase in d_F .

Note that two separate aggregations formed under a same shear condition could generate very different floc densities, which implies that there may be more factors other than the aggregation mechanism that have an influence on the floc structure. More detail on this matter will be discussed later with the listed fractal dimensions.



(b) Reductions in T and RPNC

FIG. 4.8. Effect of NaNO3 concentration on latex flocculation; 100 mg/L latex suspension aggregated at 60 rpm in the Set-up B $\,$



(b) Reductions in T and RPNC

FIG. 4.9. Effect of $Ca(NO_3)_2$ concentration on latex flocculation; 100 mg/L latex suspension aggregated at 60 rpm in the Set-up B



(b) Reductions in T and RPNC

FIG. 4.10. Effect of $Ca(NO_3)_2$ concentration on silica flocculation; 150 mg/L silica suspension aggregated at 60 rpm in the Set-up B



(c) Reductions in T and RPNC

FIG. 4.11. Effect of $Ca(NO_3)_2$ concentration on kaolin flocculation; 200 mg/L kaolin suspension aggregated at 60 rpm in the Set-up B

4.2.2 Effect of polymer concentration on flocculation of various suspensions

Organic polyelectrolytes have been widely applied to sludge thickening and flocculation processes (Bolto et al. 1996). The adsorption of polyelectrolytes at the particle/liquid interface has a profound effect on the flocculation and the destabilisation behaviour of colloidal suspensions. These polymers may be used as the primary flocculant instead of metal salts, and also in a more traditional flocculation step where the polymer binds already-formed-small-flocs into larger ones. The polymer can also act as a destablising agent via a charge neutralisation/precipitation mechanism (coagulation), as well as an agent for floc growth. Cationic polyelectrolytes have a distinct advantage over the commonly used metal salts; they generate charge neutralisation without the formation of additional solids in the form of a metal hydroxide precipitate.

During a flocculation process, the flocculation rate depends on the ionic strength of the solution. Surfaces of the particles used in this work are negatively charged and stable in deionised water. Hence, in the following tests using latex and kaolin particles, the addition of sodium nitrate to make a 5 mMol solution was aimed to give the decreased stability in suspension. This concentration is insufficient to generate aggregation and only the added polymer will play a role in flocculation.

The collision efficiency in given shear conditions (60 rpm) is still very much less than unity, although it is assumed that the repulsion between particles is reduced by a adding small amount of sodium nitrate. Therefore, adding polymeric flocculant will result mainly in the destabilisation of suspension and the increased collision efficiency.

The concentrations of suspensions were set to 100 mg/L, 150 mg/L and 200 mg/Lat 60 rpm for latex, silica and kaolin particles respectively. Percol 63 of 0.1% (w/w), which has high molecular weight and charge density of 30%, is used as polymeric flocculant. A previous investigation (Gregory and Chung 1995) suggests that charge neutralisation plays an important role when this high molecular weight polymer is employed. It was notified in Section 2.4.3 that polymer adsorption can continue beyond the point of neutrality and hence charge reversal which results in restabilisation can arise. Therefore, the maximum ratio increase achieved at 600 seconds is expected to decrease with the concentration higher than the optimum (see Section 4.1 for the definition of the optimum concentration). Since polymers became widely used in the practical processes, many researchers have carried out their works to find the best flocculation conditions, by assessing polymer performance in terms of maximum rates of subsidence, minimum residual turbidity, the isoelectric point, complete adsorption of polymer, or maximum rates of dewatering in settled beds of flocs (Eriksson et al. 1993; Somasundaran and Yu 1994; Chen 1998). Despite these attempts, the use of different experimental methods to monitor flocculation resulted in discrepancies between various flocculation studies. In this study, the character of the flocculation processes will be determined mainly on the basis of the change of flocculation rate (ratio) which consists of aggregation number, $\overline{\kappa}$ and d_F as described in equation 2.56.

4.2.2.1 Curve fitting using Sigmoid function

The curve fitting of ratio using sigmoid function was used by Gregory and Hiller (1995) to characterise the flocculation is employed in this work and it is found that the changes in ratio with time in certain conditions are well expressed with the parameters. Since the ratio value is not related in a simple manner to the floc size distribution, and the kinetics of floc growth/break-up in a stirred vessel are not fully understood, it is not possible in this stage to provide a fundamental analysis of curves. However, parameters obtained from a simple curve give good comparisons between flocculations under same condition and, where possible, will be listed in tables in this chapter (refer to Fig. 4.12). The equation employed for this fitting is :

$$ratio = a + \frac{b}{1 + \exp(\frac{-(t-c)}{d})}$$
(4.1)

where a, b, c and d are the fitting parameters. The parameter a is simply the initial value of ratio and is always low since it reflects no flocculation. The value b reflects the plateau level, achieved after a sufficient period of flocculation. The parameter c is the time required to reach the inflection point of the curve having a maximum slope, and d is related to the slope at this point and is inversely proportional to the slope. Since these parameters of fitted sigmoid curves yield some useful characteristics of each flocculation result, it may be worth tabulating parameters in a single table, if all the parameters are acquired under the same experimental conditions. As shown in Fig. 4.12, the parameters b, c and d are important in determining the effectiveness of a flocculation process. The ultimate floc size should be related to b (the greater this

value the larger the flocs). The time taken to achieve the maximum rate of increase, c, is a function of the stirring rate and depends on the nature of the flocculant and particle number concentration. The process using sigmoid function is usually well fitted with polymeric flocculation where there appears to be a lag time, corresponding to the time interval for adsorption before the onset of flocculation, in contrast to the case of dissolved salt in which sudden increase in ratio occurs as soon as the monitoring begins.



FIG. 4.12. General figure of sigmoid curve

4.2.2.2 Determination of optimum concentration of Percol 63: latex flocculation

Preliminary tests have been carried out to identify the Percol 63 concentration, and from a large range of concentration levels, the work has selected concentrations in the range of $30-230 \ \mu g/L$

It is well known that increasing the coagulant/flocculant concentration increases the floc growth rate and the steady state floc size (Spicer and Pratsinis 1996b) while the excess concentration leads to a decreasing flocculation rate and, as a result, reduced steady state size. In the results obtained from this test, the polymer concentrations of $50-170 \ \mu g/L$ could be grouped as the highly effective concentration range since greater ratio increases are found with these concentrations as shown in Figs. 4.16(a) and (b). These curves show pronounced fluctuations in the later stage. These fluctuations may arise since the large area of the transmitted beam during monitoring is blocked at random times by very large flocs with similar dimensions to the light beam. The large RPNC reduction in Fig. 4.14 and the photos shown in Figs. 4.13(a) and (b) indicate that latex flocs are formed to be larger with the Percol 63 concentration of 100 μ g/L, blocking larger beam area than the flocs with lower concentration (50 μ g/L).



(a) Latex flocs by 50 $\mu {\rm g}/{\rm L}$ of Percol 63

(b) Latex flocs by 100 $\mu {\rm g}/{\rm L}$ of Percol 63

FIG. 4.13. Latex flocs taken after 600 second aggregation by Percol 63

These photos also represent the very large flocs surrounded by primary particles and small flocs even though this kind of magnified photos only provides the view of small area. Actually, the separately performed microscopic observation has rarely found very large flocs; instead, a lot of small flocs has been observed from the sample taken at 600 seconds at high polymer concentration levels. There are two possibilities causing this unbalanced floc size distribution. One is steric stabilisation. Adachi and Kamiko (1994) have observed, using solution of polyethylene oxide and a dispersion of polystyrene latices, that flocculation stopped abruptly due to the establishment of steric stabilisation, following the rapid incipient stage. They suggested that the transport of polymer towards the colloidal surface was the controlling factor. Another possibility is non-uniform mixing of polymer. Hogg (1999) reported that the adsorption times are of similar magnitude to mixing times in agitated systems. Consequently, local overdosing in the vicinity of a polymer addition point can lead to wide variations in the extent of adsorption on different particles. Because of the effective irreversibility of the adsorption process, such variations may persist, despite continued mixing. The existence of large drops of polymer solution which is caused by an initial unsuccessful mixing might lead to producing irregular structures. Hogg (1999) suggested that metered, continuous addition of polymer from a dilute solution can be used to provide some control over the distribution of polymer.



FIG. 4.14. Effect of polymer concentration on latex aggregation; 100 mg/L latex suspension flocculated at 60 rpm in the Set-up B

One more thing to notice in Fig. 4.16(b) is that the faster process occurs in the early stage with higher polymer concentration. Among the highly effective concentrations $(50-170 \ \mu g/L)$, the higher concentrations between 110 and 170 $\ \mu g/L$ exhibit a shorter lag time than the lower concentrations in the range of 50–90 $\ \mu g/L$, even though the similar level of flocculation degrees are achieved at the end of tests. This behaviour may be encouraged by the higher rate of adsorption with higher polymer dosage as suggested by Gregory (1988) (see Section 2.4.2.3). However, the adsorption of polymer on particle surface and the collisions between particles are known to occur simultaneously. The results shown in Fig. 4.16(b) do not clearly exhibit the difference of adsorption time between the concentrations of 50–90 and 110–170 $\ \mu g/L$.

The calculation of fractal dimensions in Table 4.3 demonstrates that Percol 63, having a high molecular weight, produces very compact floc structure (The comparison between polymers with different molecular weight and charge density will follow in Section 4.3). No significant dependence of d_F on polymer concentration or ratio is observed in Figs. 4.16(a) and (b) and Table 4.3, since all the derived d_F values are almost equally high regardless of the polymer concentration or the degree of floccula-

Percol 63 conc.	Calculated d_F		a	b	с	d
$30 \ \mu g/L$	2.688 (90-600 sec)		0.12	0.23	619	171
$50 \ \mu g/L$	2.646 (90-400 sec)	about 3 (-600 sec)	0.15	0.51	277	28
$70 \ \mu { m g/L}$	2.595 (90-350 sec)	about 3 (-600 sec)	0.13	0.47	287	35
$90 \ \mu g/L$	2.580 (90-350 sec)	about 3 (-600 sec)	0.14	0.52	329	46
110 $\mu g/L$	2.626 (90-300 sec)	about 3 (-600 sec)	0.15	0.53	239	33
140 $\mu g/L$	2.550 (90-250 sec)	about 3 (-600 sec)	0.16	0.46	224	24
$170 \ \mu g/L$	2.579 (90-300 sec)	about 3 (-600 sec)	0.16	0.40	208	22
$190 \ \mu g/L$	2.535 (90-400 sec)	about 3 (-600 sec)	0.12	0.39	271	60
$210 \ \mu g/L$	2.531 (90-400 sec)	about 3 (-600 sec)	0.12	0.27	248	48
$230 \ \mu { m g/L}$	2.517 (90-300 sec)	about 3 (-600 sec)	0.10	0.15	206	45

TABLE 4.3. Calculated d_F and sigmoid parameters for latex flocculation by Percol 63

tion (ratio) although the ignorable difference is observed between fractal dimensions corresponding to higher ratio (higher d_F) and lower ratio (lower d_F). The fractal dimensions obtained in the early stage are in the range of 2.5–2.7 and the gap between these values is not considered to be significant, either. These very dense flocs formed initially become even more compact as time goes. The high values of fractal dimension at optimum polymer concentrations show good agreement with the fact that the turbidity decreases to values close to zero, i.e. close to that for water.



FIG. 4.15. Sigmoid parameter, b, obtained after latex flocculation with various Percol 63 concentration

For low polymer concentration of 30 μ g/L, there are mainly small flocs due to a lack of polymer, and these small objects may be responsible for the high fractal dimension. In contrast, the very high polymer concentrations (190–230 μ g/L) corresponds to slightly lower fractal dimensions in the early stage although the values still represent very compact floc structure. However, a detailed discussion on this aspect is of little significance in the comparison of floc properties since there is uncertainty arising from the assumption of constant scattering coefficient which limits the reliability of fractal dimensions to around 0.1 as discussed in Section 2.6.3.2.

Besides the fractal dimension, Table 4.3 also represents four parametric values of the fitted sigmoid curve. Parameter b, is used as an indicator of ratio increase from start to maximum, and c and d, are related to the flocculation rate. As shown in the table, parameters of the highly effective concentration group $(50-170 \ \mu g/L)$ have high values of b and low values of c and d. The numbers in blocked letter indicate higher ratio (b), more rapid process (c), and steeper slope (d) than the others. The changes in b demonstrated in Fig. 4.15 shows very similar pattern as reductions in T and RPNCin Fig. 4.14 but the trend is not observed for other parameters, b and c.

There exists deviations in the parameters from the expected values as considering Figs. 4.16(a) and (b) and the deviations may arise due to errors introduced during the computation of sigmoid fitting while analysing the fluctuation-dominated later part of the experimental data curve. From the obtained results, it is difficult to select one optimum flocculation but it can be said that the concentration is between 90 and 110 μ g/L and one can clearly see an overall trend in the obtained sigmoid parameters with respect to the Percol 63 concentrations.



(b) Ratio at 50–170 $\mu {\rm g}/{\rm L}$

FIG. 4.16. Effect of polymer concentration on latex aggregation; 100 mg/L latex suspension flocculated at 60 rpm in the Set-up B $\,$

4.2.2.3 Determination of optimum concentration of Percol 63: silica flocculation

Silica suspension of 150 mg/L concentration was flocculated by Percol 63 of various amounts. Silica flocculation shows the same characteristics as other polymeric flocculation; (1) there is a lag time between polymer dose and ratio increase and (2) final ratio increases are observed to be much higher than in the case of simple salt when comparing to the result in Section 4.2.1.

The represented polymer concentrations were selected from a large range of tests and the concentrations below 50 and above 250 μ g/L barely lead to aggregation detectable by current monitoring device. The concentration of 130 μ g/L is the optimum in terms of maximum ratio increase and it leads to the largest reductions in T and *RPNC* as shown in Figs. 4.19(a) and (c).

Sigmoid parameter b in Table 4.4 and Fig. 4.17 also show similar pattern as in Fig 4.19(b) although no relationship is found for other parameters such as (1) c and (2) d which are (1) time taken to reach the inflection point of the curve having a maximum slope and (2) inversely proportional to the slope of the curve (see equation (4.1)). In fact, similar to the latex case in the previous section, the most rapid process (highest c and d) has been established with the concentration higher than the optimum concentration.



FIG. 4.17. Sigmoid parameter, b, obtained after silica flocculation with various Percol 63 concentration

Table 4.4 demonstrates the calculated fractal dimensions and it is found that very
Percol 63 conc.		Calculated d_F		
100 μg/L 130 μg/L 150 μg/L 170 μg/L	2.349 (90-480 sec) 2.206 (90-200 sec) 2.326 (90-400 sec) 2.215 (90-200 sec)	2.810 (-600 sec) 2.501 (-400 sec) 2.865 (-600 sec) 2.385 (-400 sec)	2.815 (-600 sec) 2.860 (-600 sec)	
Percol 63 conc.	a	b	с	d
100 μg/L 130 μg/L 150 μg/L 170 μg/L	0.09 0.13 0.16 0.12	1.10 1.32 1.11 0.95	237 198 143 169	68 48 67 41

TABLE 4.4. Calculated d_F and sigmoid parameters for silica flocculation by Percol 63; numbers in blocked letter indicate high ratio, rapid process

compact floc structures are produced by Percol 63 (see Fig. 4.18 for photo evidence). As observed in the previous section, no significant dependence of d_F on polymer concentration or ratio is observed in Figs. 4.19(a) and (b) and Table 4.4, since all the derived d_F values are almost equally high regardless of the polymer concentration or the degree of flocculation (ratio).



FIG. 4.18. Silica flocs taken after 600 second aggregation by Percol 63

The applied shear rate gives mainly aggregation rather than break-up in the early stage where small flocs of high strength become larger (refer to Section 2.5.2.1). As small flocs are getting larger, it is expected that the floc structure becomes loose as mentioned in Section 2.5.2 but the constantly applied shear promotes more floc break-up since larger flocs do not have enough strength to endure the shear. As a result, floc break-up becomes dominant to aggregation and the fractal dimensions listed in

Table 4.4 become larger as time goes due to the continuous aggregation and break-up.

As shown in Fig. 4.19(a) and (c), the optimum concentration, 130 μ g/L results in the largest reductions in T and RPNC. Among the other concentrations, the ratio values are slightly lower with the concentration of 170 μ g/L than the other concentrations (100 and 150 μ g/L) but very similar reductions are observed for all these concentrations (85 % turbidity and 1000-fold RPNC reductions). Note that the reduction ratio in T observed in silica flocculation is enormous and this agrees with the derived fractal dimensions indicating very compact structure.



(b) Reductions in T and RPNC

FIG. 4.19. Effect of polymer concentration on silica aggregation; 150 mg/L silica suspension flocculated at 60 rpm in the Set-up B

4.2.2.4 Determination of optimum concentration of Percol 63: kaolin flocculation

The aggregation of kaolin suspension of 200 mg/L concentration has been performed using Percol 63 of the concentrations from 50 to 300 μ g/L. Increases in ratio during kaolin flocculation represented in this section occur more suddenly in the early stage and stop sooner than in the latex and silica flocculation shown in the previous sections. The obtained sigmoid parameters contain very high standard deviations due to the nature of the steeper and variable part of the logarithmic plot in Figs. 4.20 and as a result, these are not listed in the case of kaolin flocculation. Lag times after the polymer doses at 90 seconds are more reduced as shown in Figs. 4.22(a) than the previous cases and this behaviour was well expected by the influence of high particle number concentration (refer to equation (2.28)).



(a) A large floc



(b) Small flocs

FIG. 4.20. Schematic diagram of ratio change

It is found that the low polymer concentrations result in a gradual and small increase in the ratio, as shown in Fig. 4.22(a). Increasing the polymer dose results in the increase in the peak ratio values until the polymer concentrations are increased up to $200-250 \ \mu g/L$.

Percol 63 conc.		Calculated d_F	
50 μg/L 100 μg/L 150 μg/L 200 μg/L 250 μg/L 300 μg/L	1.684 (90-400 sec) 1.778 (90-400 sec) 1.701 (90-160 sec) 1.787 (90-160 sec) 1.752 (90-130 sec) 1.746 (90-140 sec)	$2.186 (-600 \text{ sec}) \\ - (-600 \text{ sec}) \\ 2.125 (-200 \text{ sec}) \\ 2.057 (-180 \text{ sec}) \\ 2.820 (-170 \text{ sec}) \\ - (-600 sec$	- (-600 sec) - (-600 sec) - (-600 sec)

TABLE 4.5. Calculated d_F for kaolin flocculation by Percol 63

As investigated in kaolin aggregation by calcium nitrate, turbidity increases as flocculation occurs, i.e. the suspension becomes more turbid for a while as flocs grow to a larger size. This implies generating flocs of a loose structure (low d_F) as well as a larger floc size. However, as the flocculation continues further, a significant scatter in the experimental data can be observed, and deciding whether turbidity increases or decreases is somewhat hampered in the later stage. During the flocculation tests, flocs which are large enough to be detected by eye are usually formed within 200 seconds and these large flocs may cause the large fluctuations, as displayed in Figs. 4.21(b) and 4.22(a). The scatters observed in the data in the later stage become greater with higher polymer concentration. This indicates that very large flocs are formed with higher concentration regardless of the average flocculation rate.

The calculated fractal dimensions of kaolin flocs are listed in Table 4.5. The flocs produced in the early stage have very low density since d_F is 1.65–1.79. According to Fig. 4.22(b) showing log R/T-log T plots, fractal dimension in the later stage by some high polymer concentrations (150–300 μ g/L) should be close to 3, indicating that flocs become very compact but the the d_F in the later stage is not listed in the table due to inaccuracies by the large fluctuations observed in the figure. The behaviour of these sharp variations is illustrated in Fig. 4.20. The photo evidence exhibits that there are very large loose flocs as well as small compact flocs together in the later stage (see Figs. 4.21(a) and (b)).

The decrease in the RPNC in 600 seconds in Fig. 4.22(c) represents the floc struc-



FIG. 4.21. Kaolin flocs taken after 600 second aggregation by Percol 63

ture containing approximately 330 particles. This decrease in the RPNC is relatively low, compared to the latex flocculation result in Fig. 4.22(c). However, kaolin flocs formed in the later stage are very large enough to be recognised by eye while latex and silica particles are not formed to be that large in the current experimental condition. Significantly larger size of kaolin flocs in spite of lower RPNC reduction can be justified by the derived fractal dimension much lower than those of latex and silica flocs.

Considering the immediate ratio increase in kaolin flocculation, small aggregation number (k) and highly variable data could mean that the unflocculated initial particles and the flocs containing a small number of particles still remain in the later stage of flocculation. This is supported by microscopic observation shown in the photo in Figs. 4.21(a) and (b).



(c) Reductions in T and RPNC

FIG. 4.22. Effect of polymer concentration on kaolin aggregation; 200 mg/L kaolin suspension flocculated at 120 rpm in the Set-up B

4.2.3 Comparison of aggregation by dissolved salt/polymer

The destabilisation of particles in suspension arises in part by charge neutralisation due to adsorbed polymer, or by reduction of electrical repulsion due to the salt effect. While added salts give an instantaneous increase in ionic strength to reduce the electrical repulsion, the adsorption of polymer involves physical reaction which needs some time to complete.



FIG. 4.23. Comparison of latex aggregation by polymer and dissolved salt; 100 mg/L latex suspension aggregated by 50 mMol Ca(NO₃)₂/70 μ g/L Percol 63 at 60 rpm in the Set-up B

The results described in this section were selected from the previous sections to compare the characteristics of aggregation by the dissolved salt and polymer. Comparisons between latex aggregations by polymer and dissolved salt, between kaolin aggregations by polymer and dissolved salt and between silica aggregations by polymer and dissolved salt are demonstrated in Figs 4.23, 4.24 and 4.25, respectively.

A clear difference between aggregation by the dissolved salt and the polymer is that



FIG. 4.24. Comparison of silica aggregation by polymer and dissolved salt; 150 mg/L silica suspension aggregated by 40 mMol Ca(NO₃)₂/100 μ g/L Percol 63 at 60 rpm in the Set-up B

the initial lag time of about 5-30 seconds exists before the onset of aggregation for the case of polymeric aggregation, whereas there is no evidence of such delay in dissolved salt aggregation. However, the observed lag times (or adsorption time) in the figures are relatively short, and thus it is difficult to determine the actual adsorption time exactly. In fact, Kislenko and Verlinskaya (1999) have suggested that the flocculation process may begin before the completion of polymer adsorption, and reported that the processes of polymer adsorption on particle surface and the flocculation of the particles proceed simultaneously for some time. Therefore, the actual adsorption time should be considered to be longer than the lag times shown in the figures.

There is an initially linear region of the curves in Figs. 4.23(a), 4.25(a) and 4.24(a), and the departure from linearity may indicate the point where floc break-up becomes significant (Gregory and Kim 1999). Comparing the maximum slopes of the ratio, the



FIG. 4.25. Comparison of kaolin aggregation by polymer and dissolved salt; 200 mg/L kaolin suspension aggregated by 3 mMol Ca(NO₃)₂/120 μ g/L Percol 63 at 120 rpm in the Set-up B

rate of flocculation by the polymer (Percol 63) is higher than that by calcium nitrate in both the latex and kaolin cases. For the case of Percol 63, the ratio increase stopped within 360 seconds for latex, and 300 seconds for silica and kaolin flocculation, and greater scatter in the ratio data appeared after these intervals. The ratio of calcium nitrate increased rather slowly but still continued to rise even after 550 seconds.

The particle number concentration of suspensions with polymer keeps decreasing by up to the order of 4 decades in Figs. 4.23(c), 4.25(c) and 4.24(c), during the steady state in terms of ratio. As expected by the difference of the flocculation degree (ratio), huge differences between in the reductions of *RPNC* generated by dissolved salt and polymer are also observed. The reductions in particle number concentration by polymer are approximately 10000-fold (latex), 20000-fold (silica) and 300-fold (kaolin) whereas, in the case of calcium nitrate, *RPNC* was reduced 15-fold (latex), 50-fold (silica) and 10-fold (kaolin). The initial adsorption time and the variations in the later stage, which are usually observed in ratio results, also appear in these figures.

In Section 2.6.3.2, it has been mentioned that the plot of $\log R/T$ against $\log T$ in certain time intervals should yields a straight line and the mass fractal dimension of aggregates can be obtained by the slope of the line. The gradient of the lines are similar in values between the polymer and dissolved salt case, indicating that flocs have the similar densities regardless of the added aggregating agents. The flocs become denser through the continuous break-up and re-flocculation due to the floc strength oppositely proportional to the maximum size enduring the applied shear. It is observed that flocs generated in the later stage by Percol 63 have higher fractal dimensions according to the gradients in Figs. 4.23(d), 4.25(d) and 4.24(d).

It was discussed in Section 2.2.2.3 that an increased ionic strength in suspension reduces the stability between particles. The role of added salt on polymeric flocculation can be of great importance since raw water contains salts of Ca^{2+} , Na^+ and Mg^{2+} , and the presence of the dissolved salts leads to a reduction in the effective range of the electric double layer of particle and polymer. This reduction encourages the bridging of particles by long adsorbed polymer molecules (in the case of aggregation of negatively charged particles by anionic polymers) as well as the reduction of repulsive interaction between charged segments of the polymer chains. Though the adsorption of segment of high charge density polymer on the particle surfaces neutralised by electrolyte may be discouraged by this. Later in Section 4.5, the effect of adding ionic strength prior to polymer dose on the overall aggregation will be discussed.

4.3 Effect of different polymers on latex flocculation

It was told in Section 2.4.2.1 that flocculation begins with a relatively weak binding between polymer segment and particle surface, and this behaviour, adsorption, has a great influence further on flocculation (Hogg 1999). The sum of a large number of such linkages leads to a relatively strong attachment of the polymer molecule as a whole to the surface. It is known that the adsorption is affected by the properties of polymer. As molecular weight increases, the strength of the individual segment-surface linkages becomes less important while the charge interactions are more important for low molecular weight polymers. Hence, the characteristics of flocculation will depend greatly on the properties of different polymers.

Six kinds of cationic polymers, i.e. Percol 63, 326 and 1697, and Zetag 64, 89 and 92, have been used in this experiment in order to examine flocculations by polymers with different properties. These polymers are best distinguished by the molecular weight as well as the charge density they possess. These properties are listed in Table 3.2 in Section 3.1.2 (see page 53). Polymers with high molecular weight are usually long chain polymers. It is reported that they are very effective where polymer bridging is an important mechanism (Adachi 1995; Hogg 1999), whereas the high charge density plays an important role in neutralising the surface charge by forming a rather thin layer on the particle surface, and eventually results in the destabilisation in suspension (Durand-Piana et al. 1987). Percol 63, which has the highest molecular weight among the Percol series, has an effective size of up to about 0.2 μ m, and usually produces flocculation by both polymer bridging and charge neutralisation. Therefore, for the Zetag series, which have higher molecular weights than those of Percol series, flocculation is dominated by polymer bridging whereas for the Percol series with lower molecular weights, charge neutralisation is the dominant mechanism in flocculation.

Note that various concentrations for each polymer were applied into latex suspension as pre-tests in order to show which concentration leads to the maximum ratio increase in a given suspension and shear condition (see Figs. 4.26 for flocculation by Percol series and 4.30 for Zetag series). The detailed result showing ratio, sigmoid parameters, T and RPNC have been achieved using the optimum concentration which leads to the highest ratio during tests of 600-second duration.

4.3.1 Percol and Latex

The tests were carried out in order to investigate different flocculations caused by three kinds of Percol series. In this work, latex suspension with a 100 mg/L concentration is flocculated in the Set-up B described in Section 3.2.2. Three different polymer stock solutions of 0.1% (w/w) were introduced separately to suspension stirred at a constant shear rate. The concentrations of polymers were determined from the preliminary tests to be the optimum concentration and are listed in Table 4.6. The stirring rate was kept constant at 60 rpm for 600 seconds.

The ratio values achieved in the preliminary tests using various polymer concentrations are shown in Fig. 4.26. Major findings in the figure are as follows; (1) molecular weight seems to have a dominant influence on the increase in the degree of flocculation since polymer with higher molecular weight leads to higher maximum ratio increase. (2) Range of polymer concentration which leads to ratio increase is observed to be narrower with polymer with lower charge density.



FIG. 4.26. Maximum ratio values obtained in the flocculation of latex particles using various concentrations of Percol series; 100 mg/L latex suspension flocculated by Percol 63, Percol 326 and Percol 1697 at 60 rpm in the Set-up B; symbols in circles indicate the optimum polymer concentration and are shown in Figs. 4.27, 4.28 and 4.29

It is found in Fig. 4.27 that the flocculation rate depends greatly on the molecular weight, where the peak ratio of about 1.7 is observed for Percol 63, while Percol 326 and 1697 only lead to the peak values of 1.5 and 1, respectively. Adachi and Kamiko (1994) suggested that the higher rate of flocculation is achieved by an increase in the



FIG. 4.27. Effect of different kind of polymer (Percol series) on latex aggregation; 100 mg/L latex suspension flocculated by 100 μ g/L Percol 63, 180 μ g/L Percol 326 and 300 μ g/L Percol 1697 at 60 rpm in the Set-up B

TABLE 4.6. Calculated d_F latex flocculation and sigmoid parameters for latex flocculation by Percol series

Polymers	Concentration	Calculated d_F		
Percol 63 Percol 326 Percol 1697	100 μg/L 180 μg/L 300 μg/L	2.477 (90-400 sec) 2.467 (90-400 sec) 2.449 (90-400 sec)	about 3 (-600 sec) about 3 (-600 sec) about 3 (-600 sec)	
Polymers	a	b	с	d
Percol 63	0.33	1.42	268	41
Percol 326	0.36	1.16	338	35
Percol 1697	0.36	0.63	265	40

collision radius of the colloidal particles due to the attached polymer. They observed that the estimated effective thickness of such polymer layer is comparable to the size of a polymer molecule.

Although the peak ratio seems to be determined by the molecular weight of polymer, the charge density plays an important role in influencing the degree of flocculation, particularly when the difference in molecular weights of the two polymers are insignificant. A lower molecular weight polymer with higher charge density, Percol 1697, leads to slightly higher ratio values initially. However, it should be noted here that different polymer concentrations could also be responsible for the above trend. Clearly, more investigation is needed in future work in order to examine the exact role of the charge



FIG. 4.28. Sigmoid parameters b and d obtained after latex flocculation by Percol series

density on flocculation at initial stage. Fig. 4.29 shows that the eventual turbidity is greatly reduced for the case of the high molecular weight polymer, whereas the initial turbidity reductions by Percol 326 and 1697 are much lower.

Compared to the Percol 326 case, the results of Percol 63 and Percol 1697 exhibit higher flocculation rate at early stages, thereby achieving the steady state sooner, and this is due to their ratio values reaching the maximum sooner (refer to Fig. 4.27). This behaviour is also clearly seen in Table 4.6 and Fig. 4.28, displaying c and d for Percol 326, which are the highest and lowest sigmoid parameter values, respectively. The behaviour of c and d indicates that the late, high increase in the ratio exceeds the maximum ratio value of Percol 1697. In spite of the finding that the high charge density could lead to the high degree of initial flocculation, there is no clear evidence that the high charge density of polymer influences the rate of adsorption.

Although the properties of polymers are very different, the fractal dimensions derived from the calculations of log R/T and log T listed in Table 4.6 are all similarly high in the early stage (2.45–2.48) and the densities become even higher in the later stage. High molecular weight polymer generates flocs with higher calculated d_F as shown in the table but the differences are negligibly small.



FIG. 4.29. Reductions in T and RPNC during latex flocculation using Percol series; 100 mg/L latex suspension flocculated by 100 μ g/L Percol 63, 180 μ g/L Percol 326 and 300 μ g/L Percol 1697 at 60 rpm in the Set-up B

4.3.2 Zetag and Latex

The tests have been performed to observe the influence of three different Zetag series on latex flocculation. Latex suspension with a concentration of 100 mg/L was flocculated at a constant rate of 60 rpm using the Set-up B. In contrast to the previous section, emphasis will be put on the charge density ahead of the molecular weight since the selected polymers have the same molecular weight but different charge densities. The polymer dosages were determined so as to produce optimum flocculation and are listed in Table 4.7.

Fig. 4.30 exhibits the ratio values achieved in the preliminary tests using various polymer concentrations. The selected Zetag series have the same molecular weight, hence the followings can be confirmed from the result ((1) and (2) are also observed in the Percol case). (1) Polymer with higher molecular weight leads to higher maximum ratio increase. (2) Polymer concentration range is observed to be narrower with polymer with lower charge density. (3) The higher the charge density, the higher amount of polymer is needed to achieve the optimum concentration. The optimum polymer concentration to achieve the similar degree of flocculation is inversely proportional to the polymer charge density. This finding agrees well with the suggestion by Chen (1998). He reported that the polymer dosage to achieve the plateau adsorption of polycations or complete neutralisation of negative particle charge increases inversely proportionally to the charge density of the cationic polymer.

by Zenag series					
Polymers	Concentration	Calculated d_F			
Zetag 64 Zetag 89 Zetag 92	140 μg/L 40 μg/L 300 μg/L	2.162 (90-300 sec) 2.194 (90-350 sec) 2.192 (90-250 sec)	2.612 (-600 sec) 2.625 (-600 sec) 2.616 (-600 sec)		
Polymers	a	b	с	d	
Zetag 64	0.09	0.36	226	48	
Zetag 89	0.08	0.47	287	73	
Zetag 92	0.09	0.27	123	19	

TABLE 4.7. Calculated d_F and sigmoid parameters for 600 seconds during latex flocculation by Zetag series

As described in Section 4.2.2, local overdosing of polymer usually arises when the solution is viscous. The Zetag series used in this work have high molecular weight and are viscous as solution. Therefore, while the previously employed Percol series have



FIG. 4.30. Maximum ratio values obtained in the flocculation of latex particles using various concentrations of Zetag series; 100 mg/L latex suspension flocculated by Zetag 64, Zetag 89 and Zetag 92 at 60 rpm in the Set-up B

been dosed into suspension as a solution of 0.1% (w/w) concentration, the solutions of the Zetag series were diluted by 10-fold in order to avoid possible mixing problems. The volume range of the diluted solution mixed into suspension to give recognisable flocculation in the measurement is chosen to be $100-1000 \ \mu$ l, which is still small enough not to affect the suspension concentration (100 mg/L in 100 ml). Although it is not certain for the actual quantitative effect of the dilution of polymer solution, in Fig. 4.31(a), all three curves have a shorter lag time before the initial ratio increase, compared to the Percol case (see the previous section).

Steady state ratio values (peak ratio) are inversely proportional to the polymer concentration. The highest peak ratio is achieved by Zetag 89 with the concentration is 60 μ g/L, while Zetag 92 of 350 μ g/L exhibited the lowest peak ratio. This behaviour indicates that the polymers with low charge density require high level of polymer dose in order to obtain optimum flocculation, regardless of the the peak value. Figs. 4.31, 4.32 and 4.33 show that the polymer dosage required to give optimum flocculation increases as the charge density of the polymer decreases. Note that sigmoid parameter d is inversely proportional to the slope of the ratio curve. Chen (1998) also reported such inversely proportional relationship between the charge density and the polymer dosage for plateau adsorption of polycations, or for complete neutralisation of negative particle charges.



FIG. 4.31. Effect of different kind of polymer (Zetag series) on latex aggregation; 100 mg/L latex suspension flocculated by 140 μ g/L Zetag 64, 40 μ g/L Zetag 89 and 300 μ g/L Zetag 92 at 60 rpm in the Set-up B

An interesting feature shown in Fig. 4.32 and Table 4.7 is that the steady state ratio values are inversely proportional to the maximum slope of the ratio curve. This implies that the flocculation degree, which is lower initially, becomes greater and the ratio reaches a higher peak. In the case of Zetag 92, which has a very low charge density, the ratio increases relatively fast initially and reaches the steady state value of about 0.7 in just 150 seconds, whereas the ratio of Zetag 89 increases slowly at first but continues to increase up to 1.1 throughout 600-second duration of the test. This result disagrees with previous studies by Eriksson et al. (1993), Smith-Palmer et al. (1994) and Chen (1998) using polystyrene latex particles. They found that the cationic electrolytes with the high charge density lead to the low flocculation rate/loose floc structure, due to their flat conformations in the adsorption layers on the particles. As investigated in the previous section with Percol series, there is no significant relationship between d_F and the type of polymers in case the optimum polymer concentrations are applied. The densities of the flocs in the initial stage are high since the range of the fractal dimensions are 2.16-2.19. Due to the continuous break-up and re-flocculation in the later stage, they become denser as flocculation continues. Turbidity and RPNC in Fig. 4.33 also exhibit a similar trend to the b changes in Fig. 4.32.



FIG. 4.32. Sigmoid parameters b and d obtained after latex flocculation by Zetag series



FIG. 4.33. Reductions in T and RPNC during latex flocculation by Zetag series; 100 mg/L latex suspension flocculated by 140 μ g/L Zetag 64, 40 μ g/L Zetag 89 and 300 μ g/L Zetag 92 at 60 rpm in the Set-up B

4.3.3 Discussion

The experiments demonstrated so far have been carried out under two different solution conditions to examine the effect of polymer properties on latex flocculation.

Comparing ratio results using optimum polymer concentrations, flocculation achieved by Zetag series (with higher molecular weight) generally corresponds to more rapid processes while it is observed in the tables that the derived fractal dimensions are lower.

Molecular weight plays an important role on the flocculation degree since high molecular weight leads to higher ratio increase regardless of charge density and optimum flocculation is achieved at lower concentration than other polymers. When polymers of high charge density are applied, narrower range of effective polymer concentration and initially fast ratio increase (reaching steady state earlier as a result) are observed.

In the case of flocculation by Zetag series where the same molecular weight but different charge density are used, polymer with lower charge density produces higher degree of flocculation in terms of the ratio, though showing relatively slow initial increase in the ratio. When polymers have the same molecular weight, the polymer dosage required to provide the optimum flocculation increases inversely proportionally to the charge density of the polymer. However, the dependence of the charge density on the floc structure, attributed to conformational changes during the adsorption/flocculation process under shear, has not been observed. All calculated fractal dimensions in Tables 4.6 and 4.7 are above 2.3, thus implying that the flocs produced by the selected Percol and Zetag series are compact. The relationship between the floc density and polymer concentration or the flocculation degree has not been evidently found.

4.4 Effect of various constant shear rates on latex flocculation

During the flocculation process, the break-up of flocs becomes more pronounced, after the dominant period of aggregation. Eventually, the break-up balances the aggregation, and the repeated break-up of the remaining flocs and re-collision of the broken flocs occur. The stage achieved by this repeated process is called the steady state. Previous researches have found that the steady state is reached faster when the shear rate increases in flocculation tests using latex particles (Oles 1992; Serra et al. 1997) and using sediment particles (Lick and Lick 1988; Burban et al. 1989; Tsai et al. 1987).

Usually, intense fluid motion and high particle concentration increase the likelihood of collision between particles, and the repeated break-up and re-collision of flocs in the steady state produce dense flocs with a high fractal dimension (i.e. by intense shear) or large flocs containing a large number of primary particles (i.e. by high particle concentration). The dependence of the number of primary particles in a floc on the collision rate of fractal objects is shown in Fig. 2.11 (see page. 33). According to this figure, it can be seen that the increase in size of flocs having relatively high fractal dimension should be slow whereas the size of flocs of low d_F increases dramatically since they have fractal dimensions below 2 which indicate loose floc strucutre. Jiang and Logan (1991) also reported this dramatic increase in the floc size using fluorescent carboxylate polystyrene microspheres-NaCl system which produces the flocs with low d_F values below 2.

In this section, in order to investigate the effect of constant shear in certain time on the flocculation rate and the density of the generated flocs, latex particles were introduced into deionised water stirred at a fixed shear rates from 60 to 240 rpm and then this suspension has been aggregated using 4 kinds of polymeric flocculants (Percol 63 and Zetag 64, 89 and 92) in the Set-up B. Note that for particles with diameter of over 1.5 μ m, orthokinetic flocculation is expected to be dominant, and hence in this case, the only relevant influence on the collision frequency is the shear rate (refer to Fig. 2.5).

The experimental study described in this section investigates the influence of various constant shear applied to flocculated suspension. In order to concentrate on the effect of the shear, the polymer doses were chosen to be twice the optimum concentration which leads to the highest ratio increase in 600 seconds at 60 rpm. Four different stirring rates were applied separately in a series of tests and each stirring rate remained constant during the test. The concentration of latex suspension is selected to be 100 mg/L by the turbidity measurement as shown in Fig. 3.7(a). Note that flocculation by fluid motion is a dominant mechanism for heavy polymers whereas the polymers with low molecular weight such as Percol 1697 are adsorbed on particle surfaces mainly by diffusion.

4.4.1 Latex and Percol 63

Latex suspension of 100 mg/L concentration has been flocculated by Percol 63 in the Set-up B. As introduced in Section 3.1.1, primary latex particles are mono-disperse and have a size of 1.7 μ m. The polymer concentration is determined to be 200 μ g/L. Four stirring rates, 60, 120, 180 and 240 rpm, have been applied separately in each test in this section. Before discussing the obtained results, it should be mentioned that the results presented in this section are consistent with the results of the preceding sections in terms of the changes in the ratio, turbidity and *RPNC* achieved in the same conditions such as the particle and polymer concentration, and the stirring rate.

TABLE 4.8. Calculated d_F and particle number reduction during 600 seconds of latex flocculation by Percol 63 under different shear condition

Stirring rate	Calculated d_F		Particle number reduction
60 rpm	2.552 (90-600 sec)		30-fold
120 rpm	2.587 (90-600 sec)		40-fold
180 rpm	2.736 (90-600 sec)		46-fold
240 rpm	2.530 (90-200 sec)	about 3 (-600 sec)	273-fold

Considering the degree of flocculation (ratio), interesting features can be observed as follows; (1) the higher the stirring rate, the shorter the time taken to reach the peak ratio (which indicates steady state). At high stirring rates, 180 and 240 rpm, the peak ratio values occur at about 420 and 360 seconds, respectively. However, as shown in Fig. 4.36(a), no peak in the ratio is observed for the case of low stirring rates (60 and 120 rpm). The steady state quickly achieved by using the rate of 240 rpm, may arise from the higher rate of collision between particles or between particles and polymers as expected by equation (2.24). (2) With the higher shear rate, the more effective flocculation throughout 540 seconds is observed in terms of the ratio. The



FIG. 4.34. Photos taken at the end of tests; latex particles (100 mg/L) were flocculated by Percol 63 at various stirring rates

highest stirring rate, 240 rpm, generated very effective flocculation since it leads to the largest increase in ratio (0.65 to 2.2) at 600 seconds while a relatively small ratio increase (0.6 to 1.2) is observed at 60 rpm. (3) The ratios obtained using the stirring rates of 120 and 180 rpm reach the almost same value of about 1.4 at the end of the measurement (600 seconds), but the curve representing the higher stirring rate, 180 rpm, has a higher slope, indicating a higher flocculation rate initially than that of the lower stirring rate, 120 rpm. This behaviour is supported by the previous studies (Lick and Lick 1988; Burban et al. 1989; Oles 1992; Tsai et al. 1987; Serra et al. 1997) introduced at the beginning of Section 5.1.

The rapid flocculation process can also be observed when the particle concentration is increased. The results shown in Figs. 4.35 are obtained from the flocculation tests using different particle concentration but under same solution and hydraulic condition. The increased particle number concentration results in the increase in collision frequency in the initial stage, according to equation (2.14), and assuming that the collision efficiencies in both processes are equal, the flocculation rate becomes higher. A reduced lag time before the onset of the ratio increase is also observed in the figure. This behaviour is also observed by Serra et al. (1997) using latex particles in a Couette flow system. It is found in the experiment that, if the particle concentration is larger than a certain value (e.g. a volume fraction of 6×10^{-5}) and the shear stress (G) is not larger than 50 s⁻¹, the high particle concentration enhances the aggregation of particles and the final diameter of aggregate increases. Higher polymer concentration may be necessary to achieve the similar experimental result. More research on the effect of particle concentration is suggested to follow in future.

Table 4.8 demonstrates the calculated fractal dimension during latex flocculation by various shear speeds. As expected, high shear rate leads to compact floc structure at the end of test. Figs. 4.34(a), (b), (c) and (d) show photos of latex flocs taken after the tests. The sizes of flocs are smaller than the flocs shown in Figs. 4.13(a) and (b) due to the different polymer concentrations. The floc size in photos agrees with the trend of ratio increase with shear rate, but it is not very clear that the compactness of flocs are related to the shear rate since the difference between the derived d_Fs in the later stage in Table 4.8 is so small and the photos were not taken in such detail. Considering the particle number reduction in the table, the result disagrees with size-



FIG. 4.35. Difference between flocculations using two particle concentrations; latex particles of 100 and 200 mg/L were flocculated by Percol 63 of 200 μ g/L at 60 rpm

density relation in equation (2.31), but the behaviour is expected to be observed when the shear speed much higher than 240 rpm is applied.

The reduction in turbidity (T) and particle number concentration (RPNC) are shown in Figs. 4.36(b) and (c), which also follows a similar trend to the ratio variation, where (1) higher stirring rates lead to faster reduction in turbidity and particle number concentration, (2) the higher shear rate results in the larger reduction at 600 seconds, and (3) the higher rate of reduction is observed at 180 rpm than that achieved at 120 rpm.



(c) Logarithmic plot of R/T against T

FIG. 4.36. Effect of stirring rate on latex flocculation by Percol 63; 100 mg/L latex suspension flocculated by 200 μ g/L Percol 63 in the Set-up B

4.4.2 Latex and Zetag series

Flocculation of latex suspension of 100 mg/L by various shear rates was monitored using the Set-up B. Zetag 64, 89 and 92 have been used in this work, and were prepared in a solution of 0.01% (w/w) to prevent the possibility of local overdosing in the vicinity of an addition point by the high viscosity of polymer. These polymers have the same molecular weight but different charge densities (see Table 3.2 on page 53).

Preliminary tests have been performed to obtain the optimum concentrations for each polymer (see Fig. 4.30). Latex suspensions of 100 mg/L concentration and 100 ml volume were flocculated by various polymer (Zetag series) concentrations and the flocculations were monitored for 600 seconds. From the obtained ratio results, polymer concentrations are chosen to be 280, 80 and 600 μ g/L for Zetag 64, 89 and 92 respectively, and these concentrations correspond to twice the optimum concentration.



(c) Logarithmic plot of R/T against T

FIG. 4.37. Effect of stirring rate on latex flocculation by Zetag 64; 100 mg/L latex suspension flocculated by 280 μ g/L Zetag 64 in the Set-up B



(c) Logarithmic plot of R/T against T

FIG. 4.38. Effect of stirring rate on latex flocculation by Zetag 89; 100 mg/L latex suspension flocculated by 80 μ g/L Zetag 89 in the Set-up B

As observed in the previous section, (1) the higher the stirring rate, the sooner the steady state is reached (i.e. the ratio reaches peak value sooner) regardless of the choice of polymers. However, in this section, (2) the most effective flocculation in terms of the ratio is achieved with 180 rpm, indicating lower floc strength of flocs generated in the later stage of flocculation. In general, (3) the reduction in turbidity shown in (b) figures in Figs. 4.37-4.39 and in particle number concentration as shown in (c) figures in Figs. 4.37-4.39, is changed in the opposite manner to the ratio change.

The comparison of each flocculation by different polymers indicates that the rate of flocculation is lower when the polymer with the higher charge density is used. The ratio values achieved at 600 seconds are about 0.7-1.1 for Zetag 64, 0.9-1.0 for Zetag 89 and 0.5-0.7 for Zetag 92 case and the Zetag 89 case exhibit slower ratio increase - showing less steep curves, compared to that of other polymers. Flocculation by Zetag 89 appears



(c) Logarithmic plot of R/T against T

FIG. 4.39. Effect of stirring rate on latex flocculation by Zetag 92; 100 mg/L latex suspension flocculated by 600 μ g/L Zetag 92 in the Set-up B

to be most effective in reducing the turbidity and the *RPNC* initially, and still manage to keep the reduction going after 600 seconds, indicating the continuous dominance of aggregation over break-up. It should be pointed out here that the gradual but continued increase or decrease of the ratio, turbidity and *RPNC* can be observed commonly for the case where, regardless of polymer type, the lowest stirring rate of 60 rpm.

Previous studies (Smith-Palmer et al. 1994; Chen 1998) suggested that the density of flocs becomes maximum with fairly low charge density (1 to 30%) and minimum with moderately high charged polymer, attributed to conformational changes (refer to Section 2.4.2) during the adsorption/flocculation process under shear. However, the derived result demonstrated that there is no clear differences in calculated fractal dimensions depending on the charge density (see Table 4.9). Most flocs produced in this work have compact structure, showing large fractal dimensions (2.64-3). It is also observed in the tables that the fractal dimension and the shear rate have bearings on each other since the fractal dimensions obtained in the early stage are higher with higher shears but the d_F in the later stage indicates that the flocs become even more compact. The exception of trend of d_F increasing with shear rate is expressed in blocked letter in Table 4.9 but the deviation from the trend is in the range of 0.02 to 0.04 and is not significant.

Stirring rate		Calculated d_F		Particle number reduction
Zetag 64 case				
60 rpm	2.122 (90-250 sec)	$2.374 \ (-450 \ \text{sec})$	2.435 (-600 sec)	1185-fold
120 rpm	2.163 (90-250 sec)	$2.375~(-450~{ m sec})$	2.500 (-600 sec)	1225-fold
180 rpm	2.175 (90-250 sec)	$2.520 \ (-450 \ \text{sec})$	$2.670 \ (-600 \ \text{sec})$	1580-fold
240 rpm	2.219 (90-250 sec)	2.614 (-450 sec)	2.672 (-600 sec)	1210-fold
Zetag 89 case				
60 rpm	2.203 (90-250 sec)	$2.370 \ (-450 \ \text{sec})$	$2.502 \ (-600 \ sec)$	1690-fold
120 rpm	2.180 (90-250 sec)	$2.442 \ (-450 \ \text{sec})$	2.559 (-600 sec)	2285-fold
180 rpm	2.246 (90-250 sec)	2.489 (-450 sec)	$2.604 \ (-600 \ \text{sec})$	2845-fold
240 rpm	2.233 (90-250 sec)	2.538 (-450 sec)	2.616 (-600 sec)	2190-fold
Zetag 92 case				
60 rpm	2.173 (90-250 sec)	2.381 (-450 sec)	2.633 (-600 sec)	325-fold
120 rpm	2.186 (90-250 sec)	$2.561 \ (-450 \ \text{sec})$	2.716 (-600 sec)	565-fold
140 rpm	2.232 (90-250 sec)	2.717 (-450 sec)	2.706 (-600 sec)	930-fold
240 rpm	2.313 (90-250 sec)	$2.747 \ (-450 \ \text{sec})$	2.817 (-600 sec)	640-fold

TABLE 4.9. Calculated d_F and particle number reduction during 600 seconds of latex flocculation by Zetag 64, 89 and 92 under different shear condition

• Latex and Zetag 64

The result obtained using a stirring rate of 180 rpm represents a typical figure of optimum flocculation in terms of ratio, turbidity and RPNC as shown in Figs. 4.37(a), (b) and Table 4.9. When the highest stirring rate, 240 rpm, is applied, the ratio value increases dramatically but reaches the steady state soon.

• Latex and Zetag 89

It is observed in Fig. 4.38(a) that the degree of flocculation are almost the same regardless of the shears applied to the suspension though during initial stage

(100-400 second), the slope of the curves is proportional to the stirring rate. The faster increase in ratio observed in the initial stage with higher shear rate corresponds to larger reduction in T in the same period as shown in Fig. 4.38(b).

• Latex and Zetag 92

Compared to the other cases using Zetag 64 and 89, the lower ratio values are achieved. Similar to the Zetag 89 case, almost the same ratio values are achieved at 600 seconds as shown in Fig. 4.39(a) except for the 240 rpm case where the maximum ratio achieved at 200 seconds decreases afterwards. Also, ratio increase to the steady state occurs relatively in short time.

4.4.3 Discussion

So far in this section, the effect of different constant shears on the latex flocculation has been discussed. With higher shear rate applying to suspension, the steady state of flocculation (plateau region of ratio curve) is reached earlier and the calculated fractal dimension increases in a very small degree.

It was mentioned early in this section that the degree of flocculation does not have a linear relationship with time while the constant shear is in charge, but floc break-up becomes dominant after a certain point. This behaviour can be considered using the previously obtained ratio and log R/T-log T data.

Figs. 4.40(a) and (b) is given from the 240 rpm case in Figs. 4.36(a) and (c) and Figs. 4.37(a) and (c) since these exhibit the steady state in 600 second test time. Analysis of the figure shows that fractal dimension of the flocs increases with the constant application of one shear rate. Assuming the steady state begins at 300 seconds (230 seconds for Zetag 64 case) in the figure, the slope of the log-log plot corresponding to the 0-300 second period decreases while the slope becomes even much lower, resulting in the fractal dimension close to 3 with the steady state. The continuous processes of the break-up of the low strength of largely formed flocs and the re-flocculation of the broken small flocs and the unflocculated particles is thought to be responsible for the formation of the compact structure. Fig. 4.34(d) and Fig. 4.41 were obtained from the flocculation using the same shear rate (240 rpm) but the floc samples were taken at different time (at 600 seconds for Fig. 4.34(d) and 220 seconds for Fig. 4.41). These photos agrees with the steeper slope of the log R/T-log T plot in the later stage since the floc taken at 220 seconds looks smaller and has more open structure than the one at 600 seconds as appeared in the photos.

Huang (1994) investigated flocculation of natural sediment particles in Couettetype flocculator and suggested that the flocs formed at higher fluid shears have higher settling speed, indicating a more dense floc structure than that formed at lower fluid shear. Incidentally, the obtained fractal dimension (d_F) values in the range of 1.83–1.97 were reported in their work. The listed fractal dimensions in Table 4.8 also exhibit a trend where the higher stirring rates such as 180 and 240 rpm produce flocs with even higher fractal dimensions from 2.73 to 3. The results obtained in this section clearly represent the dependency of floc density on shear rate.



FIG. 4.40. Changes in fractal dimension during flocculation under constant shear



FIG. 4.41. Flocs taken at 220 second; latex flocculation by Percol 63 at the stirring rate of 240 rpm $\,$

4.5 Effect of dissolved salts on latex flocculation

It is mentioned in Section 4.2 that the presence of the added salts in suspension reduces the stability of the suspension, and the valency of the counter-ions has a great influence on the electrostatic attraction between the charged particles and the counter-ions.

The results presented in Section 4.2.3 exhibited that the presence of dissolved salt in a stirred suspension does not influence aggregation greatly, compared to polymeric flocculation. It is worth observing the behaviour of the added salt in polymeric flocculation since the increase in ionic strength prior to the flocculation may improve or worsen the overall efficiency of flocculation. It is mentioned in Section 2.4.2.2 that the presence of calcium ions in suspension results in ion bonding between anionic polyelectrolytes and negatively charged particle surface, giving attraction to both sides. Also, when aggregation of negatively charged particles by cationic polymer occurs, the polymer adsorption can decrease with increasing salt concentration, either by screening effect or competition for charged surface sites between ionic segments of the polymer chain and dissolved ions. Therefore, the effect of added salts on polymeric flocculation, whether giving further destabilisation or restabilisation, will be examined in the following sections. The study will discuss the effect of electrolytes of different charge number and concentration on polymeric flocculation. In order to examine this effect, a small amount of dissolved salt (calcium nitrate or sodium nitrate) is applied to give an increased ionic strength to suspension, but not to give destabilisation in full.

In this section, therefore, results are given for latex suspension, flocculated by polymer in the presence of various dissolved salt concentrations, from very small amounts which hardly lead to any destabilisation and coagulation, to concentrations high enough to cause limited aggregation. During the main tests in this section,

- the stock suspension of high concentration is mixed with deionised water in a stirred jar to give the required concentration and high shear speed (240 rpm) is applied for 20 seconds,
- then the suspension begins to circulate at 30 seconds by peristaltic pump.
- Dissolved salts were added to the stirred suspension initially and in some cases, this caused aggregation before the actual monitoring.

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• Polymers were inserted at 90 seconds. See Fig. 4.42 for test procedure for 600 seconds.



FIG. 4.42. Schematic diagram of an experimental result in Section 4.5
4.5.1 Effect of various sodium nitrate concentrations on latex flocculation by Percol series

Latex particles of 100 mg/L have been flocculated by Percol 63, 326 and 1697 at the same polymer concentration (200 μ g/L) but in NaNO₃ solution of different concentrations (0, 10, 30 and 50 mMol). The polymer concentration of 200 μ g/L produces a high degree of flocculation in a given condition in the Percol 63 case while the same concentration is much lower than the optimum concentration for the Percol 326 and 1697 cases (see Fig. 4.26 in Section 4.3.1 for the relationship between polymer concentration and maximum ratio). As seen in Section. 4.2.1, the ratio, the degree of flocculation, hardly increases in low concentration of sodium nitrate (up to 50 mMol) in latex suspension, indicating that the collision efficiency in terms of stability in suspension is still very low although the suspension is definitely destablised in some degree. According to Fig. 2.1 and equation (2.10), the presence of electrolytes downgrades repulsive force by reducing Diffuse layer. In this section, the influence of the dissolved salt with low valency at such low concentration on latex flocculation by Percol series is discussed.

Figs. 4.43(a), (b) and (c) exhibit the flocculation rate, turbidity and RPNC at the end of test (600 seconds) and fractal dimension derived from the real time ratio data and the logarithmic plot of R/T versus T are listed in Table 4.10 to show the density of flocs. In (a) figure, considerable increase in the maximum ratio is observed in Percol 63 and 326 cases when the concentration of sodium nitrate is increased from 0 to 30 mMol while there is only slight increase in the case of Percol 1697, the highest charge density. Regardless of NaNO₃ concentration in latex suspension, the highest ratio value at 600 seconds is achieved with Percol 63 which has high molecular weight while the lowest ratio has been acquired with Percol 1697 which has low molecular weight and is 100% charged (Refer to Figs. 4.43(a)).

As described in the previous Figs. 4.8(a), the concentrations of sodium nitrate between 10 and 30 mMol, by themselves, are too low to lead significant aggregation detected by turbidity fluctuation monitoring. However, latex flocculation by Percol series can be improved if the particles are flocculated in the NaNO₃ solution of this concentration range. It is observed in Figs. 4.44(a), (b) and (c) that in all cases, the increased degree of flocculation in terms of maximum ratio at 600 seconds or steady state has been achieved in the presence of sodium nitrate. However, flocculation in the solution of high NaNO₃ concentration (50 mMol) exhibits high degree of ratio increases in the early stage, but the ratio value reaches steady state very soon and results in the low ratio value eventually at 600 seconds.

Comparing the ratio values at 600 seconds obtained in the above two conditions (0 and 50 mMol), the value obtained in 50 mMol solution is higher in the Percol 63 and 326 case, and the value achieved in 0 mMol solution is higher in the Percol 1697 case (refer to Fig. 4.43).

		-	
NaNO ₃ conc.		Calculated d_F	
Percol 63 case			
0 mMol	2.140 (90-250 sec)	2.856 (-600 sec)	
10 mMol	2.484 (90-250 sec)	$2.942 \ (-600 \ \text{sec})$	
30 mMol	2.389 (90-250 sec)	about 3 (-600 sec)	
50 mMol	2.416 (90-250 sec)	about 3 (-600 sec)	
Percol 326 case			
0 mMol	2.577 (90-400 sec)	2.983 (-600 sec)	
10 mMol	2.552 (90-350 sec)	about 3 (-600 sec)	
30 mMol	2.222 (90-150 sec)	2.704 (-450 sec) about 3 (-600 sec	
30 mMol	2.181 (90-150 sec)	2.783 (-400 sec) about 3 (-600 sec)	
Percol 1697 case			
0 mMol	2.182 (90-350 sec)	– (–600 sec)	
10 mMol	2.081 (90-350 sec)	-(-600 sec)	
30 mMol	2.150 (90-250 sec)	-(-600 sec)	
50 mMol	2.075 (90-300 sec)	- (-600 sec)	

TABLE 4.10. Calculated d_F for latex flocculation by Percol series and NaNO₃

Section 4.3.1 discussed latex flocculation by Percol series and the polymer concentration has been chosen from the optimum which leads to maximum ratio increase (see page 104). There was no significant difference between the fractal dimensions obtained from different types of polymer. Flocs generated by different polymers have similar density ($d_F \simeq 2.45$) initially then become very dense ($d_F \simeq 3$). However, floc densities are found to be higher for the flocs by Percol 63 and 326 than the flocs by Percol 1697 in case the polymer concentrations are the same at 200 µg/L. According to the fractal dimensions listed in Table 4.10, fractal dimensions of the flocs in the later stage (200-600 for Percol 63 case, 400-600 for Percol 326 and 350-600 seconds for Percol 1697 cases) are almost 3 for the cases of Percol 63 and 326 cases but 2.64 in Percol 1697 case.

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In this result, the relationship between the properties of polymer and d_F cannot be confirmed since the selected polymer has different range of effective concentration as described in Section 4.3.1. The presence of NaNO in suspension leads to higher floc density ($d_F \simeq 3$) regardless of their effect on the flocculation rate. In the cases of Percol 63 and 326 cases, the derived fractal dimension listed in Table 4.10 is observed to be higher with the higher concentration of sodium nitrate added into latex suspension though the difference is minimal. However, it is uncertain whether the Percol 1697 case also exhibits the same effect because of the large variations observed in the later stage in the logarithmic plot of R/T and T result in very high standard deviation. It is in doubt which aggregation mechanism operates to increase or decrease the flocculation rate when the NaNO₃ concentration of 10 to 30 mMol is applied, and when these concentrations are further increased to 50 mMol. On possibility for 50 mMol concentration case is that restabilisation of particles/flocs arises while with the excess of electrolytes, the repulsive interaction between the ionic group on the polymer and charged sites on the particles is achieved.



(a) Increase in ratio



(b) Reduction in T



(c) Reduction in RPNC

FIG. 4.43. Changes in ratio, T and RPNC values obtained from the flocculation tests using Percol 63, 326 and 1697 and different NaNO₃ concentrations; 100 mg/L latex suspension flocculated for 600 seconds using 200 μ g/L polymer in the Set-up B



(a) Percol 63



(c) Percol 1697

FIG. 4.44. Effect of the concentration of NaNO₃ in the latex suspension on flocculation by Percol 63; 100 mg/L latex suspension flocculated by 200 μ g/L Percol series in the Set-up B

4.5.2 Effect of sodium nitrate on latex flocculation by various Percol 63 concentrations

Latex suspension of 100 mg/L were flocculated by various polymer concentrations $(60-170 \ \mu\text{g/L} \text{ of Percol 63})$. This flocculation test has been repeated in the presence of sodium nitrate of different concentrations, 10, 30 and 50 mM to investigate the influence on the optimum polymer concentration, floc structure and flocculation rate depending on the solution condition. As mentioned earlier in the previous section, sodium nitrate of small amount (up to 50 mMol) does not influence much on the aggregation of latex particles. The experiments have performed in a way as same as described in Section 4.3.1 but a series of tests using various polymer concentrations are repeated in the presence of sodium nitrate of different concentrations.

The flocculation rate (ratio value), T and RPNC at the end of test (600 seconds) are shown in Figs. 4.45(a), (b) and (c) while fractal dimensions derived from the real time ratio data and the logarithmic plot of R/T versus T are listed in Table 4.11. Figs. 4.46, 4.47 and 4.48 show the changes in flocculation rate. Each figure are separated into two charts to make a distinction between sets of data points. Note that ratio increase begins at 30 seconds and the values are slightly higher where flocculation occurs in the NaNO₃ solution of 30 mMol concentration. This is because the stock solution of sodium nitrate was added initially before the actual monitoring beginning at 30 seconds (refer to Fig. 4.42).

The polymer concentrations which lead to the optimum flocculation in terms of maximum ratio value are proportional to the NaNO₃ concentration. It is observed in Fig. 4.45(a) that the optimum concentrations increase as concentrations of the added dissolved salts increases as follows; 60 or 70 μ g/L (10 mMol case), 90 μ g/L (30 mMol case) and 110 μ g/L (50 mMol case).

However, the increase in maximum ratio values obtained in the above conditions are not linearly related to the NaNO₃ concentration. The obtained ratio values at 600 seconds are 0.85, 0.95 and 0.7, respectively. In the presence of 30 mMol NaNO₃, the maximum ratio values for each polymer concentration are higher than the ones at the other NaNO₃ concentrations. A similar trend can be observed in (b) and (c) figures representing T and RPNC.

No significant dependence on floc structures in the later stage has been observed

since under the same salt concentration condition, the fractal dimensions obtained in the early stage are in the very similar range and the values become all very high with a few exceptions as the flocculation goes to the later stage. However, flocculation at higher NaNO₃ concentration produces denser flocs in the early stage (90-400 seconds) since fractal dimensions of 2.40-2.45, 2.50-2.54 and 2.55-2.71 are obtained in the solutions of 10, 30 and 50 mMol concentrations respectively as listed in Table 4.11.

Percol 63 conc.		Calculated d_F	
NaNO ₃ conc.:	10 mMol		
$60~\mu { m g/L}$	2.441 (90-350 sec)	about 3 (-600 sec)	
$70 \ \mu { m g/L}$	2.440 (90-300 sec)	about 3 (-600 sec)	
$90 \ \mu { m g/L}$	2.436 (90-300 sec)	about 3 (-600 sec)	
$110 \ \mu g/L$	2.415 (90 - 250 sec)	about 3 (-600 sec)	
$130~\mu { m g/L}$	2.403 (90-200 sec)	2.681 (-300 sec)	about 3 (-600 sec)
$150~\mu { m g/L}$	2.449 (90-300 sec)	2.541 (-400 sec)	about 3 (-600 sec)
$170 \ \mu g/L$	2.450 (90-300 sec)	about 3 (-600 sec)	
NaNO ₃ conc.:	30 mMol		
$60 \ \mu g/L$	2.541 (90-300 sec)	about 3 (-600 sec)	
$70 \ \mu g/L$	2.497 (90-300 sec)	2.779 (-400 sec)	about 3 (-600 sec)
$90 \ \mu g/L$	2.542 (90-300 sec)	about 3 (-600 sec)	
$110 \ \mu { m g/L}$	2.516 (90-300 sec)	about 3 (-600 sec)	
$130 \ \mu { m g/L}$	2.527 (90-300 sec)	about 3 (-600 sec)	
$150 \ \mu { m g/L}$	2.495 (90-300 sec)	2.554 (-400 sec)	about 3 (-600 sec)
$170~\mu { m g/L}$	2.525 (90-300 sec)	2.632 (-400 sec)	about 3 (-600 sec)
NaNO ₃ conc.:	50 mMol		
$60 \ \mu g/L$	2.537 (90-350 sec)	$2.851 \ (-600 \ \text{sec})$	
$70 \ \mu g/L$	2.638 (90-350 sec)	about 3 (-600 sec)	
$90 \ \mu { m g} / { m L}$	2.573 (90-300 sec)	2.628 (-400 sec)	about 3 (-600 sec)
110 $\mu g/L$	2.549 (90-300 sec)	about 3 (-600 sec)	
$130 \ \mu { m g/L}$	2.639 (90-400 sec)	about 3 (-600 sec)	
$150 \ \mu { m g/L}$	2.711 (90-400 sec)	about 3 (-600 sec)	
$170~\mu { m g/L}$	2.574 (90-400 sec)	2.630 (-600 sec)	

TABLE 4.11. Calculated d_F for latex flocculation by Percol 63 in NaNO₃ solution



FIG. 4.45. Changes in ratio, T and RPNC values obtained from the flocculation tests using different Percol 63 and NaNO₃ concentrations



(b) Changes in ratio

FIG. 4.46. Effect of the concentration of NaNO₃ in the latex suspension on flocculation by Percol 63; 100 mg/L latex suspension in 10 mM NaNO₃ solution flocculated by $60-170 \ \mu$ g/L Percol 63 using the Set-up B



(b) Changes in ratio

FIG. 4.47. Effect of the concentration of NaNO₃ in the latex suspension on flocculation by Percol 63; 100 mg/L latex suspension in 30 mM NaNO₃ solution flocculated by $60-170 \ \mu$ g/L Percol 63 using the Set-up B



(b) Changes in ratio

FIG. 4.48. Effect of the concentration of NaNO₃ in the latex suspension on flocculation by Percol 63; 100 mg/L latex suspension in 50 mM NaNO₃ solution flocculated by $60-170 \ \mu g/L$ Percol 63 using the Set-up B

4.5.3 Effect of sodium nitrate and calcium nitrate on latex flocculation by Zetag series

Latex suspension of 100 mg/L concentration was flocculated at a constant rate of 60 rpm by three polymers, Zetag 64, 89 and 92. The polymer concentrations were 120 (Zetag 64), 45 (Zetag 89) and 260 μ g/L (Zetag 92), which are about 25% lower than the optimum concentration employed in Section 4.3.2. Therefore, the obtained results by these concentrations are expected to produce a slightly lower degree of flocculation when no electrolyte exists in flocculating suspension (refer to Fig. 4.30 on page 109 for polymer concentration range). Sodium nitrate $(NaNO_3)$ and calcium nitrate $(Ca(NO_3)_2)$ have been applied to stirred suspension prior to the addition of polymer. The selected concentration values vary from 1 mMol of sodium nitrate, 1 mMol of calcium nitrate (which hardly leads to flocculation), and 10 mMol of calcium nitrate (which exhibits recognisable changes in ratio, turbidity and *RPNC*). Note that there is no identifiable difference between the results by only deionised water and 1 mMol sodium nitrate. It should be noted that the calcium nitrate concentration of 10 mMol gives an immediate ionic strength to the suspension and eventually aggregation of latex particles as soon as it is added into suspension. As can be seen from Figs. 4.49(a), 4.51(a) and 4.53(a) representing the ratio, the results curves of 10 mMol calcium nitrate concentration start at significantly higher values than other concentration cases. As described earlier in Fig. 4.42, the dissolved salts were added to suspension initially and the actual measurements took place at 30 seconds. As a result, the rise in the ratio occurs between 0 and 30 seconds in 10 mMol calcium nitrate case, its initial value of the measured ratio is observed to be high.

In the early stage (90-300 seconds), if the ratio vales are compared, higher degree of flocculation (ratio value) was obtained with the stronger charged Ca²⁺ probably because Na⁺ ion did not play an significant role as destabilising agent before the addition of polymer. Therefore, it is observed in the early stage between 90-300 seconds that the ratio values are higher at higher salt concentration due to the immediate destabilisation by the added salts.

Considering the later stage where flocs are in the continuous process of break-up and re-flocculated into account, in the cases of Zetag 64 and 89 shown in Figs. 4.49(a) and 4.51(a), flocculation rate is observed to be the highest when the concentration of



(a) Changes in ratio



(b) Changes in T

FIG. 4.49. Effect of dissolved salt on latex flocculation by Zetag 64; 100 mg/L latex suspension flocculated by 120 μ g/L Zetag 64 at 60 rpm in the Set-up B

calcium nitrate is 1 mMol. When the added concentration is higher (10 mMol calcium nitrate) or the valency of the counter-ion is lower (Na⁺), the ratio values monitored at 600 seconds are below the one in 1 mMol calcium nitrate solution. However, when the high charge density polymer, Zetag 92 is applied, Fig. 4.53(a) indicates that flocculation is more effective in calcium nitrate solution of 10 mMol concentration than the other low salt concentration (1 mMol sodium nitrate and 1 mMol calcium nitrate) although the the ratio reaching the peak value begins to decrease (Ca(NO₃)₂ cases).

Besides the ratio values at the end of tests, the decrease in ratio after reaching the peak value may arise due to the already-nearly-destabilised-nature of the suspension



(b) Logarithmic plot of R/T against T

FIG. 4.50. Effect of dissolved salt on latex flocculation by Zetag 64; 100 mg/L latex suspension flocculated by 120 μ g/L Zetag 64 at 60 rpm in the Set-up B

due to the dissolved salt added initially, and further adsorption of remaining polymers would inhibit aggregation by restabilisation. Assuming that the decrease in ratio indicates the restabilisation, the added ionic strength to cause this restabilisation is placed where the concentration is between 1 and 10 mMol of Ca(NO₃)₂, over 10 mMol Ca(NO₃)₂ and 1 mMol NaNO₃ and 1 mMol of Ca(NO₃)₂ for Zetag 64, 89 and 92 cases, respectively (refer to equation (2.10) to for the quantitative effect). With high charge density, the high κ value (high concentration and high valency) is required to get restabilised. However, it should be noted that there is definitely a favourable influence on the initial increase in flocculation rate when the dissolved salts are added,





(b) Changes in T

FIG. 4.51. Effect of dissolved salt on latex flocculation by Zetag 89; 100 mg/L latex suspension flocculated by 45 μ g/L Zetag 89 at 60 rpm in the Set-up B

but the amount is small in order to lead to the decrease in ratio. In the steady state region, scatters observed in Figs. 4.49(a), 4.51(a) and 4.53(a) are not caused by the actual aggregation, but by a largely formed floc passing through the monitoring cell (refer to Figs. 4.20 for graphical illustration).

It was mentioned earlier that the stability of suspension decreases as the electrolyte concentration increases, but at a certain point, the decrease in the stability stops. The electrolyte concentration at this point is called the critical coagulation concentration (c.c.c.). The concentrations employed in this section are lower than c.c.c. since the results in Section 4.2.1 indicate that c.c.c. is near 50 mMol of $Ca(NO_3)_2$



(b) Logarithmic plot of R/T against T

FIG. 4.52. Effect of dissolved salt on latex flocculation by Zetag 89; 100 mg/L latex suspension flocculated by 45 μ g/L Zetag 89 at 60 rpm in the Set-up B

when latex suspension of 100 mg/L is aggregated at 60 rpm in the set-up B. Now consider the 10 mMol Ca(NO₃)₂ cases in Figs. 4.49(a), 4.51(a) and 4.53(a). In all cases, adding high molecular weight polymer leads to the ratio increase in the early stage (90-300 seconds). However, after this period, each case exhibits different behaviour of ratio change. In case of Zetag 89, which has high charge density, the ratio value continues to increase throughout 600 seconds while the decrease in ratio after reaching the maximum value is observed in the case of Zetag 64 (mid charge density) and Zetag 92 (low charge density). The ratio decrease after reaching the peak at 230 seconds is also observed when 1 mMol Ca(NO₃)₂ and Zetag 92 are used. The results show that the



(a) Changes in ratio



(b) Changes in T

FIG. 4.53. Effect of dissolved salt on latex flocculation by Zetag 92; 100 mg/L latex suspension flocculated by 260 μ g/L Zetag 92 at 60 rpm in the Set-up B

charge density of polymer has an influence on the further flocculation of destabilised particles. When the particle surfaces are significantly neutralised by counter-ions such as Ca^{2+} rather than Na^+ , the adsorption of considerable amount of low charge density polymers on the surfaces is unlikely to occur probably due to the charge reversal.

Regardless of the concentrations of dissolved salts, the derived fractal dimensions become very high eventually, indicating that the flocs formed in the later stage are very dense. It is mainly due to the continuous processes of break-up and re-flocculation as described in Section 4.4.3. The presence of dissolved salt can affect the density of flocs since as shown in Table 4.12, denser flocs with higher fractal dimension were



(b) Logarithmic plot of R/T against T

FIG. 4.54. Effect of dissolved salt on latex flocculation by Zetag 92; 100 mg/L latex suspension flocculated by 260 μ g/L Zetag 92 at 60 rpm in the Set-up B

produced in the early stage when calcium nitrate of 10 mMol concentration was used. Also, in the cases of 1 mMol sodium nitrate and 1 mMol calcium nitrate using same concentration but different ion valency, the obtained fractal dimensions were slightly higher with calcium nitrate than with sodium nitrate. However, it is only a limited case for the early stage, and the effect on the later stage cannot be quantified since the flocs formed in this stage are all very dense.

Table 4.13 lists the reductions in turbidity and RPNC to determine the relationship between the flocculation rate (ratio) and the reductions. Initially, larger reductions in T values occur with higher salt concentration (10 mMol calcium nitrate). However, as

	Salt conc.	Calculated d_F		
Zetag 64 case	NaNO ₃ 1 mM Ca(NO ₃) ₂ 1 mM Ca(NO ₃) ₂ 10 mM	2.335 (90-250 sec) 2.455 (90-270 sec) 2.740 (90-200 sec)	about 3 (-600 sec) about 3 (-600 sec) about 3 (-600 sec)	
Zetag 89 case	NaNO ₃ 1 mM Ca(NO ₃) ₂ 1 mM Ca(NO ₃) ₂ 10 mM	2.313 (90-250 sec) 2.355 (90-250 sec) 2.469 (90-250 sec)	2.669 (-400 sec) 2.864 (-400 sec) about 3 (-600 sec)	about 3 (-600 sec) about 3 (-600 sec)
Zetag 92 case	NaNO ₃ 1 mM Ca(NO ₃) ₂ 1 mM Ca(NO ₃) ₂ 10 mM	2.325 (90-200 sec) 2.357 (90-200 sec) 2.612 (90-200 sec)	about 3 (-600 sec) about 3 (-600 sec) about 3 (-600 sec)	

TABLE 4.12. Calculated d_F for latex flocculation by Zetag series and dissolved salts

TABLE 4.13. Maximum ratios and reductions in turbidity reductions and approximate RPNC obtained from Figs. 4.49, 4.51, 4.53, 4.50(c), 4.52(c) and 4.54(c)

	Dissolved salt concentration	Maximum ratio	Turbidity reduction	RPNC reduction
Zetag 64 case	NaNO3 1 mM	0.45	84.6%	1000-fold
	Ca(NO3)2 1 mM	1.80	88.2%	2500-fold
	Ca(NO3)2 10 mM	0.75	80.0%	100-fold
Zetag 89 case	NaNO ₃ 1 mM	0.56	79.0%	400-fold
	Ca(NO ₃) ₂ 1 mM	0.81	86.4%	2000-fold
	Ca(NO ₃) ₂ 10 mM	0.72	83.3%	400-fold
Zetag 92 case	NaNO ₃ 1 mM	0.37	67.7%	100-fold
	Ca(NO ₃) ₂ 1 mM	0.54	94.1%	2500-fold
	Ca(NO ₃) ₂ 10 mM	0.73	93.4%	1500-fold

flocculation continues, the largest reductions were observed in calcium nitrate solution of 1 mMol concentration in all cases, indicating that this concentration level leads to the optimum latex flocculation in terms of turbidity as well, though there is an exception with Zetag 92 case since considering the ratio (The calcium nitrate concentration of 10 mMol resulted in the highest peak ratio value). The application of high calcium nitrate concentration (10 mMol) resulted in a negative influence on the enhancement on flocculation and no major effect on the reductions in T were also observed due to the lower valency of the ion (1 mMol Na⁺).

The reductions in RPNC represented in Figs. 4.50(a), 4.52(a) and 4.54(a) show very similar trend to the T reduction. The initial reduction in the particle number concentration is greatest when adding 10 mMol calcium nitrate. However, the rate of the reduction are decreased as flocculation enters the later stage and this eventually results in less overall reduction at 600 seconds than the cases of using other salt concentrations. An interference occurred by stabilisation generated due to too much added ionic strength mentioned above also applies to this case.

Studying the results reveal that the calcium nitrate concentration of 1 mMol generates the highest level of flocculation in terms of the T and RPNC. Larger number of trials using a wider range of salt concentrations should be carried out to pinpoint the salt concentration required to achieve the maximum degree of flocculation, and to determine the exact ratio of polymer and salt concentration for optimum flocculation in a given condition. Nevertheless, the results provided here at least suggest that controlling the concentration of electrolyte in suspension (based on the knowledge of the relationship between polymer concentration and flocculation rate) enhances the flocculation depending on the purpose of the practical process.

4.6 Summary

Flocculation by three types of suspensions at a constant shear rate has been monitored by turbidity fluctuation technique to investigate the effect of the solution conditions. With the known size of primary particles and polymer as well as some simplifying assumptions in the theory, the monitoring technique can give useful real-time information on the estimation of the flocculation rate and the density of flocs. Prior to the main experiments, the wide range of polymer concentration has been applied, and when it is plotted against the achieved maximum ratio, each polymer has their own distribution of concentration. It is necessary to obtain such distributions for the polymer and particles which will be used since interaction between the particle surface and the polymer segment has different mechanism depending on the polymer/particle properties.

(1) Cationic polymer with high molecular weight leads to extremely high degree of flocculation of negatively-charged latex and kaolin particles. Between the differences in the charge density and the molecular weight, the latter has a dominant effect on flocculation.

(2) The speed of the flocculation depends on various factors such as the concentration and properties of particle/polymer. The higher the polymer concentration is, the faster the steady state is reached. However, the flocculation rate decreases in the excess of the polymer dosage over the optimum concentration which demonstrates the highest maximum ratio in given time. Steric interaction or the local overdosing in the case of polymers with high molecular weight may cause this.

(3) When polymers of the same molecular weight but different charge density are applied separately into the suspension of the same condition, the polymer concentration required to generate optimum flocculation increases inversely proportional to the polymer charge density. It is also observed that the steady state is reached sooner with polymer with higher charge density. However, the effect of the charge density on the floc structure, which corresponds to conformational changes during the adsorption/flocculation process under shear, has not been observed.

(4) Considering that the other factors such as shear rate, polymer properties and concentration cannot result in the very large difference in the density, the density of flocs formed at constant shear may be dependent on the shape of primary particles

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or the initial particle size range. Spherical particles form a rather small and compact floc structure (latex and silica flocs) while plate-like particles become large, openstructured flocs (kaolin flocs) as a result of flocculation. This loose structure (low d_F less than 2) resulted in increase in turbidity as initial flocculation occurs. Also, these largely formed kaolin flocs causes large fluctuations appeared on curves since the light beam is nearly blocked by them. For further investigation and analysis of this very complicated phenomenon, the combined use of monitoring technique such as digital imaging or particle counting may be required.

When a single stirring rate is employed into latex particles with cationic polymers during a test, various behaviours of flocculation were shown, depending on the properties of the polymers.

(1) High stirring rates were usually associated with the high degree of flocculation by polymers and the compact floc structure (high fractal dimension). However, since larger flocs are more easily broken by the applied shear, break-up of flocs balances eventually the aggregation rate. The degree of flocculation (ratio value) increases initially very rapidly at very high shear rates and steady state (plateau region of the ratio curve) is reached earlier than at the lower shear rate.

(2) The higher the shear rate, the higher the floc density is achieved.

(3) Charge density of polymer affect the speed of the flocculation as well since the increase of ratio occurs in much shorter time when the higher charge density polymer is used.

(4) Regardless of the stirring rates, the density of flocs becomes larger, indicating that continuous application of a shear and increase in floc size (as a result, decrease in floc strength) result in the structural changes of flocs due to the repeated aggregation and break-up.

The followings are observed in the experiments of polymeric flocculation in the presence of dissolved salts.

(1) It was observed that the presence of dissolved salt could change polymer concentration distribution as well as the maximum ratio. When polymeric flocculation of latex particles is monitored in different electrolyte concentration, the optimum concentration increases with the concentration of dissolved salt.

(2) The electrolyte concentration between 0 and the c.c.c. (critical coagulation concentration) could enhance latex flocculation in terms of the degree of flocculation (ratio) as well as the reduction in particle number concentration. This trend becomes more significant in the case of polymer with low charge density.

(3) The presence of dissolved salts affect the density of flocs in the early stage. With added ionic strength in high degree, the calculated fractal dimension becomes high.

Chapter 5

Flocculation of silica particles by shear variable with time

5.1 Introduction

It is well known that the flocculation rate can be greatly increased by stirring suspension. The given shear provides a higher probability of collisions and as a result, particles readily form aggregates, although large flocs have lower strength to resist breakage than initially formed small flocs. Hence, it can be seen that controlling applied shear is an important aspect in practical flocculation process. It was suggested by Lu and Spielman (1985) that the particles in stirred suspension are in a continuous process of dominant aggregation and insignificant break-up for a certain time and eventually reach the steady-state where the break-up balances the aggregation process. Both aggregation and break-up rates are known to depend on the shear rate and on the probability of cohesion/break-up. It is known that the final size of the aggregates depends on the shear rate (Spicer and Pratsinis 1996b) and the volume fraction (Serra et al. 1997). Note that this was shown theoretically using equation (2.23) in Section 2.3.3 and the volume fraction (ϕ) is proportional to the surface area and the population of the particles. In cases where the rates of the aggregation and break-up process are different, the average size of aggregates increases or decreases according to whether the aggregation rate is higher or lower than the break-up rate.

In this chapter, an experimental study to show the influence of shear condition on flocculation will be presented. The change of the flocculation rate of silica particles will be mainly discussed and the possible structural changes that silica flocs undergo, depending on the variable stirring rates from the one that relatively slow flocculation occurs with to the one with which the break-up dominates, will also be suggested. And these shear rates were changed intentionally during the test for the purpose of the experiments mentioned above. As described in Section 4.1.1, (1) flocculation rate (or flocculation degree) is expressed by ratio or R and (2) T and RPNC are used to show the changes in turbidity and particle number concentration respectively. (3) The d_F obtained for a certain period will represent the density of the flocs. These terms are discussed further in the following section. It should be noted that silica particles used in this chapter are poly-disperse (size below 5 μ m) and are different with mono-disperse (1.5 μ m), amorphous ones used previously in Sections 4.2.

5.2 Effect of shear rate variable with time on silica flocculation and floc structure

5.2.1 General

Investigations of floc breakage and re-flocculation have become one of the main subjects in aggregation research over the last two decade, from which the analysis of floc structure and aggregation/break-up kinetics became possible by introducing the concept of fractals and the development of monitoring techniques. As discussed in Section 2.5.2.1, the strength of flocs and the applied shear have a great effect on these processes. Previous studies in these areas have found that the flocs imposed by the applied shear tend to break up at the weakest points in the floc structure. These broken flocs are considered to be more compact and smaller than the parent flocs (Thomas 1964). Serra and Casamitjana (1998b) found that aggregation increases the average floc size, but decreases its compactness, while fragmentation decreases the average floc size but increases the average compactness. The controlling of aggregation and fragmentation is now recognised as an essential factor for the optimisation of a flocculation process (Spicer et al. 1998).

The following sections aim to investigate the influence of different polymers and scheduled shears on the degree of flocculation and floc properties. The tests have been performed using the Set-up A described in Section 3.2.1. In this set-up, a cylinder-shaped vessel is equipped with a stirrer which has two cross-shaped paddle of 1.75 cm \times 1 cm width and four baffles of 2.2 cm width to generate a more turbulent shear to stirred suspension. In this work, silica particles of diameter below 5 μ m were used, and the concentration of silica suspension is determined to be 400 mg/L since it induces reasonable changes in the ratio and turbidity value in given set-up and suspension conditions. Fig. 3.7(d) exhibits the values of voltage which survives when it is transmitted through silica suspensions of various concentrations for selecting the concentration in the region of Beer-Lambert law.

It is mentioned that in Section 4.1 that the standardised pre-tests have been performed prior to the main tests, and these pre-tests determines the polymer concentrations which cause the highest ratio increase in a given time and this is called the optimum concentration in this work for convenience. In order to determine the optimum concentration of coagulant/flocculant, the tests have been performed for 600 seconds by taking the following steps;

- (i) Various amounts of additives such as dissolved salts or polymers were added to give the required concentration while moderate constant fluid shear (60 rpm in Set-up A) is applied by a stirrer, and
- (ii) the obtained results were examined, regarding the maximum ratio values in given test time. The optimum concentration has been found by these values, regardless of time taken to reach the maximum ratio.

In preliminary tests, silica suspensions of 400 mg/L concentration were flocculated at constant stirring rate of 60 rpm in the Set-up A, using Percol 63, 326 and 1697 of various concentrations. The results of the preliminary tests are represented in Figs. 5.1(a), (b) and (c). At the stirring rate of 60 rpm, it is observed that aggregation dominates for 300-400 seconds (ratio increases) then the steady state reached (linear region of the curve is shown after ratio increase). High flocculation degree has been achieved with relatively low concentration of Percol 63. However, in case of Percol 1697, much more than twice the amount was needed to be applied to achieve half the ratio value of the Percol 63 case. For the flocculation of poly-disperse silica particles stirred at 60 rpm, the concentrations of 70 μ l for Percol 63, 500 μ l for Percol 326 and 700 μ l for Percol 1697 during a series of preliminary tests.

5.2.2 Silica flocculation under variable shear rates

The following tests have been performed using the same procedure described above for the preliminary tests except for the shear rates applied variably with time. The prepared polymer solutions were added to silica suspension of 800 ml at 120 seconds. (1) Stirring suspension began at 120 rpm which results in increase in ratio, indicating dominant aggregation. (2) When the increase becomes smooth, higher shear rates are applied from 240 to 300 rpm. These shears caused decrease in ratio (floc breakage). (3) As the decrease stops and a plateau region of ratio curve is kept for more than 60 seconds, the shear is decreased to 60 rpm in order to observe re-flocculation of silica particles (see Fig. 5.2 for specific shear schedules).



FIG. 5.1. Determination of optimum polymer concentrations for silica flocculation; silica suspensions of 400 mg/L were flocculated by Percol series of different concentration at a stirring rate of 60 rpm



FIG. 5.2. Schematic diagram of an experimental result in Section 5.2

The results are shown in Figs 5.3, 5.4 and 5.5 and the following sections discuss the effect of variable shear rate on the silica flocculation (flocculation rate, turbidity and particle number concentration).

According to equation (2.56), increase (or decrease) in ratio indicates the increased (or reduced) aggregation number (\bar{k}) , regardless of the fractal dimension (d_F) of the flocs (With the same aggregation number, looser flocs which have lower fractal dimension result in higher ratio). The ratio value is also called the flocculation degree (or rate). Note that higher ratio indicates larger floc size in case of similar level of fractal dimension. The changes in *RPNC* is more directly related to the aggregation number since it is inversely proportional to the aggregation number (refer to equation 2.57). However, it does not contain the information on the size of flocs due to the absence of the fractal dimension in the equation. As flocs grow and the generated flocs are compact, turbidity (T) tends to decrease according to equations (2.39)-(2.41) and (2.43). Also, Fig. 2.14 exhibits that turbidity depends much on the scattering coefficient.

5.2.2.1 Ratio: Flocculation rate

Firstly, the comparison of the results in Figs 5.3, 5.4 and 5.5 demonstrates that the polymers with a higher molecular weight provide the higher peak ratio and the larger reduction in turbidity and particle number concentration in given time, indicating more effective flocculation. The peak ratio value of about 1.35 is observed at 400 seconds with Percol 63 (highest molecular weight), whereas Percol 326 and Percol 1697 (lowest

molecular weight) lead to the peak ratio of 1 at 500 seconds and 0.7 at 400 seconds, respectively.

In all three cases, the increasing tendency of the ratio value becomes slower as the stirring rate is increased. However, when the applied shear rate is below a certain level (e.g. 240 rpm), the ratio increases gradually again shortly after. This is observed in Figs. 5.3(a) and 5.4(a) while flocculation by Percol 1697 exhibits continuous decrease, as shown in Fig. 5.5(a). It can be also seen from Fig. 5.3(a), that the ratio value drops suddenly when the stirring rate is raised to 240 rpm from 120 rpm at 400 seconds but, soon thereafter, a gradual increase in the ratio is observed until a higher stirring rate of 300 rpm is applied at 600 seconds.

It is thought that the input of higher shear rate results in the immediate floc breakup and the flocs of reduced size are more resistant to breakage. Note that previous researches have used a limiting size of aggregates to judge the aggregate strength as mentioned in Section 2.5.2.1. Therefore, the results in Figs. 5.3(a) 5.4(a) and 5.5(a) exhibit that the average floc size continuously becomes smaller for 300 seconds during the application of the stirring rate of 300 rpm and as a result, the floc strength becomes higher while the dominant break-up over aggregation is kept, since for the following 300 seconds (between 600 and 900 seconds), a slow decrease in ratio takes place.

However, in the case of Percol 1697, the stirring rate of 240 rpm appears to be enough to prevent re-flocculating of the broken silica flocs since the reduced ratio value continues to gradually decrease between 400 and 600 seconds and further drop in the ratio was observed when the stirring rate of 300 rpm is applied at 600 seconds. This indicates the lower strength of the flocs produced by Percol 1697 during the application of the stirring rate of 120 rpm. The floc strength does not entirely depend on the size of the flocs or the density. More discussion related to the density will be given in Section 5.2.3.

As the highest shear of 300 rpm was decreased to 60 rpm, all the ratio values acquired by using different polymers increased immediately. The increased size of the flocs means that aggregation between the broken flocs or the broken flocs and detached particles occurs during the application of the lowered shear (60 rpm). This indicates that charge neutralisation plays an role on aggregation rather than polymer bridging since the flocs formed by bridging can not be easily re-formed after the breakup. Hence, the silica flocculation by the selected Percol series can be called reversible flocculation since the ratio value is increased again implying that the broken flocs are re-flocculated to be larger flocs after the floc breakage.

Percol 63 and 326 exhibit the behaviour where the ratio values suddenly increase at 60 rpm from the maximum value attained during the 120 rpm period. In contrast, after showing a similar dramatic increase initially, Percol 1697 displayed a gradually falling ratio behaviour 40 seconds after the stirring rate of 60 rpm was applied. This increase in ratio by the re-introduction of low shear rate indicates that silica flocculation is capable of producing a dramatic level of re-flocculation of the flocs broken by a series of very strong shears.

5.2.2.2 T: Change in turbidity

This section discusses the changes in T during tests and comparison with the ratio change will be described. Assuming the formation of aggregation lead to compact flocs $(d_F > 2)$, turbidity is expected to decrease as aggregation occurs. Turbidity (T)of silica suspensions during flocculation by three polymers initially decreased with a fairly low stirring rate of 120 rpm. Similar to the trend observed by the ratio changes in Figs. 5.3(a), 5.4(a) and 5.3(a), turbidity shows a sudden and immediate increase with the introduction of increased shear, followed by a gradual decrease. Both Percol 63 (Fig. 5.3(b)) and Percol 1697 (Fig. 5.5(b)) results display the aforementioned sudden increase in turbidity when the stirring rate of 240 rpm is applied.

The highest stirring rate, 300 rpm, leads to only a gradual increase in turbidity though large reduction in ratio is observed at the same time period. However, in Fig. 5.4(b), no initial sudden increase was observed when high shears (240 and 300 rpm) are in charge. These high shears lead to an gradual increase in turbidity for the first 100 seconds then maintain the reduction again to reach the original value achieved by previous low stirring rate, 120 rpm, at 100 seconds. The observed gradual increase may suggest that an increased shear leads to a more gradual floc breakage in the case of Percol 326, thereby indicating higher floc strength than the others. This aspect will be studied again using the logarithmic data of R/T and T in the following section.

Comparing these turbidity results, Percol 63 leads to the largest reduction in turbidity at the end of test while Percol 326 and Percol 1697 result in similar lower



(c) Logarithmic plot of R/T against T

FIG. 5.3. Effect of stirring rate on silica flocculation by Percol 63; 400 mg/L silica suspension flocculated by 70 μ g/L Percol 63 in the Set-up A



(c) Logarithmic plot of R/T against T

FIG. 5.4. Effect of stirring rate on silica flocculation by Percol 326; 400 mg/L silica suspension flocculated by 500 μ g/L Percol 326 in the Set-up A



(c) Logarithmic plot of R/T against T

FIG. 5.5. Effect of stirring rate on silica flocculation by Percol 1697; 400 mg/L silica suspension flocculated by 700 μ g/L Percol 1697 in the Set-up A

reduction. However, for the first 400 seconds, when a constant stirring rate of 120 rpm is employed, Percol 63 and 1697 lead to more reduction in turbidity (about 33%) than that by Percol 326 (about 22%). In all cases, turbidity, showing very gradual increase at 300 rpm, decreases dramatically when the stirring rate is reduced to 60 rpm.

5.2.2.3 RPNC: Change in particle number concentration

The shapes of all *RPNC* curves shown in Figs. 5.3(b), 5.4(b) and 5.5(b) are opposite to the ratio curves. Actually, according to equations (2.56) and (2.57), the *RPNC* should be inversely proportional to logarithmic value of ratio where fractal dimension is constant. The advantage of representing *RPNC* in the figure is to find out the actual changes in particle number easily during the flocculation or the break-up.

After polymers were applied to silica suspension at the stirring rate of 120 rpm, RPNC decreased initially and ratio increased. The following increased stirring rate leads to gradual (or steep) increase in particle number concentration while the ratio curve obtained in the same test shows gradual (or steep) decrease respectively, both indicating that sudden floc break-up occurs. When the stirring rate is increased to 240 rpm, a slight increase appears then RPNC value is kept decreasing until a higher stirring rate, 300 rpm, is applied. When this high stirring rate, 300 rpm, is applied, a slow increase in particle number concentration continues, indicating that the break-up process is dominant.

Polymer with higher molecular weight produced the larger reduction in particle number concentration at the end of test (at 1000 seconds). All *RPNC* results exhibit decreases in particle number concentration at 1000 seconds, indicating reflocculation, but Percol 1697 resulted in only 20-fold reduction at 1000 seconds as shown in Fig. 5.5(b) while flocculation by Percol 63 in Fig. 5.3(b) exhibits 1000-fold reduction. Percol 326 whose molecular weight is moderate, resulted in 150-fold reduction at 1000 seconds.

In the cases of Percol 63 and 326, the re-flocculation at the lowest stirring rate, 60 rpm, from 900 and 850 seconds are so effective that the reduction in particle number concentration achieved at 1000 second is larger than the reduction by initial 120 rpm at 400 and 500 seconds. However, in the case of Percol 1697, the reduction at 1000 seconds is 20-fold, less than 35-fold reduction at 400 seconds. The re-flocculation by

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Percol 63 exhibits the largest reduction in particle number concentration of 100-fold at 400 seconds and 1000-fold at 1000 seconds as shown in Fig. 5.3(b). The re-flocculations occurred by a low stirring rate, 60 rpm, does not appears to be stopped but continue at 1000 seconds.

5.2.3 Floc structure during flocculation under variable shear rates

5.2.3.1 Interpreting floc structure using logarithmic plot of R/T against T

From the findings in the previous sections, the break-up and re-flocculation of polydisperse silica particles have been observed considering the floc size, floc strength and aggregate number changes. In this section, the changes in floc density while the processes of break-up and re-flocculation occur will be discussed.

Floc structures evolve during flocculation. Initially, flocs become larger rapidly as a result of the dominant floc growth. As flocculation continues, the size of flocs increases further, maintaining open structures that are more susceptible to fragmentation by fluid shear. As a result of the balance between floc growth and breakage rates, the steady state is reached. The floc structure in the steady state should be of a more compact structure than the flocs formed initially, although the average size becomes less. If higher shear is applied in this steady state system, floc breakage will be dominant over floc growth. The flocculation process is determined to be either reversible or irreversible, depending on the solution condition or the type of flocculants.

As discussed in the previous sections, silica flocculation describes the reversible process, indicating that the floc fragments generated by high shear become larger flocs with a modified structure when the moderate shear is re-applied. Whether the flocculation process is reversible or irreversible also depends greatly on the kinetics of polymer adsorption. Polymer adsorption is clearly a non-equilibrium process, and due to the multiple polymer segment-particle surface interactions involved, the attachment process is effectively irreversible (Hogg 1999). However, the interaction models shown in Fig. 2.8 (see page. 27) suggest that the flocculation process can be reversible when charge neutralisation is dominant over polymer bridging.

Now consider the logarithmic plots of R/T against T. Note that the term T (=ln V_0/\overline{V} or τL) is employed to described turbidity and plotted here for convenience, since the use of T does not fundamentally affect the analysis of the results. If the


(a) Floc breakage into sub-units from which they were formed (Clustercluster flocculation/breakage)



(b) Floc breakage into sub-units from which they were formed (Particlecluster flocculation/breakage)



(c) Floc breakage caused by surface erosion (refer to case ii)

FIG. 5.6. Schematic diagrams of floc break-up

fractal dimension of the growing aggregates were constant in a certain time interval, the curve is expected to exhibit a positive slope when $d_F < 2$, a roughly horizontal region when $d_F \approx 2$ and a negative slope when $d_F > 2$. It is clear that the plots are not characterised by a constant slope, as might be expected by theory in equation (2.58). A significant feature can be observed in the figures where the plotted curve (line) re-trace the flocculation path. The degree of slope at which the re-tracing follows depends upon the level of stirring rate and the ways in which the aggregate distrupt occur. (refer to Fig. 5.6 for a graphical illustration);

• The line re-traces the flocculation path, showing the same slope. This implies that the flocs break into sub-units from which they were formed (see Figs. 5.6(a)

and (b)).

- The line re-traces the flocculation path, showing a steeper slope and could arise where breakage is not simply the reverse of floc formation. This could be the case if breakage involves some surface erosion of small particles (see Fig. 5.6(c)).
- The line re-traces the flocculation path, showing a less steep slope. It is uncertain as to which systematic process governs this.

At present, there is no satisfactory and accepted model to account for the floc breakage since it is very difficult to interpret in detail this complex phenomenon with large-scale fragmentation as well as surface erosion of small components occurring simultaneously (Glasgow and Liu 1991). The information on the floc density variable with shear rate obtained in this work will provide better understanding in the analysis of flocculation results.

5.2.3.2 Experimental results related to the change in floc structure

This section discusses the results displayed in Figs. 5.3(c), 5.4(c) and 5.5(c). These results were obtained from the same flocculation tests as described in Section 5.2.2.

It has been shown in the previous sections that the addition of polymers lead to flocculation at a low stirring rate, 120 rpm, during the time range of 0-400 seconds (0-500 seconds for the Percol 326 case). Considering the structure of the flocs generated in this period, these flocculations produce quite compact flocs since the curves have a negative slope. The lines appeared in this period are not very straight but curved, indicating that the flocs grow into quite an open structure initially and then becoming more dense later. Spicer and Pratsinis (1996b) reported similar findings in their observation of the dynamic evolution of floc structure with polystyrene particles and aluminum sulfate. Monitoring by image analysis of digitized floc images showed that the parameter-based fractal dimension defined by them increases initially (showing more open structure) and eventually reached a steady state. They suggested that this occurs as a result of shear-induced breakage and/or restructuring. Oles (1992) also observed that increasing the amount of floc breakage increased the floc density but decreased the average floc size. He observed a rapid initial floc growth rate that slowed as floc breakage began to occur. An equilibrium between floc growth and breakage

attributes a leveling off of the floc sizes.

During the application of high shear rates (240 and 300 rpm), the ratio curves shown in Figs. 5.3(a), 5.4(a) and 5.5(a) indicate that the sudden break-up of flocs occurs initially followed by gradual re-flocculation or break-up. Under the same shear conditions, the results shown in Figs. 5.3(c), 5.4(c) and 5.5(c) exhibit behaviour where the direction of the curve is changed when the break-up of flocs is dominant over flocculation in terms of the ratio (the degree of flocculation). When the stirring rate of 240 rpm is applied, a sudden drop, followed by a gradual increase in the ratio is observed indicating that the breakage is dominant only for the first 30 seconds. It can be seen from Figs. 5.3(c), 5.4(c) and 5.5(c) that each drop or increase in the ratio corresponds to an instantaneous change of direction in the log R/T vs. log T curve. Hence, two changes of direction are monitored in each of Figs. 5.3(c), 5.4(c) and 5.5(c)when the strring rate of 240 rpm is used. For the case of using 300 rpm as the stirring rate, only one change of direction can be observed at the point when this occurs the rate is raised to 300 rpm. No further change is detected until about 800 seconds, since after the initial drop in ratio, there is no increasing of the ratio until the stirring rate of 60 rpm is applied.

Another change of direction when the stirring rate is lowered to 60 rpm is due to the occurrence of re-flocculation of broken sub-units.

The previous section showed that molecular weight of polymer has a significant influence on the floc density since flocs generated by Percol 63, the highest molecular weight polymer, exhibit the highest resistance to shear as well as the highest degree of flocculation. It is found that the re-flocculation, following the floc break-up by high shear, does not always lead to the formation of denser structure. The way flocs are broken up and re-flocculated is generally much the same as where they are formed or broken in terms of the slope of the curves in the case of Percol 326 and 1697, while flocs formed in the final stage by the re-flocculation are more compact, showing a steeper slope in the case of Percol 63.

In the following section, results from two different shear schedule conditions will be demonstrated. These schedules are determined based on the results in this section and the tests will be concentrated on the relationship between the degree of flocculation and floc density during the processes of aggregation—break-up—re-flocculation.

5.3 Influence of different shear schedules on silica flocculation

It has been shown in Section 5.2 that varying shear rate have a great effect on various aspects of flocculation, such as the flocculation rate, turbidity and floc properties. In the previous section, the process of flocculation and break-up were mainly represented using by three different polymers. Based on these results, this section concentrates on comparing two flocculations achieved under two different scheduled shear conditions in order to investigate the effect of different variables such as shear and flocculants. The main interests are the restructuring processes during sheared silica flocculation and to verify its effect on the final properties of the flocs generated under different scheduled shear. The applied shear rates in a given time range are shown in Figs. 5.7(a) and (b). As a matter of convenience, shear conditions are divided into two different sets according to their initial stirring rates, which are 60 and 120 rpm and the terms I-60 and I-120 are used to represent these cases respectively. The initial stirring rates are gradually increased to 300 rpm which are then eventually decreased to 60 rpm at the end of the test. Each test is consisted of 4 shear phases; Phase I (initial low stirring rates), Phase II (moderate stirring rate of 180 rpm), Phase III (high stirring rates of 240 and 300 rpm), and Phase IV (final low stirring rate).

The tests were carried out with silica suspension of 400 mg/L, flocculated by Percol series (63, 326 and 1697) using the Set-up A. The polymer concentrations were determined to be around twice the optimum dosages (refer to Figs. 5.1 for the preliminary test results which determine the optimum dosages), and this is expected to result in more rapid due to higher adsorption rate (see equation (2.28)) but smaller changes in the ratio, turbidity (T) and particle number concentration (RPNC). Using the polymer concentration higher than the optimum means that polymers have less influence on flocculation and that the applied shear becomes more dominant as an influential factor. Hence, such changes in the solution condition are expected to lead to clearer exhibition of the shear effect.

It has been shown in the previous sections that (1) silica flocculation is reversible, (2) the effectiveness of flocculation in terms of flocculation rate, turbidity reduction and aggregation number reduction is dependent on the applied shear, and (3) depending on the shear schedules and the flocculants, the degree of flocculation and the final



(a) I-60 case



FIG. 5.7. Stirring rates applied in given time intervals (Section 5.3)

properties of flocs in the last stage may be very different. In this section, the comparison of two different shear schedules applying to the same flocculation condition is mainly concerned and the evolution of floc structure is also considered, based on the calculation of the data such as ratio and log R/T-log T.

5.3.1 Influence of two different shear schedules: Silica and Percol 63

The results in Figs. 5.10 (I-60 case) and 5.11 (I-120 case) were acquired from the tests carried out with 200 μ l of Percol 63 of 0.1% (w/w) solution, which is much higher than the optimum dose of 70 μ l.

• Ratio: Flocculation rate

In Figs. 5.10(a) and 5.11(a), the ratio values increase during Phase I and signifi-

cant drops in the values are observed when high stirring rates of 180 and 240 rpm are applied. The observed decrease in ratio is maintained in Phase II, indicating steady state. After a series of high shears (240 and 300 rpm), a low stirring rate of 60 rpm (or 120 rpm) was employed (Phase IV), which resulted in the ratio increasing above the highest ratio value at the end of Phase I. This indicates a reversible process which shows a high degree of re-flocculation.

The results of I-60 and I-120 cases exhibit almost the same ratio values (about 5.8) at the end of Phase IV (at 1200 seconds). When the two figures representing the ratio are compared in detail, the following differences are observed; (1) the degree of flocculation is greater during Phase I in the I-120 case than the I-60 case, since the initial stirring rate of 120 rpm leads to a steeper initial slope of the ratio curve. The application of 120 rpm for 480 seconds in I-120 case results in the ratio increase of about 5.5 which equals the increase observed in the I-60 case, obtained by applying 60 rpm for 480 seconds, followed by 120 rpm for another 180 seconds (600 seconds in total). (2) Applying a series of high shear (180, 240 and 300 rpm) results in the decreased ratio values. These ratio drops are larger in the I-60 case (about 2.4 rather than 1.8 in the case of I-120) even though time taken for Phase II and Phase III are longer in the I-120 case. (3) The similar ratio values monitored at 1200 seconds indicate that re-flocculation in Phase IV under low shear is more effective in the I-60 case in spite of its shorter application time of low shear.

• T and RPNC: Turbidity and particle number concentration

Although the reduction of the ratio is observed under high shear in the range of 180-300 rpm (i.e. decreased level of flocculation), no significant changes in the turbidity and *RPNC* are found in Figs. 5.10(b) and 5.11(b). The turbidity and *RPNC* continue to decrease slowly, except in the case where the turbidity increased when the stirring rate was 300 rpm in shown Fig. 5.11(b).

Similar to the ratio result where less increase is observed during Phase I of I-60 case than the I-120 case, the turbidity reduction in this period is larger in the I-120 case (65% reduction) than the I-60 case (55% reduction). This trend is also observed in the RPNC results. The RPNC of the I-60 case exhibits 1000-fold reduction in 660 seconds while 1500-fold reduction is observed in the I-120 case. However, the overall reductions in the turbidity and RPNC values in the I-60 case are greater at 1200 seconds, mainly due to a longer decrease in the measured values during the re-flocculation period (Phase IV). The observed overall reductions in turbidity and RPNC at 1200 seconds are 85% and 5000-fold in the I-60 case and 77% and 1500-fold in the I-120 case. It should be noted that in Figs. 5.10(a) and (b) (representing the I-60 case), decrease in turbidity and RPNC occurs at 300 rpm though the ratio in the same period also decreases and the analysis of this observation is uncertain.

• d_F by logarithmic plot of R/T vs T

The results shown in Figs. 5.10(c) and 5.11(c) represent the double logarithmic plot of R/T against T, which are obtained from the flocculation tests carried out using Percol 63 in silica suspension. Fractal dimensions have been derived from the plots and the calculated values are negatively proportional to the slope of the curves. As shown in equation (2.58), as the curve becomes steeper, d_F increases, and this indicates that the floc structure becomes more compact. Photos shown in Figs. 5.8 present silica flocs observed at the end of each phase in I-60 case. As shown in the figures, there are many small flocs and various floc sizes are observed. These cause the comparison of two cases (I-60 and 120) to be very difficult although these photos still give the representative shape and size of the formed flocs. Considering the floc size, flocs shown in (b) and (e) figures are much larger than those in (c) and (d) figures, indicating significant amount of break-up re-flocculation.

Phase I represents the initial stage of flocculation by low stirring rates in Figs. 5.10(a) and 5.11(a). (660 seconds for the I-60 case and 480 seconds for the I-120 case). As can be seen from the figures, the slope of the curves in this period changes. In the I-60 case, the derived d_F is 2.2 for the first 480 seconds where the stirring rate is 60 rpm. Then the stirring rate is increased to 120 rpm, which results in the curve becoming steeper. The derived d_F value is almost 3 in the time region of 480–660 seconds, and implies the formation of more compact floc structure due to high shear rate. In the I-120 case, despite applying one stirring rate of 120 rpm, Phase I is also divided into two regions, 60 to 250 seconds and 250 to 480 seconds. The derived fractal dimensions for the time range of 60–250 seconds

and 250-480 seconds are found to be 2.3 and 2.8. According to equation (2.56), the ratio value depends on the aggregation number and the fractal dimension of the floc and is dependent on the size of flocs. According to Table 5.1, the high ratio value can be achieved with the low fractal dimension indicating loose structure and high aggregation number (\bar{k}) which is proportional to the *RPNC*. At the end of Phase I, the obtained values agree with this since the higher d_F , and the lower *RPNC* in the I-60 case than I-120 case result in the same ratio.

$\overline{d_F}$	1.2	1.5	1.8	2.0	2.3	2.5	2.8	3.0
const. R	$\overline{k}^{1.167}$	$\overline{k}^{0.833}$	$\overline{k}^{0.611}$	$\overline{k}^{0.500}$	$\overline{k}^{0.370}$	$\overline{k}^{0.300}$	$\overline{k}^{0.214}$	$\overline{k}^{0.167}$

TABLE 5.1. Relationship between ratio and d_F based on equation (2.56)

In Phase II where the stirring rate of 180 rpm is introduced, the ratio exhibited a drop in the value initially followed by a slower increase (as shown in Fig. 5.10(a) and 5.11(a)). At the point at which the ratio curve exhibits sudden decrease in the degree of flocculation, the curve in Fig. 5.10(c) changes its direction, displaying a positive slope, though the changes are very complex to investigate in detail. The possible structural model applicable to these change is the particle-cluster re-flocculation followed by cluster-cluster break-up after the introduction of the increased shear rate (refer to Fig. 5.9).

The direction of the log-log curve can be said to be very much dependent upon the changes in the ratio curve since the direction of the curve shows an upward (or downward) movement when the ratio curve represents the change from increase to decrease (or from decrease to increase). During Phase III, where the high shear rates of 240 and 300 rpm are applied in succession, the direction of the curve is changed again, and with even steeper slope. In the I-120 case shown in Fig. 5.11(c), the direction of the curve displays a downward movement and then a steep upward movement of the curve is observed. These curves bending during Phase III may be due to sudden changes in suspension such as structural changes. Although the change of direction in the curve is clearly observed, the analysis of data is hampered by the fluctuations, especially in I-120 case.

During Phase IV, the curve follows the behaviour exhibited at the end of Phase I and the shape of the curve gradually becomes steeper with the decreased stirring

rate (60 rpm in the I-60 case or 120 and 60 rpm in succession in the I-120 case). The re-flocculation occurred in this period generate flocs with almost the same compactness as those produced at the end of Phase I. The derived fractal dimensions are about 3 in the I-60 case and 2.8 in the I-120 case. It can be said that more effective flocculation in terms of the flocculation rate and the turbidity reduction occurs in the I-60 case.



(e) after re-flocculation

FIG. 5.8. Photos of silica flocs taken during flocculation test by Percol 63 (I-60 case)



FIG. 5.9. Possible structural change during Phase II



(c) Logarithmic plot of R/T against T

FIG. 5.10. Effect of initial stirring rate on silica flocculation by Percol 63 with stirring rate starting at 60 rpm (I-60 case); 400 mg/L silica suspension flocculated by 200 μ g/L Percol 63 in the Set-up A



(c) Logarithmic plot of R/T against T

FIG. 5.11. Effect of stirring rate on silica flocculation by Percol 63 with stirring rate starting at 120 rpm (I-120 case); 400 mg/L silica suspension flocculated by 200 μ g/L Percol 63 in the Set-up A

5.3.2 Influence of two different shear schedules: Silica and Percol 326

The experiments were carried out with Percol 326 of 0.1% (w/w) with 1000 μ l volume, which is twice the optimum. As observed in Section 5.2.2, Percol 326 produced a lower degree of flocculation, compared to that by Percol 63.

• Ratio: Flocculation rate

The changes in the degree of flocculation are represented in Figs. 5.14 (for the I-60 case) and 5.15 (for the I-120 case). In Phase I, the increase in the ratio is faster with a higher stirring rate (120 rpm) than with 60 rpm as expected with equation (2.23) though the peak value at 480 seconds is higher in the I-60 case than in the I-120 case. The drop in the ratio is instant in the I-60 case when the stirring rate is increased to 120 rpm at 480 seconds. This indicates that the initial stirring rate of 60 rpm produces flocs with low strength. This aspect will be discussed further in the following sections regarding the calculated fractal dimensions.

In Phase II and Phase III, introducing high shear over 180 rpm resulted in sudden drops in the ratio, and the decreasing trend remained during the application of the shear. This is in contrast to the Percol 63 case where the steady state in terms of the ratio was maintained for a while after instant drops by high shears. The lower strength of flocs with Percol 326 may be responsible for the ratio decrease at high shears. Similar to the previous section, reversible flocculation is also demonstrated in Phase IV but with less effective re-flocculation than in the Percol 63 case. The ratio value, which goes up again at 60 rpm, does not reach the maximum achieved in Phase I, i.e. applying a lower shear rate gives the higher degree of re-flocculation. As observed in the Percol 63 case, the steeper increase in the ratio is observed in the I-60 case than in the I-120 case.

It should be noted that, the appearance of some peaks on the ratio curve in between 780 and 900 seconds in Fig. 5.14(a) (and the later stage in Figs. 5.10(b) 5.11(b) in the previous sections) is thought to be not due to the changes in the degree of flocculation, but probably due to the passage of occasional large flocs through the light beam in the measuring tube (refer to Figs. 4.20). The photos of the flocs produced are taken during Phase III, and Fig. 5.12 represents the presence of very large flocs as well as the very small flocs rather than flocs of the similar size even though the analysis and characterisation of the period is so difficult due to various characters of the existing flocs.



FIG. 5.12. Photo of silica flocs taken during Phase III

• T and RPNC: Turbidity and particle number concentration

For the case of Percol 63 in the previous section, the turbidity usually decreased even if the rate of flocculation is reduced. However, in Figs. 5.14(b) and 5.15(b), an increase in the turbidity is clearly observed in Phase III indicating further break-up due to lower strength of flocs formed in Phase I and II. The reduction is about 47% at the end of Phase III in both the I-60 and I-120 cases but in Phase IV (re-flocculation period), a slightly greater reduction of 59% is observed in the I-120 case than in the I-60 case. These figures also show that the reductions in the particle number concentration are 200-fold at the end of Phase I and 125fold at the end of Phase IV in the I-60 case, and 290-fold at the end of Phase I and 125-fold at the end of Phase IV in the I-120 case. During Phase IV, the Percol 326 cases represents smaller reductions in turbidity and particle number concentration, indicating less re-flocculation than the previous Percol 63 case.

• d_F by logarithmic plot of R/T vs T

The results shown in Figs. 5.14(c) and 5.15(c) represent the plot of log R/T against log T obtained from the flocculation tests carried out using Percol 326 in silica suspension.

During Phase I, it has been shown in Fig. 5.14(a) that the ratio of the I-60 case



FIG. 5.13. Possible structural change during Phase I

increases for the first 480 seconds, followed by the sudden decrease in the value when the stirring rate was increased to 120 rpm. The logarithmic plot in the same period in Fig. 5.14(c) shows that the curve gradually decreases for the first 480 seconds, and then becomes very steep when the stirring rate of 120 rpm is applied. The derived fractal dimensions are 2.22 for the first 480 seconds and 2.75 between 480 and 660 seconds. In the I-120 case, an initial increase in the ratio value occurs dramatically, followed by the steady state from 360 to 480 seconds (as shown in Fig. 5.15(a)) and Fig. 5.15(c) depicts the curved plot in the same period, from which the fractal dimensions of 2.22 for the first 250 seconds and 2.75 for the remaining part of Phase I, are evaluated. The small change in ratio shown in I-120 case may be due to the continuous break-up and re-flocculation followed by the surface erosion by the introduction of the increased shear rate (refer to Fig. 5.13).

From the results shown in Figs. 5.14(a) and 5.15(a), it was found that the silica-Percol 326 flocs, when exposed by the stirring rate of 180 rpm, are likely to be broken up and the dominant break-up is observed in Fig. 5.14(c) and 5.15(c) during Phase II. The curve shows the vertical shape in the I-60 case (see Fig. 5.14(c)) while I-120 case shows that the curve traces with the derived fractal dimension of 2.65 (see Fig. 5.15(c)). During Phase III, Fig. 5.14(c) exhibits the curve tracing the behaviour of Phase I, and the calculated fractal dimension=2.75 which again is almost the same as that achieved in Phase I. The changes in the curve direction occur more often in the I-60 case than in the I-120 case. This is because of the observed spikes in the ratio at the points due to the very large flocs (see Fig. 5.12 for the example of the photo evidence) passing through the light beam when the increased stirring rates are introduced during Phase II and III (as shown in Fig. 5.14(a)).

As re-flocculation occurs with the re-applied low stirring rates during Phase IV, the curves also take up their original direction. The structures of flocs in both the I-60 and I-120 cases are thought to be very compact, having the derived fractal dimensions of 2.76 and 2.95 respectively. However, compared to the floc compactness achieved in Phase I, flocs generated at 1200 seconds in the I-120 case became denser whereas similar floc density ($d_F=2.75$ at the end of Phase I) is observed at the end of test in the I-60 case.



(c) Logarithmic plot of R/T against T

FIG. 5.14. Effect of stirring rate on silica flocculation by Percol 326 with stirring rate starting at 60 rpm (I-60 case); 400 mg/L silica suspension flocculated by 1000 μ g/L Percol 326 in the Set-up A



(c) Logarithmic plot of R/T against T

FIG. 5.15. Effect of stirring rate on silica flocculation by Percol 326 with stirring rate starting at 120 rpm (I-120 case); 400 mg/L silica suspension flocculated by 1000 μ g/L Percol 326 in the Set-up A

5.3.3 Influence of two different shear schedules: Silica and Percol 1697

The tests were carried out using Percol 1697 of 0.1% (w/w) with the amount of 1400 μ l, which is twice the optimum dose.

• Ratio: Flocculation rate

As shown in the results presented in Section 5.2.2, Percol 1697, which has the high charge density and the low molecular weight, leads to much lower ratio values compared to the results by the other polymers. The obtained results are plotted in Figs. 5.16(a) and 5.17(a).

The peak ratio values achieved at the end of Phase I are higher in the I-120 case ($\simeq 2.4$) than in the I-60 case ($\simeq 2.0$) even though the low stirring rates were applied longer in the I-60 case (60 and 120 rpm in succession for 660 seconds). The ratio decrease during the high shear application (180 to 300 rpm) occurs almost immediately after a stirring rate steps up. During re-flocculation by the low shear rates, the ratio in the I-120 case does not increase greatly within the given times of 180 (1020-1200 seconds in the I-60 case) and 300 seconds(900-1200 seconds in the I-120 case). In both cases, the values obtained at 1200 seconds are almost the same as the value achieved in Phase I and the ratio is expected to increase continuously even after 1200 seconds, thus the final degree of re-flocculation would be much higher indicating the effective re-flocculation during the Phase IV. Percol 1697 has high charge density and low molecular weight, and in this case, the charge neutralisation is the dominant aggregation mechanism. Unlike high molecular weight polymer whose long chains adsorbed on the particle surface, causing particle bridging, are not reproducible from the breakage, re-flocculation is likely to occur due to the reduced repulsive force between particles or broken flocs in the case of Percol 1697.

• T and RPNC: Turbidity and particle number concentration

Similar to the ratio case where a slight difference in the ratio values at the end of Phase I and at 1200 seconds is observed, the difference in the turbidity reduction is also not very significant. In Phase I, the initial flocculation in the I-60 case resulted in the 17% turbidity reduction while 24% reduction is observed in the I-120 case. These values are relatively low compared to the Percol 63 and 326 cases. Re-flocculation in Phase IV led to almost the same reduction to that achieved in Phase I. As observed in the results representing the ratio, the turbidity continues to decrease even at 1200 seconds for both cases (as shown in Figs. 5.16(b) and 5.17(b)).

Since a slightly greater decrease in turbidity of I-120 case than in the I-60 case is observed, the overall reduction in the RPNC is more pronounced in the I-120 case. The obtained reductions in the particle number concentration are 7-fold at the end of Phase I and Phase IV in the I-60 case while the I-120 case exhibits 125-fold drop at the end of Phase I and 143-fold at 1200 seconds. Finally the RPNC curves also continue to decrease at 1200 seconds. The obtained result agrees with the observation of Ditter et al. (1982), who reported that the higher shear sensitivity observed with a higher charge density polymer may be due to the predominance of electric patch attraction over polymer bridging mechanism, thereby conferring a more or less constant formation, break-up, re-formation of floc structure under sheared conditions. More on this matter will be mentioned later in discussion in Section 5.3.4.

• d_F by logarithmic plot of R/T vs T

The results shown in Figs. 5.16(c) and 5.17(c) represent the plot of log R/T against log T obtained from the flocculation tests carried out using Percol 1697 in silica suspension.

From the slope of the curves in the I-60 and I-120 cases, the fractal dimensions of flocs generated in Phase I are calculated to be about 2.17 and 2.21 respectively. The curve in Fig. 5.16(c) becomes steeper when the increased rate of 120 rpm is applied and the obtained fractal dimension increases to 2.45. However, the curve in Fig. 5.17(c) decreases at a slower rate, and consequently at 480 seconds, d_F is found to be 2.32.

The ratio shown in Fig. 5.16(a) which corresponds to the I-60 case, increases slowly until the stirring rate of 180 rpm is applied where a sudden drop in the ratio is observed, and during Phase II, the ratio increased again. However, the ratio shown in Fig. 5.17(a) (I-120 case) continued to decrease after the application of 180 rpm stirring rate. These changes in the behaviour of the ratio values can

be correlated to the change of direction in the log R/T vs log T curves. During Phase III, the curves re-trace until the low stirring rates (60 or 120 rpm) are re-applied. The re-traced curves have the similar slope to that achieved during Phase I, and exhibit the fractal dimensions of about 2.45 and 2.32 for the cases of I-60 and I-120, respectively.

During Phase IV, the curves re-trace in the same direction to the curve of Phase I, with a slightly steeper slope. The derived fractal dimensions of flocs during this re-flocculation period are 2.46 (I-60 case) and 2.5 (I-120 case). These values are relatively low compared to the others obtained with Percol 63 and 326, although the obtained fractal dimensions in Phase I are almost the same.



(c) Logarithmic plot of R/T against T

FIG. 5.16. Effect of stirring rate on silica flocculation by Percol 1697 with stirring rate starting at 60 rpm (I-60 case); 400 mg/L silica suspension flocculated by 1400 μ g/L Percol 1697 in the Set-up A



(c) Logarithmic plot of R/T against T

FIG. 5.17. Effect of stirring rate on silica flocculation by Percol 1697 with stirring rate starting at 120 rpm (I-120 case); 400 mg/L silica suspension flocculated by 1400 μ g/L Percol 1697 in the Set-up A

5.3.4 Discussion

The flocculation rate, ratio varies depending on shear rate applied in various time interval. Two different shear schedules, I-60 and I-120, lead to disparity between the cases at the same moment. (1) Taking the results obtained at the end of test into account, two different shear schedules lead to almost same level of flocculation rates eventually at 1200 seconds although RPNC shown in the figures indicates that the floc properties in two cases are different since aggregation numbers (k) derived using the gap between the initial and final RPNC values (refer to Section 4.1.1) are higher in the I-120 case when Percol 63 and 326 were used and the same when Percol 1697 was applied. (2) Generally, applying 120 rpm for 480 seconds leads to more effective flocculation than applying 60 rpm and 120 rpm for another 220 seconds in terms of the achieved ratio, T and RPNC. (3) Flocs formed during Phase I and II by Percol 326, the lowest charge density polymer, are observed to have lower floc strength than those by the other polymers since the break-up rate based on *RPNC* in Table 5.3 is higher than the others when the high shear rate during Phase III is applied. (4) Charge neutralisation plays a dominant role on aggregation of particles since the re-flocculation occurs with downgrading shear rate. However, it is problematical to compare the reflocculation degree in quantitative manner since the each case shows different break-up rate.

		Т	reduction	RPNC	reduction
Polymer type	Shear schedule	Phase I	Phase IV	Phase I	Phase IV
Percol 63	I-60	55%	55%	1000-fold	5000-fold
	I-120	65%	77%	1200-fold	2000-fold
Percol 326	I-60	52%	49%	200-fold	125-fold
	I-120	60%	59%	290-fold	125-fold
Percol 1697	I-60	17%	16%	7-fold	7-fold
	I-120	24%	32%	125-fold	143-fold

TABLE 5.2. Reductions in T and RPNC during Phase I for initial flocculation and IV for re-flocculation

Table 5.3 lists the calculated d_F in the regions where it can be derived. All flocs generated in the initial stage have almost the same density, having d_F of about 2.2. The initially formed floc structure becomes more compact under one or two moderate shears. Although the polymers produced similar level of fractal dimension in the early stage regardless of the type of polymer, it is observed that the floc structure can be affected by the shear schedule since the obtained fractal dimension is higher in the I-60 case when Percol 63 and 1697 were used and lower in the I-60 case when the other polymers were added.

Polymer type & shear condition		(1) Calculated d_F (interval in seconds)	(2) Break-up rate during Phase III	
Percol 63				
I-60 case	2.20 (60-480)	about 3 (480-660)	about 3 (1020-1200)	40%
I-120 case	2.30 (60-250)	2.80 (250-660)	2.80 (960-1200)	62%
Percol 326				
I-60 case	2.22 (60-480)	2.75 (480-660)	2.76 (1020-1200)	75%
I-120 case	2.22 (60-250)	2.75 (250-660)	2.95 (960-1200)	98%
Percol 1697				
I-60 case	2.17 (60-480)	2.45 (480-660)	2.46 (1020-1200)	64%
I-120 case	2.21 (60-250)	2.32 (250-660)	2.50 (960-1200)	64%

TABLE 5.3. Floc properties in initial and final stage; (1) fractal dimensions derived from the various time ranges and (2) break-up rate, based on *RPNC*, during Phase III

According to the floc formation mechanism proposed by Langer et al. (1994), the higher the charge density of a cationic polymer, the more stable are the flocs and the more energy required to destroy the floc structure. In this result, during the break-up process by high shears (180–300 rpm), flocs produced by Percol 1697, which has the highest charge density, experiences less floc breakage than the Percol 326 case but it is Percol 63 which leads to the least breakage, lower than the Percol 1697 case when the floc breakage is considered based on the RPNC. In Section 2.4.3, it is mentioned that flocs by bridging used to lead to high floc strength than by charge neutralisation. The capability of both adsorption processes of Percol 63 may lead to the higher floc strength due to the combined bridging and charge neutralisation.

5.4 Summary

Monitoring flocculated suspensions using turbidity fluctuation technique has been performed to show the influence of flocculation kinetics. As for the applied shear conditions, the main interests is on the effect of the break-up and re-flocculation by shears variable with time.

From the results presented in this chapter using stirring rates variable in each time interval, the following are observed.

(1) flocculation of poly-disperse silica particles by Percol series is a reversible flocculation since the particles are re-flocculated after a significant break-up by the increased shear rate.

(2) During the break-up and re-flocculation, the density of the flocs is found to remain constant since the re-tracing lines of logarithmic plot of R/T against T during the same period can be mostly described by the same slope. There are some periods in which the curve has a positive slope before it takes the opposite direction to re-trace. These transition periods are usually found when a relatively moderate stirring rate, 180 rpm (often including 120 and 240 rpm), is applied. However, the slope found in these areas do not provide much information on floc structure by itself. Therefore, d_F derived from the following slope in the stage of dominant breakage (Phase III) or re-flocculation (Phase IV) has only been used to give relative information on floc structure. Except for the transition periods, there is no significant difference between the initial slopes (at 120 rpm) and the slopes of the re-traced curves (usually at 240 and 300 rpm). This implies that the sub-units of similar densities are separated and re-flocculated and silica flocs may break into sub-units from which they were formed.

(3) It is also found that the re-flocculation followed by the break-up can still produce the compact flocs, which indicates that flocculation of silica particles are carried out mostly by charge neutralisation and re-flocculation is made possibly by the reconfiguration of adsorbed polymers on particle surfaces (This also applies to (1)).

(4) The properties of polymers used in the experiments have little effect on the floc density at the initial stage of flocculation. Regardless of their properties, very similar fractal dimensions are obtained. However, the flocs formed initially become more compact and have different densities after a series of various high shear. This may depend on the stirring rate and the polymer properties but the correlation between d_F and polymer properties or the initial stirring rate has not been found. Flocs generated in re-flocculation become more compact than the flocs in the very initial stage, as indicated by the different fractal dimensions.

Chapter 6

Conclusions

6.1 Summary

6.1.1 Measurement technique

The fundamental principles of the experimental techniques have been discussed in Section 2.6 and the monitoring methods have also been described in Section 3.2.1. The use of the light transmission technique has been well examined in previous works (Gregory and Chung 1994). While suspension is being flocculated, ratio and dc (or V) are obtained directly from the monitoring measurement. The dc is the voltage that survives after light passes through a suspension and turbidity can be derived from the obtained dc value using equation (2.38). The ratio and dc values respond in different ways as flocculation occurs, depending on conditions.

According to equation (2.57), $(R/\tau)^2$ indicates aggregation number, \overline{k} which is inversely proportional to particle number in the suspension and, hence, the values of $(T/R)^2$ should increase or decrease proportionally to particle number concentration. The value before adding flocculants is multiplied to give 100. The values during flocculation are multiplied by the same factor. The converted values are *RPNC* and are plotted against time.

The values of log R/T and log T are plotted against each other and the the curve generally contains straight regions indicating constant fractal dimension of the growing flocs. The slope of the curve is converted to d_F using equation (2.58) which corresponds to $d_F = 4/(2 + s)$ where s is a slope of a linear region of the curve. If the obtained slope is negative (or positive), $d_F > 2$ (or < 2). The present work was carried out in order to measure the floc properties using the light transmission technique since the obtained properties are important to understand how polymeric flocculants and shear conditions play a role in determining the optimal flocculation conditions depending on the purpose of the water treatment. The represented experimental results show that a simple pre-test routine under standard conditions, and the main experimental procedure to analyse and characterise the flocculation behaviour, can both be used to determine the effect of the solution and hydraulic conditions.

6.1.2 Effect of shear rate on flocculation

Flocculation of poly-disperse silica particles by Percol series is a reversible flocculation since the particles are re-flocculated after a significant break-up by the increased shear rate. The re-flocculation following the break-up can still produce the compact flocs. This implies that the separated sub-units by re-flocculation form flocs at a similar level (or higher) of fractal dimension at which they were formed during breakage/reflocculation of silica flocs. This indicates that flocculation of silica particles is caused mostly by charge neutralisation or the re-configuration of adsorbed polymers on particle surface make re-flocculation possible.

When the higher or lower shear rate is introduced into a stirred suspension, the density of the flocs remains constant since the re-tracing lines of logarithmic plot of R/T against T during the same period can be mostly described by the same slope. This implies that the sub-units of similar densities are separated and re-flocculated and silica flocs may break into sub-units from which they were formed.

The properties of polymers have little effect on the floc density at the initial stage of poly-disperse silica flocculation while they play an important role on the flocculation rate. Regardless of their properties, very similar fractal dimensions are obtained. The flocs formed initially become more compact and have different densities after a series of various high shear. Although the floc density is very dependent on the stirring rate, the correlation between d_F and polymer properties or the initial stirring rate has not been found.

When a single stirring rate is employed with latex particles and cationic polymers during a test, high shear rate were usually associated with the high degree of flocculation and the compact floc structure. However, the increased flocculation rate leads to steady state and the floc density becomes higher through the continuous aggregation and break-up. The higher shear rate leads to higher floc density since the strength of shear and flocs balances and small, compact flocs are more endurable.

Fractal dimensions by other studies are listed in Table 6.1 with the used materials and system.

6.1.3 Effect of solution conditions on flocculation

Large amount of the standardised pre-tests are usually required prior to the main experiments to obtain the general idea on the relationship between specific polymer and particles. Each polymer and particle has its own concentration range which includes the maximum flocculation rate. The concentration giving the highest maximum rate (ratio value), is called optimum concentration for convenience. This is related to the interaction between the particle surface and the polymer segment which has different mechanism depending on the polymer/particle properties.

Molecular weight and charge density of polymer has a great effect on the flocculation rate. The flocculation rate increases with molecular weight and decreases with charge density. Charge density and polymer concentration play an important role on the speed of flocculation process. The higher the charge density or the polymer concentration is, the faster the steady state is reached. This may be due to the nature of adsorption mechanism in which charge neutralisation (or electrostatic patch) is dominant over polymer bridging. Charge density also affects the polymer concentration required to generate optimum flocculation and the higher amount is required to be the optimum concentration in the case of low charge density. While the critical coagulation concentration (c.c.c.) is found in aggregation by electrolyte, the flocculation rate decreases significantly in the excess of the polymer dosage over the optimum concentration which demonstrates the highest maximum ratio in given time. Steric interaction or the local overdosing in the case of polymers with high molecular weight may cause this.

It was observed that the presence of dissolved salt could change polymer concentration distribution as well as the maximum ratio. When polymeric flocculation of latex particles is monitored in different electrolyte concentration, the optimum concentration increases with the concentration of dissolved salt. The electrolyte concentration below the c.c.c. could enhance latex flocculation in terms of the degree of flocculation (ratio). This trend becomes more significant in the case of polymer with low charge density.

6.2 Suggestions for further work

The present experimental investigation has provided information on flocculation rate and floc density using turbidity fluctuation technique. The following suggestions emerge from the present research and should be examined more closely in future work.

Prior to the main experiments, it is necessary to perform considerable amount of pre-tests to obtain the polymer concentration range which demonstrates the relationship between polymer concentration and the degree of flocculation. Each polymer has its own effective concentration range depending on their properties.

When flocculation occurs, various shapes of aggregates are formed from the earliest stage and the number of possible structures rapidly increases. In microscopic observation, there are significant small flocs still existing in the later stage. Therefore, some values obtained in this study such as RPNC and fractal dimension can not be applied to the specific flocs collected for microscopy but stand for the averaged quantity though this technique is still very useful to monitor flocculation with simple procedures. For further analysis of this complicated structural changes, the combined use of digital imaging of flocs or particle counting for floc size distribution will be required.

Primary particles used in this study have size ranges much larger than conventional size range of colloidal particle (1-1000 nm) and the flocs monitored in this study becomes very large and/or dense in relatively short time (within 300-500 seconds). When the volume of flocs increases into a certain degree, the flocs can block the effective cross-sectional area completely from the transmitted light regardless of the floc density. Inaccurate result can be caused in the later stage where flocs become large and the use of smaller particles is recommended for modelling purpose.

TABLE 6.1. Fractal dimension in colloidal systems

Fractal dimension	Literature
$\overline{1.79 - 2.25^a}$	Johnson et al. (1996)
(1) $1.59 - 1.68$ (2) $1.89 - 1.92^{b}$	Logan and Klips (1995)
$1.39 - 1.52^{c}$	Logan and Wilkinson (1990)
$1.28 - 1.86^{d}$	Kilps et al. (1994)
$1.4 - 2.85^{e}$	Li and Ganczarczyk (1989)
2.3^f	Amal et al. (1990)
$1.25 - 1.5^{g}$	Gardner et al. (1998)
$1.5 - 1.9^{h}$	Clark and Flora (1991)
$1.83 - 1.97^{i}$	Huang (1994)
(1) 2.25 (2) 2.52^{j}	Jung et al. (1996)
(1) $1.43-2.08$ (2) $1.77-1.83^k$	Jiang and Logan (1996)
(1a) 1.87 (2a) 1.68 (3a) 1.75 (3b) 2.2^{l}	Zhang and Buffle (1996)
(1) 2.1 (2) 2.5^m	Spicer et al. (1998)
(1) $1.8-1.9$ (2) $2.2-2.8^{n}$	this study

^a0.87 and 2.6 μ m latex spheres destabilised with NaCl solution and flocculated in flat paddle mixer at 5 s⁻¹; d_F measured by an aggregate cross-sectional area and the number of particles in the aggregate (d_F varies with mixing time)

^b0.92 μ m latex spheres in (1) rolling cylinder, and (2) paddle mixer, assumed to be completely destabilised; d_F measured by aggregate property scaling, steady state size distributions, and dual-instrument multiple-size distribution techniques

^cMarine snow; d_F determined by size-porosity and settling velocity data collected by others. The assumption was made that differential settling was dominant among collision kinetic mechanisms

^{*d*}Marine snow; d_F by microscope and image analysis

^eAggregates from sludge, alum, iron, clay and mixtures; Analysis of data collected by others on settling rates and size-density relationships

^fHematite particles destabilised with salt; d_F estimate assumes that aggregate size (R) is proportional to time as $R \propto t^{1/d_F}$. d_F estimated by curve fitting

 g 0.07 μ m hematite spheres with no applied shear; d_{F} Estimated by fitting Smoluchowski equation to experimental aggregation data

^h0.36 μ m latex spheres flocculated with aluminum sulfate in Rushton vessel with a six-blade diskmounted turbine; d_F determined by microphotographic analysis

ⁱNatural sediment of size range $0-10 \ \mu m$ flocculated in Couette-type flocculator; Estimation by settling speed measurement

^jIron hydroxide flocculated by the hydrolysis of FeCl₃ solution in a vessel equipped with a motor driven stirring unit; d_F determined by small-angle light scattering

^k0.92 and 0.83 μ m latex particles fully destabilised with salt. Aggregates generated in (1) Couette reactor and (2) paddle mixer; d_F by estimated using the two-slope method applied to cumulative size distributions measured by electrical resistance

¹0.025 μ m hematite in (a)DLA, (b)RLA conditions; d_F measured by (1) dynamic light scattering, (2) TEM image analysis, (3) static light scattering.

^mRestructured flocs of 0.87 μ m mono-disperse polystyrene spheres in a baffled, stirred tank (1) small and (2) large structure; Small-angle light scattering method

ⁿ(1) 1.5 μ m kaolin and (2) 1.7 μ m latex particles flocculated by cationic polymers in stirred vessel; d_F determined by turbidity fluctuation technique

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