INFLUENCE OF DISSOLVED SILICA ON FLOCCULATION OF CLAY SUSPENSIONS WITH HYDROLYSING METAL SALTS

A thesis submitted to the University of London for the degree of Doctor of Philosophy

by

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To my wife, MinHua
and my daughter, MuBing
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ABSTRACT

Silicic acid or dissolved silica exists abundantly in natural waters. Hydrolysing metal salts such as aluminium sulphate and ferric chloride are widely used coagulants in the water industry. Interactions between the metal ions, such as Al$^{3+}$ and Fe$^{3+}$, and silicic acid in aqueous solution have been reported over wide concentration ranges. At typical concentrations in water, the presence of dissolved silica could exert some effects on flocculation of particles by these hydrolysing metal salt coagulants.

Using a standard flocculation set-up equipped with a Photometric Dispersion Analyser (PDA), coupled with Electrophoretic Mobility (EM) measurements of the suspended particles, the influence of dissolved silica on the flocculation of kaolin suspension has been investigated. The precipitation of aluminium has also been examined with and without the presence of dissolved silica in order to explain the observed effect.

The results showed that the presence of dissolved silica could either improve or prevent the flocculation depending on silica concentration, solution pH and coagulant concentration. These effects can be attributed to the interactions between aluminium and dissolved silica, which alters electric charge of dissolved aluminium hydrolysis species, modifies the colloidal properties of the precipitate and hence affects the aggregation of the primary precipitate particles. Therefore, at low coagulant dosage, the influence of dissolved silica will be characterised by the charge modification of aluminium hydrolysis products; while at high coagulant dosage, the influence will depend on the precipitation. When the interactions promote the aggregation of primary precipitate the flocculation will be improved; while the interactions prevent such precipitation process the flocculation will be prevented. It has been found that the effect of dissolved silica is much more sensitive at high pH (e.g., 8), which corresponds the isoelectric point of aluminium hydroxide. At this pH, flocculation can be readily prevented at low levels of dissolved silica (e.g., 10-20 mg/L). The effect of common ions, such as calcium, on aggregation of kaolin with aluminium salts in presence of dissolved silica is also examined.
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CHAPTER ONE

INTRODUCTION

1.1 Research Background

Coagulation and flocculation are very important in solid-liquid separation processes, which are widely used in water and wastewater treatment processes (Bernhardt and Schell 1993; Bratby 1980; Camp 1955; Dentel 1991; Graham 1986; Gregory 1983, 1989; Ives and Bhole 1973; Faust and Aly 1983; Tambo and Watanabe 1979). Generally, coagulation is defined as the destabilisation of colloids after addition of metal salts (coagulants) in waters and the subsequent primary growth of aggregates; whereas flocculation is designated as the growth of the aggregates (flocs) after the stage of destabilisation (Bratby 1980). Since stability of colloids largely depends on factors, such as, interfacial properties of colloids and solution chemistry, coagulation is essentially a physico-chemical process. On the other hand, flocculation, which mainly concerns the dynamic conditions of aggregate growth, such as mixing time and conditions, etc., is more like a physical process. In some case, for convenience of discussion, the term of flocculation could cover the whole process through destabilisation to aggregation (Gregory 1989).

In solid-liquid separation processes, such as filtration, flotation, and sedimentation, effective removal of impurities or colloids can only be obtained after the destabilisation and aggregation of the colloids, and in many cases large aggregates have to be formed. In order to destabilise the colloids and to promote aggregation of particles, in the water treatment process, electrolytes or coagulants are added to raw waters. Among the coagulants, metal salts, such as aluminium and ferric salts, are most commonly used around the world (Bratby 1980, Dentel 1991).
Chapter 1 Introduction

There has been extensive work done in studies on the coagulative behaviour of these coagulants (Ching et al. 1994 a and b, Matijevic 1973, O'Melia and Stumm 1967, Stumm and O'Melia 1968). The influence of solution chemistry on the metal salts coagulation has also been studied (Marion and Thomas 1946, Letterman et al. 1979). From these studies, the mechanisms of coagulation of colloids by the hydrolysable metal ions can be generally understood.

The mechanisms of coagulation by the hydrolysable metal salts are closely related to the hydrolysis reactions and precipitation of these metal ions. This is because various kinds of dissolved hydrolysis species and even precipitates can form in aqueous solution or suspensions due to these reactions. These species and precipitates play an important part in the coagulation process (Matijevic 1973, Stumm and O'Melia 1968). Therefore, any influences which affect these hydrolysis reactions and/or precipitation will change the coagulative properties of these metal ions. Generally, the speciation of these metal ions and their precipitation in aqueous solution is dependent on concentration of the metal ions, solution pH, and even solution chemistry. Presence of impurities or particles in solution might also affect this process.

The mechanisms of coagulation by hydrolysing metal ions can be characterised by adsorption of these hydrolysis products on to surfaces of colloidal particles, or by deposition of precipitates, or by heterocoagulation between particles and precipitates, or even by enmeshment of colloids by precipitates depending on the concentration of added metal salts. Since these metal ion hydrolysis products are observed to be adsorbed more readily than simple metal ions, the coagulation behaviour does not follow the simple model of double layer compression described by the DLVO theory in case of indifferent electrolytes at a low level coagulant dose (Matijevic 1973). While at a high dose of the coagulant, coagulation may be dominated by formation of precipitates.

There have been several models in describing the destabilisation or coagulation mechanism of colloids by these metal ions (Dentel 1991, Farley et al. 1985, Stumm
1992, Stumm and Morgan 1996). Among them are surface adsorption, surface precipitation, and precipitation charge neutralisation, etc. The surface adsorption and surface precipitation models describe the ways in which the metal ions species were absorbed on particle surfaces through co-ordination chemistry, while the precipitation and charge neutralisation model explain the general adsorption process of these species with emphasis on the charge neutralising effects on coagulation based on the practical water treatment process.

The effects of solution chemistry on coagulation has been focused on the influence of some anions on coagulation (Marion and Thomas 1946, Letterman and Vanderbrook 1983). The general observation of these effects is to shift the optimum range of pH for coagulation. These effects are suggested to be related to the competition of bonding between metal ions and hydroxyl and these anions. Modification of the metal ions hydrolysis reactions are also suggested by presence of certain anions. These studies could allow a general understanding of the solution effects on coagulation.

However, the mechanisms of coagulation by metal ions and effects of solution chemistry are still not entirely clear. This is especially true in case of influences of solution chemistry on coagulation. Following a development of a simple optical technique in monitoring the aggregation processes (Gregory and Nelson 1984, Gregory 1985), kinetics of coagulation by these metal ions was examined in recent years (Ching et. al. 1994). It was demonstrated that the growth rate of aggregates strongly depends on concentration of aluminium sulphate and solution pH and it cannot be explained simply by solubility of the metal ions and the charge effects. Although it is postulated that these kinetic characteristics are related to precipitation of metal ion at high level of the coagulants, there has been no direct experimental evidence to prove this. Moreover, the conventional approach, which broadly defines coagulation in terms of four zones (Stumm and O'Melia 1968, Dentel 1991), also faces a challenge in explaining the observed phenomena. Most interestingly, based on this experimental observation, one question can arise: what is the role of solution chemistry on the kinetics of coagulation in such case.
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It seems rather clear that if direct evidence of the relationship between kinetics of coagulation and metal ion precipitation can be obtained at the same time scale, a better understanding of coagulation could be achieved. For the same reason, if the influence of solution chemistry on coagulation can be directly supported by experimental evidence of the influence of solution chemistry on the metal ion precipitation, a better picture of influence of solution chemistry on coagulation by the metal ions could be obtained.

There are many aspects of solution chemistry, which could exert great influences on coagulation by the hydrolysable metal ions, such as presence of anions (PO₄³⁻, SO₄²⁻, Cl⁻, etc.) in solution. Apart from these anions, some chemical substances in the waters could also exhibit profound effects on the coagulation which may be important but not yet well understood. Among them, one possible chemical is silicic acid or dissolved silica, the influence of its presence in solution on coagulation is unknown. Study on this influence might be of great theoretical and practical importance, because of the universal occurrence of silica in water environments, and as well as its relevance in other areas.

Silicon, with its great abundance in the earth’s crust, exists in natural waters in the concentration range: 0.02 to 0.5 mM or more (Siever 1957, Clesceri 1989). It occurs dominantly as Si(OH)₄ monomers in the natural aquatic environment (Farmer 1986, Siever 1957). Interactions between aluminium species and silicic acid in aqueous solution are of great interest in environmental studies and reactions have been reported with fairly wide concentration range of aluminium and silicic acid. The concentration may vary between different researchers due to their own research interests, and reported results up to now may indicate a general range of aluminium from 4 M to 0.1 M and silica range from 0.1 mM to 0.1 M SiO₂ (Brace and Matijevic 1977; Farmer and Lumsdon 1994; Birchall 1990; Exley and Birchall 1992). At the same time, although not receiving so much interest as aluminium, interactions between iron(III) and dissolved silica are also reported (Schenk 1968, Meng and Letterman 1996). With
such concentration of silicic acid in natural waters, and the chemical interaction
between the aluminium (or iron(III)) and silicic acid, there could be some influence on
coagulation of colloids by aluminium (or iron(III)). At present, there is little known on
this point.

1.2 Objectives of this Research

The objective of this research is to investigate the influences of silicic acid or dissolved
silica on flocculation of kaolin suspensions by the two commonly used coagulants,
aluminium sulphate and ferric chloride, with emphasis on aluminium sulphate.

This examination of the influences will focus on several aspects. Firstly, the effects of
presence of dissolved silica on flocculation of kaolin suspensions will be investigated.
The purpose of this is to show whether the presence of silicic acid (or dissolved silica)
can promote or prohibit the coagulation by these hydrolysable metal salts. Because the
coagulation by these metal salts is strongly dependent on solution pH, this examination
will be conducted at pH values, which are of practical importance for water treatment
process. Therefore, it may show that how these effects depend on pH and at what
levels of dissolved silica the effects become important.

Secondly, another interest is focused on how presence of certain levels of silicic acid
(or dissolved silica) affect the optimum pH range under the experimental conditions.
This would provide some information on selection of optimum pH range for
coagulation, which is very important in water treatment process.

Thirdly, the charge effects of presence of dissolved silica in the coagulation system will
also be examined. This is intended to reveal how the presence of dissolved silica affects
the charge neutralisation ability of these metal salt coagulants.
Finally, based on the experimental evidences, the mechanisms of these influences of silicic acid (dissolved silica) on coagulation will be discussed and proposed. This will be made on the bases of mechanisms of coagulation, aluminium precipitation and interactions between aluminium and dissolved silica.

In addition, if the presence of dissolved silica at some levels would prevent the coagulation by the metal salts, it would be interesting to examine what would happen if common ions like Ca^{2+} are present in solution. So, the role of this simple ion in the coagulation system will be also examined. Because simple ions like Ca^{2+} can exist at high levels in waters, this investigation would be of practical importance.

1.3 Study Methods

In order to fulfil the proposed objectives, the experimental strategies include:

(1) Measurements of kinetic influence of dissolved silica on coagulation. This will be carried out by the turbidity fluctuation technique, using a Photometric Dispersion Analyser (PDA). With this instrumentation, the coagulation process can be monitored continuously throughout the whole process; the information about growth of aggregate size versus mixing time can be obtained. A comparison between the measurements of coagulation with and without presence of dissolved silica can be carried out directly based on the experimental results, which would provide the information about the influence of dissolved silica on kinetics of flocculation.

(2) Measurements of charge effects in presence of dissolved silica on the colloids in the coagulation system. This will be conducted by the measurements of electrophoretic mobility of the colloids under varying conditions. This will provide the information about the influence of dissolved silica on charge neutralising ability of aluminium hydrolysing products.
(3) Measurement of kinetic aggregation of primary aluminium hydroxide precipitates with and without presence of dissolved silica. The dynamic precipitation of aluminium with and without dissolved will be investigated by the particle monitor (PM). Using this technique, the kinetics of aggregation of the primary precipitates versus time can be obtained. This will provide experimental evidence on the relationship between aggregation of primary precipitate and the aggregation of kaolin suspension by aluminium sulphate. The mechanism of this influence can be discussed based on the results. As will be seen in this work, the coagulation by aluminium is largely controlled by the dynamics of precipitation in certain stages of coagulation.

Finally, we also would like to state that, in this study, we have decided to re-examine some aspects of the behaviour of aluminium coagulation, this is not because of an overriding interest in aluminium coagulation, but because kinetic aspects of aluminium coagulation remain unclear at present. This re-examination will prove to be important in understanding the influence of dissolved silica, and it would shed some light on the solution influence on coagulation as general.
CHAPTER TWO

THEORY OF FLOCCULATION

2.1 Colloids and their Properties

Dispersed particles are commonly encountered in water and waste water treatment process. The size of dispersed particles can range from fractions of a millimetre down to macromolecular dimensions. There has been a traditional distinction between colloidal and suspended particles, with the former having at least one dimension within the nanometre \(10^{-9}\) m to micrometre \(10^{-6}\) m range (Elimelech et. al, 1995; Shaw 1991). Despite this boundary, it may not be expected that there is a sudden change from one type of behaviour to another at a given particle size; on the contrary, there is only a gradual transition.

Particles of colloidal dimensions can stay stable, i.e. remain as separate entities in a dispersed state, due to their inherent characteristics. One of the characteristic features of colloidal dispersions is the large area-to-volume ratio for the particles involved. This makes the effects arising from interfacial interactions much more important than the effects of external forces such as gravity. These interfacial properties include nature of surface charge, electric double layer and electrokinetic phenomena. All these interfacial properties are essential in understanding colloid stability, and the processes, such as destabilisation, aggregation or coagulation.
2.1.1 Hydrophilic and hydrophobic colloids

In colloidal dispersions, there are two general classes of colloids, which are called lyophobic and lyophilic colloids. In the case of aqueous colloidal dispersions, more specific terms are used: hydrophobic and hydrophilic colloids. Here, hydro - refers to the aqueous phase in which the colloids are embedded and - phobic and - philic describe the degree of affinity of the colloids or the tendency of a surface to become wetted by the liquid phase. That is, the hydrophobic colloids possess a surface which repels water and on the other hand the hydrophilic colloids possess a surface which has a strong affinity for water molecules.

Despite these general definitions, it would be difficult to classify one particular colloidal system. This is because both types may co-exist in a particular system or both hydrophobic and hydrophilic areas may exist on the colloids (Bratby 1980). In his book, Shaw (1991) even warned that the general usage of the terms lyophilic and lyophobic in defining colloidal systems is somewhat illogical. Some liquid dispersions of solid or liquid particles traditionally described as lyophobic, there is often a high affinity between the particles and dispersion medium. He further argued that if the term lyophobic is taken to imply no affinity between particles and dispersion medium, then the particles would not be wetted and no dispersion could be formed.

However, the terms lyophilic and lyophobic are normally used to distinguish between one-phase and two-phase colloidal system respectively (Hiemenz 1977). From this point of view, the lyophobic colloids are treated as systems with two distinctively different phases, while lyophilic colloids are treated as colloid systems with solvent and solute.

In water and wastewater treatment, mineral particles, such as kaolin, may be called hydrophobic colloids, whereas the impurities, such as humic and fulvic compounds and viruses may be put in the category of hydrophilic colloids (Bratby 1980, Stumm and

2.1.2 The electrical double layer (EDL)

The surface charge of colloids is essential in discussing colloidal behaviour. This section will review these aspects of colloids: the origin of surface charge and the electric double layer.

2.1.2.1 Origin of surface charge

The surface charge of colloids may arise in three principal ways (Stumm 1992, Stumm and Morgan 1996; Elimelech et al. 1995):

1) The electrical charge may originate from chemical reactions at the colloid surface. Many solid surfaces possess ionizable functional groups, e.g., -OH, -COOH, -OPO$_3$H$_2$, -SH. The charge of these particles is dependent on the degree of ionisation (proton transfer) and consequently on the pH of the liquid. For example, most oxides and hydroxides exhibit amphoteric behaviour and the surface charge can be explained by the acid base behaviour of the surface hydroxyl groups S-OH. The reaction at the interface can be expressed as:

$$\text{S-OH}_2^+ \rightarrow \text{S-OH} \rightarrow \text{S-O}^-$$

Another example of this kind is organic surface, such as bacterium or of biological debris. In this case, the surface charge may result from protolysis of functional amino and carboxyl groups. In addition, surface charge may also arise when solutes become coordinatively bound to solid surfaces, e.g.,
\[ \equiv \text{Fe-OH} + \text{Cu}^{3+} \rightarrow \text{FeOCu}^+ + \text{H}^+ \]

2) Surface charge at the phase boundary could be caused by lattice imperfections at the solid surface. This is especially important for clay minerals. For example, if in an array of solid SiO₂ tetrahedra a Si atom is replaced by an Al atom, a negatively charged framework is established:

\[
\begin{array}{c}
\text{HO} \\
\text{Si} \\
\text{HO}
\end{array} \quad \begin{array}{c}
\text{O} \\
\text{Si} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{O} \\
\text{Al} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{O} \\
\text{Si} \\
\text{OH}
\end{array}^{-}
\]

3) Surface charge may be established through adsorption of a hydrophobic species or a surfactant ion. Preferential adsorption of a surface active ion can arise from so-called hydrophobic bonding, from hydrogen bonds or from van der Waals interactions.

2.1.2.2 The Gouy-Chapman and Stern double layer models

Since colloids possess surface charge from one way or another, it will surely affect the distribution of ions nearby in the liquid. Generally, ions with opposite electrical charge, counter-ions, will be attracted towards the surface, while ions with the similar charge, co-ions, will be repelled away from the surface. Also, there is the mixing tendency of thermal motion and mutual ionic repulsion or attraction in the liquid. All these, as a result, lead to the formation of an electric double layer made up of the charged surface and a neutralising excess of counter ions over co-ions distributed in a diffuse manner in the nearby liquid (Figure 2.1).

Generally, the electrical double layer is composed of two regions: an inner region which may include water molecules and adsorbed ions (see Stern model), and a diffuse
region in which ions are distributed according to the influence of electrical forces and random thermal motion (see Gouy-Chapman model).

In explaining the electrical double layer quantitatively, several models have been developed. Among them, the *Gouy-Chapman* and *Stern* models are fundamental.

1) The *Gouy-Chapman* double layer description

The simplest quantitative description of the diffuse part of the double layer is the Gouy-Chapman model. In this model, the electrical double layer was regarded as consisting of a charged surface and a diffuse region of ions around that surface. The model is based on the following assumptions:

1. The surface is flat, of infinite extent and uniformly charged.
2. The ions in the diffuse part are point charges, able to approach up to the interface.
3. The solvent dielectric constant has the same value throughout the diffuse part.
4. A single symmetrical electrolyte of charge number \( z \) will be assumed.
Figure 2.1 The electric double layer of the Stern model; the variation of potential close to a charged surface: (a) low concentration of indifferent electrolyte; (b) higher concentration of indifferent electrolyte; (c) in case of specifically adsorbing counterions (charge reversal occurring at the Stern plane).
Considering the electric potential to be \( \Psi_0 \) at a flat surface and \( \Psi \) at a distance \( x \) from the surface in the electrolyte solution, then \( n_+ \) and \( n_- \), the respective numbers of positive and negative ions per unit volume at points in solution where the potential is \( \Psi \), can be expressed by using the Boltzmann expression:

\[
n_+ = n_0 \exp \left[ -\frac{ze\Psi}{kT} \right] \quad \text{and} \quad n_+ = n_0 \exp \left[ -\frac{ze\Psi}{kT} \right]
\]

where \( z e\Psi \) and \( -ze\Psi \) are the electric potential energy, \( n_0 \) is the bulk concentration of each ionic species. \( e \) is the electron charge and \( k \) is the Boltzmann constant.

The net charge density \( \rho \) at points where the electric potential is \( \Psi \), is given by

\[
\rho = ze(n_+ - n_-)
\]

\[
= zen_0 \left\{ \exp \left[ -\frac{ze\Psi}{kT} \right] - \exp \left[ -\frac{ze\Psi}{kT} \right] \right\}
\]

\[
= -2 zen_0 \sinh \frac{ze\Psi}{kT}
\]

2.1

The relationship between \( \rho \) and \( \Psi \) is expressed by Poisson's equation as follows (for a flat double layer):

\[
\frac{d^2\Psi}{dx^2} = -\frac{\rho}{\varepsilon}
\]

2.2

where \( \varepsilon \) is the permittivity of the medium.

Combination of equations (2.1) and (2.2) gives the Poisson-Boltzmann expression:
The solution of this equation (2.3) can be easily obtained, with the following boundary conditions ($\psi = \psi_0$ when $x = 0$; $\psi = 0$ and $d\psi/dx = 0$ when $x = \infty$):

$$\psi = \frac{2kT}{ze} \ln \left( \frac{1 + \gamma \exp[-\kappa x]}{1 + \gamma \exp[-\kappa x]} \right)$$

where

$$\gamma = \frac{\exp[ze\psi_0 / 2kT] - 1}{\exp[ze\psi_0 / 2kT] + 1}$$

$$\kappa = \sqrt{\frac{2e^2n_0z^2}{\varepsilon kT}}$$

If $ze\psi_0 / 2kT < 1$ or $\psi_0$ less than about 25 mV at 25°C, then the equation (2.4) can be simplified to

$$\psi = \psi_0 \exp[-\kappa x]$$

Equation (2.7) is useful approximation to equation (2.4); it shows that the double layer potential $\psi$ follows a simple exponential form when the surface potential $\psi_0$ is not high. The potential decreases by an exponential factor over a distance $1/\kappa$ at low potentials, and the distance is customarily referred to as the "thickness" of the diffuse double layer. In equation 2.6, the $\kappa$ is for z-z electrolytes; for general case of electrolyte solutions with a number of dissolved salts, the sum is taken over all ions present in the solution. In this case, at 25°C and giving numerical values, $\kappa$ can be taken the form (see Hunter 1981, Elimelech et. al. 1995):

$$\kappa = 2.32 \times 10^3 \left( \sum c_i z_i^2 \right)^{1/2}$$
Chapter 2 Theory of Flocculation

where the unit of $c_i$ is in mol dm$^{-3}$ and $\kappa$ is in m$^{-1}$. With this expression, the values of the double layer thickness can be estimated. For typical solutions, the values are in the range 1-100 nm (e.g. 4 nm for Thames water and 0.4 nm for sea water, while for distilled water, the value is 1 µm).

2) The Stern double layer model

Treatment of diffuse double layer by the Gouy-Chapman model assumes point charges in the electrolyte medium. However, ions in solution are not point charges - they have a finite size. Assuming the ion charge as being located at the centre of a sphere of finite size, then the charge cannot be on the interface, but limited to a distance equal to the sphere radius. This distance, symbolised by $\delta$, defines a region which is inaccessible to counterion charge. This concept is originally proposed by Stern and the modified Gouy-Chapman model using this concept is called the Stern model (Figure 2.1).

In the Stern model, the plane at distance $\delta$ from the surface is usually known as the Stern plane, and the region between this plane and the surface is known as the Stern layer. Outside the Stern layer is a diffuse layer of counter ions and co-ions, just as in the Gouy-Chapman model.

One important point is that, surface charge at the Stern layer could change drastically when specific adsorption takes place. If specifically adsorbing ions are polyvalent or surface active counter ions, counter-ion adsorption and charge reversal can be brought about within the Stern layer as in the case of hydrolysing metal ions (see Figure 2.1). This is of great practical importance in particle aggregation. More details of this model can be found in the works (Elimelech et al. 1995, Stumm 1992, Bratby 1980, Shaw 1991).
2.1.3 Electrokinetic phenomena

2.1.3.1 Phenomena

Electrokinetic phenomena take place whenever there is relative movement of a charged interface with respect to the adjacent electrolyte solution, so that the mobile part of the electric double layer is sheared off from a charged surface. One important concept of these phenomena is the plane of shear (see Figure 2.1). The electrical potential at the shear plane is the electrokinetic potential, or the so-called "zeta potential" $\zeta$, which may be derived from electrokinetic data. Electrokinetic effects include the four phenomena:

1) particle electrophoresis
2) electro-osmosis
3) streaming potential
4) sedimentation potential

One of these phenomena, electrophoresis, will be reviewed briefly here.

2.1.3.2 Particle electrophoresis

Particle electrophoresis is the movement of a particle with charged surface together with attached material relative to stationary liquid by an applied electric field. The motion of particles in an electric field can simply be observed microscopically, and the velocity can be determined. The electrophoretic mobility (EM), $U$, is usually defined as the velocity per unit field strength with a standard unit ($\mu m s^{-1} V^{-1} cm$).

In practice an electrophoresis cell has usually either a rectangular or circular cross-section, with an electrode at each end. Because the internal surfaces of the cell are charged, there is an electro-osmotic flow of liquid near the tube walls together with a
compensating return flow of liquid with maximum velocity at the centre of the tube, giving a parabolic distribution of liquid velocity with depth. Usually, measurements are conducted at the *stationary levels*, where the liquid velocity is zero. In this way, the true electrophoretic velocity is directly observed at the locations.

For particles large compared with the double layer thickness ($\kappa a >> 1$), the electrophoretic mobility can be taken a simple form, known as the *Smoluchowski equation* (see Elimelech *et. al.* 1995):

\[
U = \frac{e\zeta}{\mu}
\]  

2.9

$\mu$: viscosity of fluid

For particles with 1 $\mu$m diameter in a 10 mM solution of 1-1 electrolyte, $\kappa a$ is about 160 and equation (2.9) could be used with very little error. For aqueous solution at 25° C, the zeta potential can be expressed as

\[
\zeta \text{ (mV)} = 12.8U \text{ (\mu m s}^{-1}\text{V}^{-1}\text{cm)}
\]  

2.10

There are other expressions for some different conditions (Hunter 1981).

### 2.2 DLVO Description of Colloidal Stability

If colloids stay uniformly distributed throughout an aqueous solution and no aggregation occur, the system is said to be stable. It is quite possible for a system to be unstable with respect to sedimentation, but relatively stable (kinetically) with respect to coagulation (the kaolin system, as used in this study, might be described as stable in the latter sense).
Addition of indifferent electrolytes (e.g. simple ions such as Na\(^+\) and K\(^+\)) may alter the stability and even initialise aggregation/coagulation. One important theory to explain this phenomenon is the DLVO theory, which was developed independently by Derjaguin and Landau (1941) and Verwey and Overbeek (1948). In this theory, two basic colloidal interactions are fundamental: van der Waals attraction and electrical double layer repulsion. Here, we will first deal with the two interactions and then have a brief review of this theory.

### 2.2.1 Double layer interaction

When two charged particles approach each other in an electrolyte solution, their diffuse layers may overlap. In the case of similarly charged particles a repulsion may arise between them due to the similar electric potentials (or charges). Theoretical calculation of the interaction energy due to the overlapping of the diffuse layer have been made for two parallel charged plates of infinite area and thickness, and for two spherical particles (see Elimelech et. al. 1995, Shaw 1991).

Many expressions can be found in the colloid science literature developed for the calculation of repulsion energy between two colloidal particles in solution (Gregory 1975). One commonly used expression is given here in the following equation which is developed through application of the *linear superposition approximation* (LSA) method (Gregory 1975):

\[
V_r = 64\pi \frac{a_1 a_2}{a_1 + a_2} \left( \frac{kT}{2} \right)^2 \gamma_1 \gamma_2 \exp(-\kappa h) \tag{2.11}
\]

where \( h \) denotes the (minimum) surface-to-surface separation between the spheres; \( z \) the valency of the ions (a symmetric \( z\)-\( z\) electrolyte is assumed) and \( e \) is the elementary charge. The \( \gamma_1 \) and \( \gamma_2 \) are dimensionless functions of the surface potentials (see equation 2.5).
For two identical particles, equation 2.11 reduces to:

$$V_R = 32 \pi \varepsilon a (kT/e)^2 \gamma \exp(-\kappa h)$$  \hspace{1cm} 2.12

where $\varepsilon$ is the permittivity of the medium.

For small values of surface or zeta potential, equation 2.12 can further simplified to:

$$V_R = 2\pi \varepsilon a \zeta^2 \exp(-\kappa h)$$  \hspace{1cm} 2.13

where $\zeta$ denotes the zeta potential, and $1/\kappa$ is the “effective thickness” of diffuse double layer. If we only consider the condition in which no specific ion adsorption occurs, the interaction energy $V_R$ should decrease in an exponential fashion with increasing separation distance $h$; and the range of $V_R$ should be decreased by increasing $\kappa$ (i.e. by increasing electrolyte concentration and/or counter-ion charge number). Because the effect of salt addition on the repulsion is two-fold: a decrease in the zeta potential and an increase in $\kappa$, addition of salt will result in a decrease in the repulsion at a given separation distance.

### 2.2.2 Van der Waals interaction

It has long been recognized that attractive force always exists between colloidal particles of the same material. This attraction between two closely separated surfaces is generally called the London-van der Waals force.

In evaluation of the London-van der Walls attraction, commonly used expressions are Hamaker expressions, which are based on the assumption of pairwise additivity of intermolecular forces (Hamaker 1937, Hunter 1993, Elimelech \textit{et. al.} 1995).
For two spheres of radii \( a_1 \) and \( a_2 \), separated by a distance \( h \), the interaction energy at close approach \((h \ll a)\) is taken the form:

\[
V_A = -\frac{Aa_1a_2}{6h(a_1 + a_2)}
\]  \hspace{1cm} (2.14)

For equal spheres of radius \( a_1 \) separated by a distance \( h \) (at a close approach \( h \ll a)\), the interaction energy is simply given by:

\[
V_A = -\frac{A_{11}a_1}{12h}
\]  \hspace{1cm} (2.15)

From equation 2.15, two important features should be noted: the inverse dependence of the interaction energy on the separation distance, and the direct dependence on particle size.

The Hamaker constant \( A_{11} \) is for the interaction of media across a vacuum. For interaction through a liquid, the Hamaker constant need to be modified. Many attempts have been made for calculation of the constants (Gregory 1969, 1989; Visser 1981). Since the constant is affected by many factors, such as nature of liquid, ionic strength and temperature, etc., there would be difficulties in obtaining reliable data. However, in some cases, experimental values of the constant have been reported fairly to agree with the calculated values (Gregory 1977). For practically aqueous dispersions, Hamaker constants is in the range 0.3 - 10 \( \times 10^{-20} \) J. That is, \( A/kT \) is in the range 0.7-24 (Elimelech 1995). Dense mineral particles may have a higher value than those with low-density.
2.2.3 Colloidal stability in terms of the DLVO theory

Based on the Gouy-Chapman model, and only considering the double layer interaction and the Van der Waals interaction energy, Derjaguin and Landau (1941) and Verwey and Overbeek (1948) independently developed a quantitative theory. In this theory, the stability of colloids is evaluated by the total interaction energy, i.e. the energy of attraction (van der Waals) and the energy of repulsion (overlapping of electric double layer) in terms of the distance between particles.

Assuming van der Waals attraction and EDL repulsion to be additive, the total interaction, usually expressed as potential energy \( V_T \), is calculated as the sum of van der Waals attraction \( V_A \) and the EDL interaction \( V_R \):

\[
V_T = V_A + V_R
\]  

One conceptual potential energy versus distance diagram is presented in Figure 2.2. The repulsion energy is an exponential function of the separation distance with a range of the order of double layer thickness \( (1/\kappa) \) as indicated by equation 2.11, 2.12 and 2.13. The attraction energy decreases as an inverse power of distance (see equation 2.14 and 2.15). The total energy profile will depend on the strength of each of the two contributions as a function of separation distance: at small distance, attraction energy will predominate and a primary minimum energy exist; at intermediate distance, repulsion may predominate and a maximum energy exist (called the energy barrier); at a larger distance a secondary minimum may exist.

There are two conditions in which colloidal particles may come into true contact and stick together in the discussed situation here. Firstly, if the maximum energy or the energy barrier is large in relation to thermal kinetic energy of particles, the colliding particles could not come into true contact and no aggregation could occur, so the system is stable; but if the kinetic energy is large enough to surmount the energy
barrier, then the particles can be held by van der Waals attraction in a deep primary minimum, the particles will aggregate and the system is not stable. Secondly, addition of indifferent electrolytes can compress the double layer and reduce the maximum energy (energy barrier), so that colloids can come together and destabilised, or even a rapid aggregation may occur (see Figure 2.2(b). Besides, it is suggested that fairly weak aggregates may form due to the existence of second minimum repulsion energy (see Figure 2.2). However, no detailed information is available on this aspect at present.

One important concept in discussing the stability of colloids concerning the energy barrier is the critical coagulation concentration (CCC), which is generally defined as the lowest coagulant concentration giving the maximum rate of coagulation. It is usually estimated theoretically by assuming that no energy barrier exists, i.e. $V_T = 0$. Suppose $V_T = 0$, and $dV_T/dh = 0$, the CCC is given by (Elmelech et. al. 1995):

$$CCC \propto z^6A^2 \tanh^4 \left( \frac{ze\zeta}{4kT} \right) \quad \left(ze\zeta/4kT \gg 1 \right) \quad 2.17$$
Figure 2.2 Schematic representation of DLVO theory. Total energy of interaction as a function of separation distance of colloidal particles: (a) at low electrolyte (indifferent) concentration, great energy barrier exists, preventing true contact between particles. (b) at high electrolyte (indifferent) concentration, energy barrier is eliminated due to double layer compression, colloidal particles may come into true contact and aggregate.
From equation 2.17, it is clear that, at large zeta potentials CCC is proportional to $z^6$, so it is the valence of the counterions that has the main effect on the stability on colloids. This dependency has been known as the Schulze-Hardy rule. However this $z^6$ dependence is far from universal, there are only a few case where the rule is followed (Greene and Saunders 1970). At small zeta potentials (i.e. $ze\zeta/4kT < 1$), as commonly encountered, the CCC has a much weaker dependence on the counterion charge. Also, there are some differences among different counterions of the same valence, probably due to the differences in size of the hydrated counterions and the consequent effect on the potential at the Stern layer (and hence on the zeta potential) (Russel et. al 1989; Pieper et. al. 1975).

From the DLVO theory, it follows that neither size nor concentration of particles should affect CCC if an indifferent electrolyte is added; and no charge reversal and restabilisation of colloids could occur. If particle concentration has an effect on CCC, this may indicate an occurrence of specific adsorption of counterions on the surface of colloids. In this case, the DLVO theory is no longer applicable. The effects of such specific adsorption on colloid stability and aggregation has been found with hydrolysing metal salts such as aluminium sulphate and ferric chloride (see 2.3 and 2.4).

It worth noting that, in the DLVO theory, only the two interaction are considered: the double layer and van der Waals interactions. There are some other effects, namely non-DLVO forces, playing important part in stability of colloids and these include hydration effects, steric interaction, and polymer bridging. These effects also has significant effects on colloidal stability (Gregory 1993).
2.3 Mechanisms of Flocculation

Aggregation is an important step in many solid-liquid separation processes and is widely used in water and wastewater treatment. Particles in waters are often in the colloidal size range, between 1 nm and 1 μm, which is too small for effective separation in common unit operations such as filtration, flotation, and sedimentation. In many cases, aggregation is brought about deliberately to increase particle size in order to enhance solid-liquid separation. In water treatment, there are two terms concerning the aggregation process: coagulation and flocculation. Generally, coagulation is defined as the process of destabilisation of colloidal suspensions. That is, the purpose of coagulation is to overcome those factors promoting the stability of a given colloidal system (often the charge on suspended particles). On the other hand, flocculation is the process through which destabilised particles are induced to stick together to form settleable (or filterable) aggregates (flocs). However, in most cases, these processes occur simultaneously and it is difficult to distinguish one from the other. Therefore, it is more convenient for the term “flocculation” to cover the whole aggregation process, whilst drawing attention to distinctions in terminology which are commonly made (Gregory 1989). In this work, “flocculation” will be used as such a generic term; while if destabilisation of colloids is more interested, the terms, “coagulation and/or destabilisation” will be used.

Flocculation of colloidal particles is assumed to proceed in two consecutive steps:

a) Transport of particles, leading to inter-particle collisions

b) Attachment of colliding particles, leading to aggregates

Particle transport can be brought about by either Brownian diffusion or fluid motion, while attachment will be dependent on inter-particle forces or colloidal interaction. The former is related to the collision frequency and the latter has a great influence on collision efficiency.
In this section, we will have a brief review of the mechanisms of particle destabilisation or coagulation and then of kinetics of flocculation.

### 2.3.1 Particle destabilisation or coagulation

Stability of dispersed particles may be affected by several mechanisms. These include double layer compression, adsorption, bridging, and sweep flocculation.

1) Double layer compression

As described by the DLVO theory (see 2.2), addition of *indifferent electrolytes* to a colloidal suspension can compress the diffuse double layer, or reduce the effective double layer thickness \((1/\kappa)\), as a result, the energy barrier of colloidal particles is reduced or even eliminated. If energy of particles provided by Brownian or fluid motion surmount the energy barrier, true contact between particles may occur and the colliding particles can stick together by van der Waals attraction in a deep *primary minimum*. In addition, the formation of fairly weak aggregates may occur at a large separation distance, a *secondary minimum* in the potential energy curve. Since the interaction energies are directly proportional to particle size, secondary minimum effects are more significant with larger particles (greater than 1 \(\mu m\) in diameter). They are also more important at moderately high salt concentrations, so that the range of electrical repulsion is reduced, allowing the particles to approach closer, where van der Waals attraction is greater.
2) Adsorption

Adsorption, the accumulation of matter at the solid-water interface, is very important in destabilisation/coagulation. The main reason is that, adsorption of ions can affect the electrostatic properties of suspended particles and colloids as described in the Stern model (see 2.1.2.2), which, in turn, influences their tendency to aggregate and attach. Adsorption of ions at solid-water interface may occur through:

   a) Surface complexation reactions (surface hydrolysis, the formation of coordinative bonds at the surface with metals and with ligands).
   b) The electric interactions at surfaces.

Hydrolysis products of metal ions, such as Al³⁺ and Fe³⁺, have been found to adsorb readily on mineral particle surfaces. Adsorption of these hydrolysis product exert great effects on destabilisation/coagulation of suspended particles. Detailed explanation of this will be given separately in 2.4 and 2.5.

3) Polymer bridging

Adsorption of polymers can greatly influence colloid stability. A great deal of empirical information existing on the flocculation of dispersions by long-chain polymers shows the importance of bridging between surfaces by polymer chains (Dickenson and Eriksson 1991). It was originally postulated by Ruehrwein and Ward (1952) to account for the aggregation of clay particles by polyelectrolytes. In this mechanism, polyelectrolytes are long-chain structures which extend itself into the aqueous phase. Suspended particles may be attached to different part of a single polymer molecule, and thus may be bridged by adsorbed polymer. In this way, particle destabilisation and flocculation occur. However, excess addition of polymer would cause steric interaction between particles- adsorbed polymer layers overlap and a short-range repulsion arise between particles (Napper 1983, Gregory 1996). For this reason, there
is an *optimum dosage* of polymer in generating good flocculation. At higher dosages, restabilisation may occur.

4) The electrostatic patch mechanism

When particles and polyelectrolyte are of opposite charge, adsorption of polyelectrolyte on particle surfaces may reduce electric charge on its surface. As a result, destabilisation may occur. This simple charge-neutralisation picture has been refined to the "electrostatic patch" model (Gregory 1973) (see Figure 2.3).

![Figure 2.3 Schematic representation of the "electrostatic patch model", in the case of negatively charged particles and cationic polymer.](image)

In the electrostatic patch mechanism, adsorption of electrolyte on particle surfaces are supposed to occur in a patchwise manner so that there are patches of adsorbed polyelectrolyte and areas of unoccupied surfaces on a particle. This condition can arise when the charge density of the polyelectrolyte is much greater than that of the particle surface. Strong electrical attraction will take place between particles when positive and negative areas of different particles are adjacent. In this way, particles can be held together and aggregation occurs.
5) Sweep flocculation

Particles can be destabilised through “sweep flocculation”. This will take place when excess hydrolysing metal salt coagulant with respect to solubility is added and the concentration of colloid is not high. In this case, massive metal hydroxide precipitates will form in suspension, they enmesh the colloidal particles, so that the particles are destabilised and flocculated.

### 2.3.2 Flocculation kinetics

#### 2.3.2.1 General

When particles are destabilised, it is often assumed that every collision is effective (collision efficiency \( \alpha = 1 \)), and aggregation is irreversible (no break-up of aggregates). Under this assumption, the kinetics of flocculation is described by the classic work of Smoluchowski (1917). In this case, flocculation can be thought to be a second-order rate process, in which the rate of collision is proportional to the product of concentrations of two colliding species. For a dispersion of initially identical particles, after a period of aggregation, the rate of change of concentration of \( k \)-fold aggregates (formed by \( k \) primary particles) can be expressed as:

\[
\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} k_{ij} n_i n_j - \sum_{k=i} n_k \sum_{i=1}^{k} k_{ik} n_i
\]

where \( k = i + j; n_i \) and \( n_j \) -number concentrations of aggregates with size “i-fold” and “j-fold”; \( k_{ij} \) and \( k_{ik} \) -second-order rate constant, which depends on a number of factors, such as particle size and transport mechanism, which will be discussed briefly in section 2) and 3) below.
In equation 2.18, the first term on the right hand side represents the rate of formation of $k$-fold aggregates by collision of any pair of aggregates, $i$ and $j$, such that $i + j = k$. The second term accounts for the loss of $k$-fold aggregates by collision, and aggregation, with any other aggregates.

### 2.3.2.2 Perikinetic flocculation

Small particles in suspension undergo continuous random movements or *Brownian motion* due to the thermal energy of the system. If particle transport is brought about by *Brownian* diffusion, the aggregation is called perikinetic flocculation.

Under *perikinetic flocculation*, the collision frequency or the total number of collision $(J_{ij})$ between particles of type $i$ and $j$ in unit volume per unit time can be derived by Smoluchowski approach as follows:

$$J_{ij} = 4\pi R_{ij} (D_i + D_j)n_i n_j$$  \hspace{1cm} 2.19

where $D_i$, $D_j$ are the diffusion coefficients of particles of types $i$ and $j$; and $R_{ij}$ is the collision radius for particles $i$ and $j$, which is the centre-to-centre distance at which the pair of particles may be taken to be in contact. In practice, it can usually be assumed to be the sum of the particle radii:

$$R_{ij} = a_i + a_j$$  \hspace{1cm} 2.20

Using the Stokes-Einstein expression for the diffusion coefficient of a spherical particle:

$$D_i = \frac{kT}{6\pi a_i \mu}$$  \hspace{1cm} 2.21
Equation 2.19 then becomes:

\[ J_y = \frac{2kT}{3\mu} n_i n_j \left( \frac{a_i + a_j}{a_i a_j} \right)^2 \]

Comparing this with equation 2.18 gives the rate constant for perikinetic collisions:

\[ k_y = \frac{2kT}{3\mu} \left( \frac{a_i + a_j}{a_i a_j} \right)^2 \]

This result has the very important feature that, for particles of approximately equal size, the collision rate constant becomes almost independent of particle size. The term \((a_i + a_j)^2/a_i a_j\) has a constant value of about 4 when \(a_i = a_j\). Physically, this is because increasing particle size leads to a lower diffusion coefficient, but a larger collision radius and these two effects cancel each other out when the particles are of nearly the same size. Under these conditions, the rate constant becomes:

\[ k_y = \frac{8kT}{3\mu} \]

Inserting values for aqueous dispersions at 25°C gives \(k_y = 1.23 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}\). For particles not too different in size, the rate constant may be assumed to be equal and may expressed by equation 2.24. Under this assumption, for an initially uniform dispersion of particles, the initial collision rate can be calculated from equation 2.18 and the initial rate of decrease of the total particles concentration, \(n_T\), follows directly from the collision rate. Hence, a very simple result can be derived (Gregory 1989):

\[ \frac{dn_T}{dt} = -k_F n_T^2 \]

where \(n_T = n_1 + n_2 + n_3 \ldots\) and \(k_F = 4kT/3\mu \) (6.13×10^{-18} \text{ m}^3 \text{ s}^{-1}) in water at 25°C).
With the boundary condition \( n_r = n_0 \) when \( t = 0 \), integration of equation 2.25 leads to the form:

\[
n_r = \frac{n_0}{1 + \frac{t}{\tau}}
\]

2.26

where \( \tau = 1/k_F n_0 \), this characteristic time is called the coagulation time or the half life of the aggregation.

It is worth noting that this expression is based on the assumptions of constant \( k_{ij} \) values and that the colliding particles are spherical. It may be reasonably applied in the early stage of the process, but cannot be expected to apply after substantial aggregation has occurred.

In many practical applications of flocculation, such as the process in water treatment, formation of large aggregates is required, containing thousands of primary particles. This may mean a very large reduction in total particle number. From equation 2.26, one can see that a reduction of particle concentration, by a factor of 1000, would require a time of about 1000\( \tau \). For dilute suspensions this could represent many hours or days. For this reason practical flocculation process can rarely be carried out relying only on Brownian motion to bring about the required collisions.

2.3.2.3 Orthokinetic Flocculation

As mentioned above, the rate of perikinetic flocculation is quite slow for fairly dilute dispersions. In fact, it has been observed that flocculation rates can be greatly increased by stirring a suspension. An aggregation process, in which particle transport is brought about by fluid motion, is known as orthokinetic aggregation.
Chapter 2 Theory of flocculation

Again, Smoluchowski (1917) first tackled the rate of orthokinetic aggregation in a uniform laminar shear field, in which the fluid velocity varies linearly in only one direction. He assumed that particles would follow straight fluid streamlines and collide with particles moving on different streamlines, according to their relative position. Considering a fixed central sphere of radius \( a_j \) and flowing particles of radius \( a_i \), then those moving particles on streamlines that bring their centres within a distance \( a_i + a_j \) of the central particle will collide with it. The collision frequency can then be calculated by considering the flux of particles through a cylinder of radius \( R_{ij} \). With this model, the total number of collisions occurring between \( i \) and \( j \) particles in unit volume and unit time is given by:

\[
J_y = \frac{4}{3} n_i n_j G (a_i + a_j)^3
\] 2.27

By analogy with equation 2.18, the rate constant for orthokinetic collisions between \( i \) and \( j \) particles can be taken:

\[
k_y = \frac{4}{3} G (a_i + a_j)^3
\] 2.28

There is a very important point in the equation 2.28 that the rate constant for orthokinetic collisions is dependent on the sizes of the colliding particles; more precisely, is proportional to the cube of the collision radius. This is very different from perikinetic collision, in which collision rate constant is nearly independent of particle size.

It is worth saying that the assumption that particles are in a uniform laminar shear field is not appropriate for real flocculation process. In practice, flocculation is carried out under turbulent conditions. In order to cope with this problem, Camp and Stein (1943) developed one way to calculate a mean velocity gradient \( \overline{G} \) from the power input per unit mass of fluid, \( P \):
\[ G = \sqrt{\frac{P}{\nu}} \]

2.29

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

In discussing these two kinds of collision, one interesting thing is the comparison between the two collision rate constants, defined by equation 2.23 and equation 2.28. The orthokinetic collisions become much more important for particle sizes greater than 1 \( \mu \)m. (Gregory 1989, Elimelech et.al 1995).

2.3.2.4 Collision efficiencies

All above discussions on kinetics of aggregation is based on the assumption that every collision between particles will be effective leading to a formation of a new aggregate. This would mean that aggregates could grow up quickly and indefinitely in their sizes in such an aggregation process. However, this would not be true, for rate of aggregation can be very different and aggregates can only grow up limited sizes in practical conditions. Even before the limit of size, in some case, not every collision can lead particles to have real contact. In practice, collision efficiency (\( \alpha \)) or the fraction of successful collisions, has to be considered. That is, a factor \( \alpha \) must be incorporated into the rate expression in equation 2.18 in estimation of the rate of change of particle concentration in an aggregation process.

The collision efficiency (\( \alpha \)) can be affected significantly by several factors. It can be greatly reduced due to colloidal repulsion, such as double layer repulsion. Also, it can be affected by hydrodynamic or viscous interaction, which tends to hinder the approach of colliding particles. In discussion of perikinetic aggregation, the term of a stability ratio is normally used instead of collision efficiency (Gregory 1989, Elimelech 1995). It is shown that the stability ratio, so the collision efficiency, is related to the energy barrier (Reerink and Overbeek 1954). For modest barrier values, of the order of
a few $kT$ units, stability ratios can be very high indicating a very low collision efficiency; it keeps a constant low value after the energy barrier disappears, showing a high collision efficiency. For orthokinetic aggregation, viscous interaction can be very important, and the collision efficiency has been expressed by a limiting collision efficiency (Van de Ven and Mason 1977). It has been shown that the collision efficiency decreases as the particle size and the shear rate increase.

### 2.3.3 Fractal nature of aggregates

When solid particles aggregate, it is not possible for them to form solid particles. Instead, some porous aggregates or fractal clusters will be formed. In this way, aggregates are recognized as fractal objects (Meakin 1988, Wiesner 1992). One important feature of these fractal objects is that they have a self-similar structure. This self-similarity in fractals leads to power-law relationship between length scale and properties such as mass density. The relationship between aggregate mass, $M$, and size, $L$, can be generally expressed as:

$$M \propto L^{d_F} \quad 2.30$$

where $M$ is mass of aggregate, $L$ is length scale of size, and $d_F$ is the fractal dimension ($d_F < 3$). From the definition of fractal dimension, if an aggregate consists of $i$ primary particles with radius $a_p$, the radius of the aggregate ($a$) can be expressed as:

$$a = a_p i^{d_F} \quad 2.31$$

From this equation, the volume of the aggregate at certain fractal dimension can be calculated.
2.4 Chemistry of Metal Ions $\text{Al}^{3+}$ and $\text{Fe}^{3+}$

Aluminium and ferric salts are widely used coagulants in water treatment. Although there is great concern about toxicity of aluminium to human body, scientific research shows that the average daily Al intake from drinking water is less than 1 percent of the total (Reiber et. al. 1995), and moreover using aluminium as a coagulant does not substantially increase the total overall Al content of the distributed water (Letterman and Driscoll 1988, Miller et. al. 1984). In cases of using Al as a coagulant, in only 30 percent of utilities is there meaningful increase of Al concentration in finished water; whereas 40 percent of the cases the total Al content is diminished.

The metal ions, $\text{Al}^{3+}$ and $\text{Fe}^{3+}$, share some common traits in solution. Both of the metal ions can undergo a series of hydrolysis reactions and as a result, many dissolved species and even solid phases can form in an aqueous system. Properties such as adsorptivity and electrical charge of these dissolved species and precipitation of the metal ions are of fundamental importance in understanding the coagulative behaviour of the aluminium and ferric salts with suspensions. So, it is necessary to have a brief review of these aspects: hydrolysis reaction and resulting species and the precipitation process.

2.4.1 Hydrolysis reaction of metal ions $\text{Al}^{3+}$ and $\text{Fe}^{3+}$

When the metal ions such as $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ are added in water, they undergo a series of hydrolysis reactions, and as a result, many aluminium (or ferric) hydrolysis products are formed in aqueous solution. As the concentrations of these metal ions increase and exceed the solubility with respect to the amorphous hydroxides, precipitation of aluminium (or ferric) hydroxide may occur.

Hydrolysis of metal ions ($\text{Al}^{3+}$, $\text{Fe}^{3+}$) were first described as a stepwise consecutive replacement of $\text{H}_2\text{O}$ molecules in the hydration shell by (OH)$^-$ ions (for example, $\text{Al(\text{H}_2\text{O})}_6^{3+} \rightarrow \text{Al(\text{H}_2\text{O})}_5\text{OH}^{2+} \rightarrow \text{Al(\text{H}_2\text{O})}_4(\text{OH})^+ \rightarrow \text{Al(\text{H}_2\text{O})}_3(\text{OH})_2 \rightarrow \text{Al(\text{H}_2\text{O})}_2(\text{OH})_3 \rightarrow \text{Al(\text{H}_2\text{O})}_3(\text{OH})_4$). However, this scheme of consecutive stepwise hydroxide binding is an oversimplification.
It has been reported (Hem and Roberson 1988, Sposito 1989) that in the hydrolysis process, apart from dissolved monomeric aluminium (or ferric) species, polymeric aluminium (or ferric) species with general expression of Meq(OH)p+ exist. Stol et al (1976) suggested in their study that hydrolysis of aluminium at low concentration (c_{Al}^{3+} \leq 5 \times 10^{-5} M) over the entire OH/Al range will be dominated by only formation of the monomeric species Al(OH)^{3+}, Al(OH)^2^+, and Al(OH). In aluminium solution with c_{Al}^{3+} > 5 \times 10^{-5} M and over the range 0.5 < OH/Al < 2.2, polymerization will occur. It is now generally recognized that such multimeric hydroxo-metal complexes are of almost universal occurrence in aqueous solution, although there is still uncertainty or argument concerning the precise nature of some particular polynuclear species. Typical hydrolysis species, and some polynuclear species, which are well documented in many papers on water treatment (O’Melia et al. 1989, Dentel 1991, Ching et al. 1994), and their corresponding equilibrium constants are listed in Table 2.1.

2.4.2 Solubility diagram

Solubility diagrams show the total concentration of dissolved hydrolysis species in equilibrium with the solid phase. Obviously, the total concentration depends on concentrations of various dissolved hydrolysis complexes (hydrolysis products), with different electrical charges. As the concentration of each hydrolysis product depends on solution pH, so does the total concentration. The whole story of solubility and the dissolved species can be most conveniently illustrated by using a logC-pH diagram.

From the reaction equations and equilibria listed in Table 2.1, the logC-pH solubility diagram of aluminium (III) and iron (III) species can be constructed, as shown in Figure 2.4. and Figure 2.5.

In these diagrams, the region where amorphous aluminium hydroxide (Al(OH)₃(am)) (or Fe(OH)₃ (am)) may form in solution is sketched. All the lines in it represent the
concentration that may exist at various pH values in equilibrium with respect to the corresponding solid phase (here the amorphous form); so, for a concentration of a particular species above the line in the diagram, the solution will be supersaturated with respect to the solid phase for that species. The \( \text{Al(OH)}_3\text{(am)} \) (or \( \text{Fe(OH)}_3\text{(am)} \)) boundaries represent the total concentration of all these dissolved hydrolysis species that are in equilibrium with the solid phase and these are indicated by thick lines.

It may be worth noting that there are two solid phases: amorphous aluminium hydroxide precipitate (\( \text{Al(OH)}_3\text{(am)} \), \( \log K = -31.5 \)) and crystalline aluminium hydroxide precipitate (such as gibbsite, \( \text{Al(OH)}_3\text{(c)} \), with solubility given by \( \log K = -33.5 \)). There are some difference between the two: the amorphous precipitate denotes the freshly precipitated solids without definite ordered structure, formed by addition of an aluminium to an aqueous solution; while the crystalline precipitate represents the solid with identifiable crystalline phases, formed in solution after a long standing or ageing. It can be shown that crystalline aluminium hydroxide (gibbsite form) predominates over a much larger region than does freshly precipitated (\( \text{Al(OH)}_3\text{(am)} \)). However, in water treatment, after addition of metal salt coagulants into water, the whole flocculation (including coagulation) process may need less than twenty minutes to process (ASCE&AWWA 1990). Therefore, for most reactions of concern in water treatment, only the amorphous aluminium (or ferric) hydroxide precipitate is important in the coagulation/flocculation process (Reiber et al. 1995).

In the case of amorphous aluminium oxide, as shown in Figure 2.4, aluminium hydrolysis and solubility are evaluated by considering three polymeric species (\( \text{Al}_2\text{(OH)}_2^{2+} \), \( \text{Al}_3\text{(OH)}_4^{5+} \), and \( \text{Al}_{13}\text{O}_4\text{(OH)}_{24}^{7+} \)) and five monomers (\( \text{Al}^{3+} \), \( \text{AlO}_2^{2+} \), \( \text{Al(OH)}_2^{+} \), \( \text{Al(OH)}_3^- \), \( \text{Al(OH)}_4^- \)) in equilibrium with solid (\( \text{Al(OH)}_3\text{(am)} \)).

It can be seen from the diagram that, in equilibrium with amorphous aluminium hydroxide, the polymeric aluminium hydrolysis species rather than \( \text{Al}^{3+} \) will be predominant below pH 6. In the more acidic region (pH < 3), soluble \( \text{Al}^{3+} \) will prevail; on the other hand, at alkaline region (pH > 8), the principal soluble aluminium species in equilibrium with the amorphous solid is the aluminate anion, \( \text{Al(OH)}_4^- \). When total soluble aluminium species
exceed solubility, precipitation occurs. From Figure 2.4, it is seen that aluminium is least soluble at a pH around 6.9; and the values of solubility for aluminium at pH 6, 7, 7.5, 8, 8.5, are listed below:

Table 2.2 Solubility of aluminium at values of pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>6</th>
<th>7</th>
<th>7.5</th>
<th>8</th>
<th>8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (M)</td>
<td>$10^{-4.09}$</td>
<td>$10^{-3.29}$</td>
<td>$10^{-4.95}$</td>
<td>$10^{-4.47}$</td>
<td>$10^{-3.97}$</td>
</tr>
</tbody>
</table>
Figure 2.4 Solubility diagram for amorphous aluminium hydroxide: equilibrium concentration of hydroxo aluminium (III) complexes in a solution in contact with freshly precipitated amorphous Al(OH)₃ (s) (made based on the reaction constants from Baes and Mesmer (1976), see Table 2.1).
Figure 2.5 Solubility of Iron (III) at equilibrium with amorphous ferric hydroxide (reaction constants from Flynn (1984), or see Table 2.1).
Table 2.1 Aluminium and Iron (III) Equilibria

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>log K (25°C)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Al}^{3+} + H_2O = \text{Al}(OH)^{3+} + H^+$</td>
<td>-4.97</td>
<td>Baes and Mesmer (1976)</td>
</tr>
<tr>
<td>2</td>
<td>$\text{AlOH}^{2+} + H_2O = \text{Al}(OH)_2^{+} + H^+$</td>
<td>-4.3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$\text{Al}(OH)_2^{+} + H_2O = \text{Al}(OH)_3 + H^+$</td>
<td>-5.7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$\text{Al}(OH)_3 + H_2O = \text{Al}(OH)_4^{-} + H^+$;</td>
<td>-0.8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$2\text{Al}^{3+} + 2H_2O = 2\text{Al}^2(OH)_2^{4+} + 2H^+$</td>
<td>-7.7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$3\text{Al}^{3+} + 4H_2O = 3\text{Al}(OH)_4^{5+} + 4H^+$</td>
<td>-13.94</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$13\text{Al}^{3+} + 28H_2O = 13\text{Al}(OH)(OH)_{24}^{7+} + 32H^+$</td>
<td>-98.73</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$\text{Al}(OH)_3(\text{am}) = \text{Al}^{3+} + 3OH^-$</td>
<td>-31.5</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$\text{Al}(OH)_3(c) = \text{Al}^{3+} + 3OH^-$</td>
<td>-33.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$\text{Fe}^{3+} + H_2O = \text{FeOH}^{2+} + H^+$</td>
<td>-2.2</td>
<td>Flynn (1984)</td>
</tr>
<tr>
<td>11</td>
<td>$\text{FeOH}^{2+} + H_2O = \text{Fe}(OH)^{2+} + H^+$</td>
<td>-3.5</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>$\text{Fe}(OH)^{2+} + H_2O = \text{Fe}(OH)_3 + H^+$</td>
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<td></td>
</tr>
<tr>
<td>13</td>
<td>$\text{Fe}(OH)_3 + H_2O = \text{Fe}(OH)_4^{-} + H^+$</td>
<td>-10</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>$2\text{Fe}^{3+} + 2H_2O = 2\text{Fe}_2(OH)_2^{4+} + 2H^+$</td>
<td>-2.9</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>$3\text{Fe}^{3+} + 4H_2O = 3\text{Fe}_3(OH)_4^{5+} + 4H^+$</td>
<td>-6.3</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>$3\text{Fe}^{3+} + 4H_2O = 3\text{Fe}_3(OH)_4^{5+} + 4H^+$</td>
<td>-38.7</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>$\alpha\text{-FeOOH}(c) + H_2O = \text{Fe}^{3+} + 3OH^-$</td>
<td>-41.7</td>
<td></td>
</tr>
</tbody>
</table>
Although identification of these species has not been possible to date in systems containing colloidal materials or in actual process environments, polymeric or polynuclear species such as \( \text{Al}_3\text{O}_4(\text{OH})_{24}^{7+} \) have been identified in aqueous solution (Bottero and Bersillon 1989, Bottero et al. 1982, Bottero et al. 1987). The significance of these polynuclear species in the relevant pH region for coagulation has been demonstrated (Ching et al. 1994).

Note that the solubility diagram will show some differences if different equilibria are chosen, or different number or kinds of the hydrolysis species are included. Due to the uncertainties in the values of the equilibria, particularly for formation of soluble \( \text{Al(OH)}_3 \), these differences are often observed in different reference. Furthermore, the situation could be more complicated in actual flocculation systems due to presence of colloids and some anions. So, it would be difficult to establish a relationship between coagulation/flocculation and the solid or the dissolved species of these metal ions quantitatively. However, in many cases, it can provide useful information for general discussions. The implication of the diagrams to coagulation/flocculation and their limitation in interpreting these process will be discussed later (see 2.5).

Note that solubility of aluminium can be greatly affected by presence of other chemicals. Effects of fluoride, sulphate and silicate on aluminium solubility have been reported (Reiber et al. 1995).

### 2.4.3 Precipitation of aluminium

For a slightly supersaturated solution with respect to a solid phase, the solution may remain stable indefinitely (Stumm 1992). When the degree of supersaturation increases or when fine particles of a substance are mixed with this solution, precipitation occurs. Precipitation of aluminium (or iron) in an aqueous solution or suspension is of great importance in understanding coagulation by these metal salts. In order to get a better understanding of precipitation and the effects on coagulation, three aspects should be mentioned:
(1) the general steps of precipitate formation;
(2) the nature of precipitates (stability and charge);
(3) kinetics of precipitate formation.

2.4.3.1. General steps of precipitate formation

Generally, the term precipitation refers to the formation of a solid phase from a supersaturated solution by a chemical reaction. One important feature of precipitation processes is that they are generally initiated at high supersaturation, resulting in fast nucleation and the consequent creation of large numbers of very small primary crystals. It consists of three basic steps and two subsequent secondary steps. The three basic steps are: supersaturation, nucleation and crystal growth; and the two secondary steps are: agglomeration, ripening or ageing (Mullin 1993, Snoeyink and Jenkins 1980).

(1) Nucleation

Nucleation is the initial step of precipitation, during which very fine particles called nuclei form and precipitation begins. There are two kinds of nucleation: homogenous nucleation and heterogeneous nucleation. If the nuclei are formed from clusters of a few molecules or ion pairs of component ions of the precipitate, the initial phase of precipitation is referred as homogeneous nucleation; if foreign particles, with some similarity of crystal lattice structure, are the nuclei, the nucleation is said to be heterogeneous. In aqueous solution, due to existence of fine particles of various types, most nucleation occurs heterogeneously.

(2) Crystal Growth

Crystal formation is an intermediate step in precipitation, which takes place through the deposition of the precipitate constituent ions onto nuclei. The rate of crystal growth is of
critical importance in water treatment process involving precipitation that often does not reach equilibrium in the available time. Crystal growth rate can be expressed as

\[
\frac{dC}{dt} = -k_s S(C - C^*)^n
\]

where

- \(C^*\) = saturation concentration, mole/liter
- \(C\) = actual concentration of limiting ion, mole/liter
- \(k_s\) = rate constant, liter\(^n\) time\(^{-1}\), mole\(^{1-a}\)
- \(S\) = surface area available for precipitation, mg/liter of a given particle size
- \(n\) = constant

(3) Agglomeration

The initially formed solid, the very small primary crystals, might cluster together due to interparticle collision and van der Waals attraction forces. In this stage, such terms as agglomeration, aggregation, coagulation and flocculation can all be applied in this area, although agglomeration is normally used for simplicity (Mullin 1993). It is most likely that during this process, the amorphous precipitates will form. In this case, the kinetics of aggregation can be described by the Smoluchowki theory.

(4) Ageing

Dispersed particles in their own saturated solution tend to undergo a process, during which the smaller particles dissolve and the solute is deposited subsequently on the large particles. As a result, the small particles disappear and the large grow larger towards to a monosized dispersion. In this process, the crystal structure of the precipitate may change to that of the stable phase. This ageing period may take a very long time. In the water treatment process, coagulation and flocculation are usually completed in less than twenty minutes. So the ageing may not be important for this process.
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It is likely that, among these steps, crystal growth and agglomeration will be important for coagulation by the hydrolysing metal salts. Although for some divalent ions, the crystal growth may be a slow kinetic process (e.g. precipitation of calcium carbonate in supersaturated solution 10 or 20 minutes will be needed (Nancollas and Reddy 1974)), it may take a few seconds for $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ to complete this step of precipitation. However, quite possibly, the agglomeration or aggregation of the small primary crystals might take relatively longer time depending on the particular conditions. So that, it may exert some important influence to the coagulation and flocculation by the hydrolysing metal salts as shown in this study.

2.4.3.2 The nature or characteristics of precipitate

Despite the general description of precipitation as stated in preceding section, the term \textit{precipitation} is quite often used ambiguously, for various reasons. In some cases, although precipitation of an insoluble phase occurs, a settleable precipitate may not always form. Sometimes a precipitate is colloidaly dispersed during its formation either because of adsorption of potential determining ions or through peptization during washing or dilution. Different scientists may have different definitions. Most chemists, especially analytical chemists (Latinen 1960, Scoog and West 1963) view precipitation as the formation of a solid phase when the product of the active masses of the reactants exceeds the solubility product. Colloid chemists sometimes refer to the settling of sols after coagulation as precipitation. In their study, Hayden and Rubin (1974) defined precipitation as a result of active masses or concentration of a chemical substance exceeding that predicted by the solubility product, without regard to the settleability of that phase. This definition would be in accordance with the general description (in 2.4.3.1), and will be accepted in this study.

It is worth noting that the stability of a solution and the colloidal stability of the precipitate are different concepts, and must be carefully distinguished. Stability of a solution refers to a state or condition of that solution with respect to formation of the most insoluble or inactive solid phase, whereas stability of the precipitate means whether or not the solid of
precipitate is dispersed or settleable. So, a colloidally-stable precipitate is dispersed as a sol and may not settle even after long periods of time. An unstable precipitate will not be colloidally dispersed and therefore would settle if allowed to stand undisturbed.

Bearing this conception in mind, one must realise that the solid phase in the solubility diagrams (Figure 2.4 and Figure 2.5) may possess distinct colloidal properties due to the heterogeneous aqueous reactions of aluminium, solubility and solution pH; some may be stable colloids while others settleable fine aggregates. This difference in colloidal properties of precipitates and together with electrical charges of them will be discussed below.

The characteristics of aluminium precipitate, the colloidal stability (stable or settleable) and electrical charge, has been observed as a function of solution pH.

Hayden and Rubin (1974) investigated the precipitation of aluminium systematically. In their study, using light scattering techniques, the critical pH limits of precipitation and dissolution were determined by observing curves of scattering intensity as a function of pH at a given aluminium salt concentration. For $1.0 \times 10^{-3}$ M aluminium nitrate, it was found that the pH range of precipitation after one hour was 4.55 to 9.25. Moreover, the precipitate is colloidally dispersed in acidic solution pH region. Above neutrality (as shown in Figure 2.6), the precipitate settled rapidly. The same phenomena are also observed at a concentration of $5.0 \times 10^{-4}$ M Al(NO$_3$)$_3$. Although the solutions in the acid pH range where the stabilised precipitate formed were perfectly clear to naked eye, a well-defined Tyndall beam was observed when placed in the nephelometer. This might indicate that the size of colloidal aggregates formed in the acidic solution were very small.

In addition, measuring fresh solutions by using a Streaming Current Detector, the charge of the aluminium hydrolysis products was examined as a function of solution pH at a concentration of $5.0 \times 10^{-4}$ M Al(NO$_3$)$_3$ (Hayden and Rubin 1974). The results indicated that the aluminium hydroxide hydrosols are strongly positively charged at low pH, and that the precipitate in the alkaline pH range was weakly negative. An isoelectric point (IEP) at approximately pH 8 that corresponds to the middle of the pH range where the settleable
precipitate forms. This result is consistent with results obtained by other methods (Hall 1966, Gayer et. al. 1958).

There is a discrepancy about the pH value of IEP. A value of pH around 9 for the IEP was found by Matijevic and co-workers (1971). They prepared alumina flocs for mobility measurements in aluminium nitrate (1×10^{-2}M) solutions precipitated with sodium hydroxide. The samples were centrifuged, supernatants were decanted and the precipitates were allowed to stand for 24 hours before the pH and the mobility were measured with a microelectrophoresis cell. So, the difference between the values pH of IEP might be attribute to difference of the sample preparation and instruments.
Figure 2.6 Typical turbidity-pH curves for fresh solution of $1.0 \times 10^{-3}$ M Al(NO$_3$)$_3$. The pH range between pH$_p$ and pH$_d$ define the range of insoluble aluminium (III) at the given concentration; The precipitate between pH$_p$ and pH$_c$ was colloidally dispersed, the precipitate between pH$_c$ and pH$_d$ settled rapidly. (□) denotes the turbidity measurements at two minute; (O) denotes the measurements at ten minute; and (●) denotes the measurements at sixty minutes. (From Hayden and Rubin (1974)).
2.4.3.3 The Factors of Affecting Precipitation

Several factors affect the aluminium precipitation process kinetically. These factors include solubility, concentration of total aluminium in solution, formation of polymeric hydrolysis species, and even the physical factors such as mixing conditions. Among them, the solubility and formation of dissolved species are very much related to the solution pH.

Using a base titration method, with simplified aluminium chemistry models, Clark and Srivastava (1993) showed that there is competition between polymeric and solid aluminium species during base titration. This indicates that formation of polymeric aluminium species may reduce the formation of solid aluminium species. Their results also showed that mixing conditions affect the aluminium precipitation. With mixing speed either 500 or 2000 rpm, and Al concentration either 1.0×10^{-2} or 4.0×10^{-4} M, their results show that mixing speed influences the shape of the pH titration curve.

The kinetic expression for the solid aluminium hydroxide (assuming amorphous precipitate formation) was proposed as below (Clark and Srivastava 1993):

\[ r_s = k_s \left( [Al]_r - [Al]_p \right)^{2/3} \left( K_s [Al^{3+}][OH^-]^3 - [Al(OH)_{3}]^* \right) \]  \tag{2.33}

where

- \([Al]_r\) the total aluminium concentration
- \([Al]_p\) the concentration of polymeric aluminium species
- \(Al(OH)_{3}\) the solubility or critical concentration of aqueous aluminium hydroxide
- \(k_s\) the solid kinetic constant (m^2·mol^{-2}·s^{-1})

Equation (2.33) shows that the rate of solid formation becomes very low if most aluminium has been converted to polymeric forms. Formation of solid phase will be impossible if the critical concentration of aluminium hydroxide is not exceeded.
2.4.3.4 Influence of solution chemistry on aluminium precipitation

Effects of certain anions on aluminium precipitation have been studied (Marion and Thomas 1946; Hayden and Rubin 1974; Letterman et al. 1979, Letterman and Vanderbrook 1983). Although anions such as nitrate have almost no effect on aluminium precipitation, other anions such as bicarbonate \((\text{HCO}_3^-)\), sulphate \((\text{SO}_4^{2-})\) and \(\text{PO}_4^{3-}\) can influence the precipitation of aluminium in several ways. These effects include shifting pH range of precipitation, altering colloidal stability of precipitate and moving IEP of aluminium hydroxide precipitate to a lower pH.

Sulphate ion at relatively low concentrations was found to affect both the pH range of precipitation and colloidal stability of precipitate (Rubin and Hayden 1974). The presence of sulphate ion in solution may only slightly extend the pH limit of aluminium precipitation to the acidic side, but it has considerable effect on stability of aluminium hydroxide precipitate (Hanna and Rubin 1970). For example, precipitate of aluminium sulphate \((5 \times 10^{-4}\text{M})\) was observed to be settleable nearly along the whole range of precipitation from pH 4.5 to 8.9, while precipitate of aluminium nitrate was seen settleable only in the pH range from 7 to 9 (Hanna and Rubin 1970). The effect of sulphate ion on the IEP of aluminium hydroxide precipitate was reported by Mattson (1930); the presence of sulphate in solution might shift the isoelectric point of aluminium hydroxide to a lower pH value. More evident effects on pH values of IEP was reported in case of phosphate and silicate ions in the same study. The relevance of these effects to aluminium precipitation and coagulation by aluminium salts will be discussed later (see 5.4.4).

Presence of bicarbonate ion in solution was suggested to alter the physico-chemical characteristics of the aluminium hydroxide precipitate (Letterman et al. 1979). Accordingly, these effects of anions on aluminium precipitation will influence the aluminium coagulation with particles; more details will be given later.

In explaining the effect of anions on the pH limits of maximum precipitation of aluminium hydroxide, Marion and Thomas(1946) suggested that the behaviour of anions in aluminium
precipitation will depend on the basicity of the anion, the co-ordinative binding affinity of the anion for aluminium and the resistance of bound anion to displacement by added hydroxyl ion. If the anion is a very strong co-ordinator with aluminium and not replaced by hydroxide ion, the pH of optimum precipitation will drop sharply with increasing anion concentration. If the anion is a strong co-ordinator with aluminium but can be displaced by hydroxide ion, the pH of optimum precipitation increases with a very basic anion, and decreases with a weakly basic anion. If the anion is only a very weak co-ordinator with aluminium, it gives only a slight effect on optimum precipitation, generally in the direction of lower pH value.

2.4.3.5 Conclusion

From all above, several important points can be put as follows:

Firstly, before supersaturation with respect to amorphous Al(OH)$_3$, the dissolved mononuclear and polynuclear aluminium hydrolysis products will exist in solution depending on aluminium concentration and solution pH. Second, when the supersaturation of aluminium in solution is increased, the precipitation of aluminium occurs resulting in the formation of amorphous solid phase, which may be in a meta-stable state and undergo a long-term ageing. Thirdly, the precipitate can be colloidaly stable and remain dispersed; or may be colloidaly-unstable and be readily settleable depending on pH. The hydrolysis products are strongly positively-charged in acidic region and weakly negatively charged in alkaline region with the IEP around pH 8. Fourthly, rate of formation of precipitate is a function of concentration of total [Al$^{3+}$], and pH, which affects solubility and formation of polymeric species. Mixing conditions may also be important. Finally the precipitation can be greatly affected by presence of anions in solution; the effects include colloidal stability and electrical charge of precipitate.
2.5 Mechanism of Coagulation by Hydrolysing Metal Salts

2.5.1 General

Coagulation of colloids by hydrolyzable metal salts is determined by several factors: (1) solution pH; (2) concentration of metal ions; and (3) concentration of colloids. There are a number of reasons for this. Firstly, the coagulative properties of metal ions such as Al$^{3+}$ (or Fe$^{3+}$) depend on hydrolysis species and precipitation of these metal ions, which vary according to solution pH and concentration of total metal ion employed. Second, in the coagulation process, adsorption of the hydrolysing species on surface of colloids is important, different ratio of surface concentration of colloid to concentration of coagulant will give a specific surface coverage of adsorption which may result in a specific coagulation condition.

As discussed in 2.4, metal ions such as Al$^{3+}$ (or Fe$^{3+}$) undergo hydrolysis reactions in aqueous solution resulting formation of monomeric and polymeric species before supersaturation with respect to amorphous Al(OH)$_3$(am) or Fe(OH)$_3$(am); a further increase of supersaturation may lead to precipitate formation (Al(OH)$_3$(am) or Fe(OH)$_3$(am)). Speciation of these metal ions is dependent on solution pH and total concentration of metal ion: (1) before supersaturation, there are only dissolved hydrolysis species present, including various mononuclear and polynuclear species (2) after supersaturation, there are both dissolved hydrolysis species and amorphous precipitate in the system (see 2.4). Only for pH below 3, will simple free ions, Al$^{3+}$, be dominant in solution (for Fe$^{3+}$, pH below 2). In typical conditions of coagulation process in water treatment, monomeric and polymeric species, as well as the amorphous precipitate will play an important part in this process (Dentel 1988, 1991).

Adsorptivity of metal ions species is very important to coagulation. Adsorbable species are observed to destabilise colloids at much lower concentrations than nonadsorbable simple ions (Stumm 1968). Hydrolysed metal ion species are reported to adsorb much more
readily then a simple metal ion (Matijevic 1972). Because of this, the coagulation initiated by them will not follow the double layer compression model of coagulation described by the DLVO theory as in the case of indifferent ions (see 2.2). On the contrary, destabilisation of colloids is promoted by reduction of surface charge through adsorption of these hydrolysing metal species on surfaces of colloids, most likely at the Stern layer as described by the Stern model in case of specific adsorption (see Figure 2.1), or by co-precipitation at the colloid-water interface, or even by deposition of precipitates formed in bulk solution, depending on the total metal concentration or the concentration ratio of coagulant and colloid.

The energy of interaction for adsorption is a composite function of interaction of solid surface, solvent, and solute. The attraction of the surface for the adsorbate may result from chemical interactions such as hydrogen bonding, coordination reactions, covalent bonding, and ion exchange reactions, along with electrostatic effects. It was demonstrated that, in certain case the adsorption from chemical interaction may overweigh that from electrostatic interaction (Stumm 1968, Matijevic 1973). In addition, it has been reported that extent of adsorption of a species increases with the size of the species (Stumm 1968).

Due to the importance of adsorption, complex reactions in the medium and at the solid-solution interface is essential in understanding sol stability (Matijevic 1973). Particularly, highly charged complexes have tremendous effects upon the coagulation of hydrophobic colloids, although may constitute only a negligible fraction of the total electrolyte content of the dispersion medium (Tang and Stumm 1987; O'Melia et al. 1989). Below, several important descriptions on these interactions will be briefly reviewed. Coagulation based on this conception will be discussed.
2.5.2 The models for the sorption of cations on mineral surfaces

From 2.5.1, we know that adsorption of the metal ions hydrolysing species on the surfaces will play an important role in coagulation of hydrophobic colloids. It is obvious that, here the adsorption means accumulation of cations or especially their hydrolysing species on surfaces of mineral particles leading to certain level surface coverage of these species. Precise description of adsorption of all these various species on mineral surface would be very difficult if not impossible. However, simplified models, which describe the sorption of cations on metal oxides, may be helpful in understanding the process although they cannot give exact explanation of all the metal ion hydrolysing species. Here, two basic models are briefly reviewed, they are: (1) Surface Complexation; (2) Surface Precipitation.

2.5.2.1 Surface complexation model

The surface complexation model is principally based on the concept of co-ordination of the metal ions with the oxygen donor atoms and the release of protons from the surface (Stumm et. al. 1976; Schindler et, al. 1976), e.g. $\text{S-OH} + \text{Cu}^{2+} \leftrightarrow \text{S-OCu}^+ + \text{H}^+$ (Stumm 1992). So, the reactions between solutes and functional groups on the solid surface are co-ordination reactions that obey mass law equations for equilibrium. In this model, adsorption of cations on oxide surfaces is viewed as analogous to the formation of soluble complexes, and only monolayer adsorption can occur with a complete surface coverage at the final stage. For a fixed pH, the model in its simplest form can be expressed mathematically by the Langmuir isotherm (Stumm 1992). The surface complexation model can be used to describe the adsorption of cations at low concentrations of the sorbable cations. However, at a higher concentration, experimental data follow the empirical Freundlich isotherm with no apparent saturation of the adsorbing surfaces. Furthermore, it is often found that a sharp increase in adsorption occurs at the point when the solubility product is exceeded. So, in this case, the surface complexation model is no longer applicable to explain the observed sorption phenomena.
2.5.2.2 Surface precipitation model

The surface precipitation model was proposed by Farley et al (1985). In this model, when cations adsorb to the surface of a mineral a precipitate of the cation with the constituent ions of the mineral surface may form at high surface coverage. This allows sorption to occur through a continuum between surface complex formation and bulk solution precipitation of the sorbing ion. So, as the cation is complexed at the surface, a new hydroxide surface is formed. In the model, cations at the solid (oxide) water interface are treated as surface species, while those not in contact with the solution phase are treated as solid species forming a solid solution. In this case, at low sorbate cation concentration, surface complexation is the dominant mechanism. However, as the sorbate concentration increases, both the surface complex concentration and the amount of the surface precipitate increase until the surface sites become saturated. Surface precipitation then becomes the dominant sorption mechanism. Furthermore, as bulk solution precipitation comes closer, the amount of the surface precipitate becomes large. It follows that as metal is adsorbed on a surface, a new hydroxide surface will be formed, allowing further mass transfer of metal to the solid phase. This can be effectively a multilayer sorption process. A schematic representation of the two models, surface complexation and surface precipitation on hydrous ferric oxide (Fe(OH)$_3$(s)), is presented in Figure 2.7 (Farley et. al. 1985).

(a) \[
\text{Fe(OH)}_3(s) + \text{OH}^- + \text{Me}^{2+} \leftrightarrow \text{Fe(OH)}_3(s) + \text{O Me}^+ + \text{H}^+
\]

Surface complex formation

(b) \[
\text{Fe(OH)}_3(s) + \text{O Me}^+ + \text{Me}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \left(\text{Fe(OH)}_3(s)\right)_{\text{Me(OH)}}(s) + \text{O Me}^+ + 2\text{H}^+
\]

Surface precipitation

“solid solution”

Figure 2.7 Surface complex and Surface precipitation.
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The surface precipitation model only addresses precipitation which occurs at the solid-liquid interface. It is reasonable to think that precipitation can also occur in bulk solution before deposition, if applied metal ion concentration is high. The model of *heterogeneous nucleation precipitation* is proposed to explain this continuum from the heterogeneous nucleation to surface precipitation. Unlike the surface precipitation model, in which the interface is described as a mixing zone for the ions of the new solid phase and those of the substrate, the model "heterogeneous nucleation precipitation", considers the interface to be fixed, and no mixing of ions to occur across the interface. It seems that in this model, precipitates formed in bulk solution will simply be deposited on particle surfaces.

Whether in an actual case precipitation of a new phase follows one or the other limiting model will depend on the mixing energies of the pure phase and the substrate (Stumm 1992). However, it would be very difficult to distinguish them in a practical process.

The above models delineate the way in which cations adsorbed onto the oxide surfaces. Below, we will discuss coagulation models of metal ions such as Al$^{3+}$ and Fe$^{3+}$ in the light of these models.
2.5.3 Model of coagulation of hydrolysing metal salts

The surface complexation and surface precipitation models for adsorption (see 2.5.2) provide a theoretical base in explaining the destabilisation or coagulation of colloids by hydrolysing metal salts from the perspective of adsorption. In the light of the two surface adsorption models, the coagulation by hydrolysing metal salts such as $\text{Al}^{3+}$, $\text{Fe}^{3+}$ can be discussed accordingly. The significance of these models is that they give depiction of the adsorption at different concentration of metal ions, and that ultimate adsorption can lead to characterisation of the surface of colloids by the adsorbed solid phase. If the hydrolysing metal ion species is highly positively charged in certain pH range, the adsorption of these species can lead to a charge neutralisation of the negatively charged colloidal particles.

2.5.3.1 Coagulation through Surface Complexation

When aluminium concentration is low so that only dissolved aluminium species exist in solution, destabilisation of colloids can be described by adsorption through surface complexation (see 2.5.2.1) which involves the coordination of the metal ions with the oxygen donor atoms and release of protons from the surface. Aluminium (or iron) adsorption onto particle surfaces might affect the speciation of aluminium (or iron) in solution and change surface properties of the particles. In this case, surface complexation reactions on mineral particles surfaces can occur between aluminium and surface hydroxyl groups of the mineral. For kaolinite, although cation adsorption can involve both ion-exchange and surface complex formation, the latter occurs predominantly since the former only occurs at low pH. The complexation reaction is supposed to occur both at the basal gibbsite and edge surfaces of the clay mineral (Stumm, 1992). Reaction with monomeric aluminium hydrolysis species may be written as

$$\equiv\text{SOH} + \text{Al(OH)}_n^{(3-n)+} \leftrightarrow \equiv\text{SOAl(OH)}_{n-1}^{(3-n)+} + \text{H}_2\text{O}$$
where $\equiv S$ indicates a surface species. Suppose the original surface charge of the mineral, before adsorption, is due to the presence of charged surface species ($\equiv \text{SOH}_2^+$ and $\equiv \text{SO}^-$, without any adsorbing species other than protons). Therefore, formation of aluminium surface complexes can change surface charge (Stumm and Morgan 1996; Stumm 1992); especially for highly charged species of polymeric aluminium species adsorption can have a dramatic effect on surface charge (Tang and Stumm 1987; O’Melia et al. 1989). It seems that, in this case, certain limiting surface coverage or total site density has to be assumed due to the site-binding approach as described by James and Healy (1972) and James and Parks (1982) in their studies. This limit can be much less than the surface coverage observed when adsorption experiments are conducted (see Hahn and Stumm 1968) indicating that when concentrations of metal ions increase, this model is inapplicable.

2.5.3.2 Coagulation through Surface Precipitation

As the aluminium concentration increases, the destabilisation of colloids may be explained by the surface precipitation (see 2.5.2.2). This model allows for the formation of a surface phase with a composition that varies continuously between that of the original solid and that of a pure precipitate of the adsorbing cation, leading to a possibility of multilayer adsorption (Farley et al. 1985) as described in 2.5.2.2. Under this model, formation of the aluminium (or iron) precipitate at the mineral surface can occur; sorption density of the precipitating metal ion(s) on the surface increases. The Al(OH)$_3$(am) can be formed at the surface of mineral particles even though solubility product for Al(OH)$_3$(am) is not exceeded in the bulk solution. Finally, surface of particles can be characterised by the acid-base properties of Al(OH)$_3$(am). Letterman and Vanderbrook (1983) showed that: the surface of coated kaolin particle by aluminium and pure aluminium precipitate share nearly the same trait as a function of solution pH.

It is worth noting that when suspension is supersaturated with respect to amorphous precipitate, precipitation might also occur through heterogeneous nucleation on the mineral particle surface or through homogeneous nucleation in bulk solution. This probably is the
case in the Precipitation Charge Neutralisation model (see 2.5.3.3), for a large dosage of coagulant is assumed in this model.

2.5.3.3 The Model of precipitation charge neutralisation (PCN)

The surface complexation and surface precipitation models describe the ways in which metal ions are adsorbed onto the surfaces of colloids. It is obvious that, if the metal ion species are highly charged, adsorption of them on negatively charged colloid will result in a charge neutralisation of the colloid. Since surface charge of colloids is very important to colloid stability and coagulation, models specially for coagulation in water treatment process have more emphasis on adsorption and charge neutralisation (Letterman and Iyer 1985; Dentel 1988).

Letterman and Iyer (1985) developed a model of coagulation of kaolin by hydrolysed aluminium, using a computer program that allows self-consistent calculations to be made simultaneously for solution and surface chemical equilibria. In this model, both adsorption and charge effects were considered and stability behaviours of colloids in the four zones (see 5.4.2) were given. However, determination of the parameters would be very complicated and this may make this model less useful.

Compared with Letterman’s model, one model proposed by Dentel (1988) seems more practical. This is the precipitation charge neutralisation model (PCN) (see also Dentel 1991 and Dentel and Gossett 1987). Basically, this model is to explain coagulation by aluminium and iron (III) salts in water treatment process. Considering the normal dosage of metal salts in practice, it assumes that adsorption and precipitation of alum hydrolysis products on particle surfaces proceed after addition of high dosage of metal salts, enough to give a supersaturation with respect to amorphous precipitate, so that precipitate can form even in bulk solution. Therefore, the adsorption is supposed to occur continuously from monomers, polynuclears up to precipitate. The detailed description of adsorption or deposition process leading to a charge neutralisation or charge reversal are schematically
shown in Figure 2.8. According to this model, the coagulation with aluminium or iron salts involves three steps:

1). Destabilisation begins after addition of a high dose of aluminium (or iron) that exceeds the operational solubility limit of aluminium (or iron) hydroxide.

2). Aluminium or iron hydroxide species are then deposited onto colloidal surfaces, as represented in Figure 2.8. As shown in this figure, metal hydroxide could end up on particle surfaces by several possible pathways.

3). Under typical conditions, metal hydroxide is positively charged, while the original colloidal particles are negatively charged. So the deposition process can result in charge neutralisation or charge reversal of the colloidal particles at certain doses.

Therefore, the state of colloids will depend on the charge neutralisation and charge reversal: normally a charge neutralisation may lead to coagulation whereas a charge reversal may lead to restabilisation. When water becomes over-saturated with respect to amorphous aluminium hydroxide, a kinetic transition occurs. During this transition, monomeric, multimeric or polynuclear soluble intermediates are formed by progressive hydrolysis reactions (see 2.4.1). In the pH range below the IEP of the metal hydroxide precipitate, positively charged hydroxo-metal polymers will prevail. In solution more alkaline than the IEP, anionic hydroxo complexes exist. Ultimately polymeric complexes of indefinite size are formed. Adsorption of these positively-charged aluminium hydrolysed products reduces the negative surface charge of particles at the Stern layer (see 2.1.2.2 and Figure 2.1) so that coagulation can occur.
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SOLUTION

hydratation → polymerization → nucleation/precipitation

Al (III) → MONOMERS → POLYMERS → PRECIPITATE

↓ adsorption ↓

↓ hetero-

↓ coagulation

MONOMERS → POLYMERS → PRECIPITATE

SURFACE

(a)

(b)

Figure 2.8 Schematic representation of precipitation-charge neutralisation (PNC) model: (a) various pathways followed by aluminium hydroxide species in solution or at a surface in contact with the solution; (b) if the particles are of opposite charge to the metal hydroxide, charge neutralisation and charge reversal can occur as depicted (Adapted from Dentel 1991).
The difference with the surface precipitation models lies in the way in which the deposition of precipitate occurs. In the surface precipitation model, precipitation occurs only at the particle surface, whereas in the PCN model, precipitate can form in bulk solution, so that hetero coagulation may be brought about between colloid particles and the precipitates, as described in heterogeneous nucleation precipitation.

It is worth noting that the charge of the aluminium hydroxide as a function of pH shows a marked difference between aluminium sulphate and aluminium nitrate (Matijevic et al. 1971). This will be discussed later.

It should be also pointed out that all of the models above emphasise surface adsorption effects on coagulation, so they will be less applicable to sweep flocculation or Zone 4 coagulation. This is because enmeshment of colloidal particles by massive amount of precipitates is decisive in sweep flocculation; surface adsorption of hydrolysing metal salts products is not so important in this case.

**2.5.4 Coagulation of hydrophobic colloids by hydrolysing metal salts**

From the models above, destabilisation or coagulation by metal ions such as Al^{3+} and Fe^{3+} depends on adsorption of the charged metal hydrolysis products; or at a very high dosage of coagulant, precipitation alone can decide the coagulation. Conditions of surface coverage will depend on surface concentration of colloids (S, m^2 L^{-1}) and concentration of metal ion (C mg/L or M) or ratio of S:C. Also, the charge of hydrolysed species or precipitate depends on solution pH. Consequently, coagulation of hydrophobic colloidal particles by hydrolyzable metal ions will be dependent on: (1) concentration of metal ions. (2) concentration of the colloids. (3) solution pH. Certain anions can also have a great influence; this will be discussed separately (see 2.5.4.4). The influence of these factors on coagulation of hydrophobic colloids by hydrolyzable metal ion will be discussed below.
2.5.4.1 Effect of the metal salt concentration.

Assuming the pH is at a constant value in the acidic region, effect of the coagulants on coagulation can be conveniently discussed. This will give several different coagulation condition, which are important in understanding metal salt coagulation.

If a solution pH is in the acidic region, and the concentration of colloids is not very high, there are two coagulant concentration regions where destabilisation is obtained with increasing coagulant concentration. A typical example is shown in Figure 2.9, adapted from Stumm and O'Melia (1968) for destabilisation of a silica dispersion with Fe(III) at a pH around 4. Similar results are also observed in our experimental system with kaolin 50mg/L and aluminium sulphate, at solution pH 6 and 7 (see Chapter 5). The first region of destabilisation identified as CCC₁ (critical coagulation concentration), occurs when sufficient metal hydrolysis products are present to become adsorbed and therefore destabilise the suspension. The mechanism here is most likely adsorption of charged hydrolysing species, leading to reduction of charge or charge neutralisation. The mechanism could be well explained by the *electrostatic patch* model (Gregory, 1973,1976). Adsorption of polymerised metal hydrolysis species giving rise to a bridging mechanism of destabilisation has also been suggested (Bratby 1980), but extended bridges seem unlikely. At higher coagulant dosages, restabilisation occurs as a result of charge reversal. Bratby (1980) also suggested that the restabilisation may be due to excess adsorption of polymeric species occupying too many adsorption site so that bridge formation between adjacent particles is prevented. However the bridge formation mechanism in this case is not well established. The initial concentration of coagulant required for restabilisation is symbolised by CSC (critical stabilisation concentration). Clearly the behaviour of charge reversal is an evidence that destabilisation does not follow the simple DLVO theory in case of indifferent electrolytes (see 2.2.3).
If the initial applied coagulant concentration is increased sufficiently, a further destabilisation region will occur which is generally referred to as the Zone 4 coagulation, and the critical coagulant concentration for this region is identified as $\text{CCC}_4$ in Figure 2.9. The mechanism of coagulation in this case was broadly described as arising from a sweep mechanism of colloid enmeshment by precipitation (Stumm and O'Melia 1968). However, the actual situation might not be so simple. The coagulation may most likely be dominated by kinetics of metal ion precipitation as discovered in our study (see Chapter 5). It may be due to this complication that there are some arguments concerning the mechanism. Matijevic (1976) suggested that surface precipitation of aluminium hydroxide takes place (to some extent) in all regions or zones of coagulation but it is the solution chemistry, particularly the pH and destabilising anion concentrations, which determine whether or not the precipitate coated particles will be flocculated. Moreover, Letterman et al. (1983) suggested that the Zone 4 coagulation is controlled by the solubility of the adsorbed aluminium hydroxide precipitate and surface ionisation and sulphate complex formation reactions. This indicates that solution chemistry, especially the influence of certain anions on coagulation, has to be considered carefully (see 2.5.4.4).
2.5.4.2 Effect of colloid concentration

A schematic demonstration of the relation between coagulant dosage and colloid concentration is shown in Figure 2.10 as a typical example (adopted from Stumm and O'Melia 1968), noting that the following discussion may be taken as applicable for a pH approximately 4 to 5, coagulant Fe(III).

The shaded area indicates zones where destabilisation occurs and four conditions for destabilisation and restabilisation can be specified:

Zone 1 - indicates that insufficient coagulant has been employed to the colloidal suspension and destabilisation does not occur.

Zone 2 - refers to the region where destabilisation of colloids has taken place;

Zone 3 - refers to the region where restabilisation of colloids has taken place due to excessive coagulant addition.

Zone 4 - indicates the region where the coagulant dosage is high enough that oversaturation with respect to solid phase is achieved, and precipitation of metal hydroxide species occurs.

In Figure 2.10, there are three concentrations (labelled as $S_1$, $S_2$, $S_3$) under which increasing coagulant concentration lead to different behaviour of destabilisation.

In the case of very low concentration of colloids ($S_1$), there will be very little collision opportunity among colloids. When a quantity of metal coagulant is introduced, even though it may be sufficient to cause destabilisation, the collision rate will be too low to give significant coagulation in the available time. With further increase coagulant concentration, the ratio of coagulant dose to colloid concentration increases, resulting in excessive
adsorption, charge reversal and restabilisation of dispersed colloids. Only when very high concentration $\text{CCC}_1$ of metal salts is applied and massive metal hydroxide precipitate is formed, enmeshment of the dispersed particles by metal hydroxide precipitate (sweep floc formation) leads to destabilisation and removal of the particles.

![Diagram](image)

**Figure 2.10** Destabilisation (Zone 2), restabilisation (Zone 3), and “sweep flocculation” (Zone 4) region for the aggregation of colloidal suspensions by Al(III) or Fe(III) (adapted from Stumm and O’Melia (1968)): (a) schematic coagulation curves at constant pH (in acidic region) for four colloid concentrations; (b) effect of colloid concentration ($m^2/L$) on the dosage of coagulant required to produce destabilisation, restabilisation and sweep flocculation region.

At a higher concentration of colloid such as $S_2$, the suspension behaves differently from one with low concentration such as $S_1$, with increasing of coagulant concentration. The suspension is destabilised at low coagulant concentration, and the destabilisation occurs only over a relatively narrow range of coagulant dosage. It is quite possible that no substantial colloid removal will be obtained during this stage. Further increasing the coagulant concentration beyond a critical dosage (CSC) causes restabilisation of the suspension. The suspension will remain restabilised until a high coagulant dosage ($\text{CCC}_2$) is applied. As mentioned in 2.5.4.1, the coagulation may be controlled by kinetic formation of precipitate at certain stages, which may involve not only metal ion concentration but also
polymerisation species formation and solution pH, as will be discussed later. Once the suspension is destabilised after coagulant concentration (CCC), a significant colloid removal will be achieved. In the coagulant dosage between CCC and CSC, the mechanism of destabilisation is the adsorption of highly positively charged aluminium hydrolysis products onto the surfaces of colloids, which may be described by the surface complexation or even surface precipitation (see 2.5.3) at the Stern layer (see 2.1.2.2 and Figure 2.1).

In contrast to medium colloid concentration such as S, at high colloid concentration as S, restabilisation will not occur with increasing coagulant dosage, where nonstoichiometric sweep coagulation (Zone 4) and stoichiometric destabilisation (Zone 2) overlap (Stumm and O'Melia 1968). The mechanism of destabilisation was explained by Bratby (1980) in terms of kinetics of adsorption and collision rate of particles. However, this aspect was not considered by Stumm and O'Melia (1968) in their study, whereas a mechanism of rapid precipitation of aluminium leading to the overlap Zone 2 and 4 coagulation was suggested. It is suggested by Matijevic (1976) that surface precipitation of aluminium hydroxide takes place (to some extent) in all regions of zones of coagulation; adsorption or surface precipitation may still play an important part in the overlap zone 2 and 4. Moreover, Letterman et al. (1983) suggested that the Zone 4 coagulation is controlled by the solubility of the adsorbed aluminium hydroxide precipitate and surface ionisation and sulphate complex formation reactions. This consideration can not be neglected. All these arguments seem to indicate that the mechanism of coagulation is complicated in this region, and in postulating the mechanism in a particular system, all these factors have to be considered carefully.

In conclusion, at low colloid concentration, the destabilisation mechanism is governed by precipitate formation of metal salts (sweep floc). At medium concentration, the mechanism of destabilisation may be governed through adsorption and precipitation, so the kinetic formation of precipitate. At high concentration, the mechanism of destabilisation may be attributed to some of these factors: charge neutralisation resulting from adsorption of charged metal salts hydrolysis species, surface precipitation and precipitation in bulk solution, as well as solution chemistry.
2.5.4.3 Effect of pH

In the preceding section, the effect of colloid concentration on coagulation is discussed at a particular pH in acidic region. The profile of coagulation described in Figure 2.10 could change with increasing (or decreasing) pH, and could be totally different when the pH goes to alkaline region. So, a further factor, of great importance in destabilisation is the solution pH.

As discussed in 2.4, the predominance of a specific hydrolysis species in an aqueous solution is strongly dependent on the pH value. It is reasonable to think that with certain concentration of coagulant and particular colloid concentration, the state of colloid in suspension will be different depending on the pH. This is because the charges of hydrolysis products are different at different pH. For example, there are some hydrolysis species most effective for destabilisation by virtue of the adsorptivity and charge at certain values of pH (see Figure 2.4 and Figure 2.5). A systematic demonstration of the relationship among coagulant dosage, solid concentration and pH for the case of a silica dispersion using Fe(III) as coagulant is shown in Figure 2.11 (Stumm and O'Melia 1968), which is quite important and often quoted by others such as Bratby (1980).

At solution pH 1, it is seen from Figure 2.11 that, at low colloid surface concentrations, destabilisation does not occur; on the other hand, at high colloid concentration, destabilisation occurs but no restabilisation is observed. Moreover, it is seen that the critical coagulant concentration (CCC) is independent of colloid concentration. The mechanism for destabilisation or coagulation is determined by the species present at this pH. Since at pH 1, the dominant form is simple hydrated aquo metal ions, the destabilisation of colloids is caused by double layer compression as described by DLVO theory (see 2.2.3). The absence of destabilisation at low colloid concentration can be explained kinetically.
caused by double layer compression as described by DLVO theory (see 2.2.3). The absence of destabilisation at low colloid concentration can be explained kinetically.

![Figure 2.11 Schematic representation of the coagulation domain for coagulation of a negatively charged colloid by Iron (III). Interrelationships between coagulant concentration (C), pH, and colloid surface concentration (S) are presented. Shaded areas indicate coagulation region (adapted from Stumm and O’Melia (1968)).](image)

At pH 2, there is a similar behaviour as with pH 1 at low colloid surface concentration; however unlike at pH 1, from low to medium colloid concentration destabilisation occurs. This shows that, at pH 2, hydrolysis products begin to have a significant effect on destabilisation. So, destabilisation is dominated by the adsorption mechanism of the hydrolysed metal ion species, rather than ionic strength effects.

At pH 3 to 5, as has been discussed in 2.5.4.1, in a medium range of surface concentration, colloids are first destabilised at a low coagulant concentration (CCC₁); and then restabilised when coagulant dosage is increased to a certain level (CSC); further increase of coagulant concentration to a high level (CCC₂) destabilisation occur the second time. The mechanism for the destabilisation and restabilisation has been given in the preceding section.
quite questionable for the point of zero charge (the net surface charge) of ferric hydroxide precipitates ($\alpha$-FeOOH) is close to value of pH 7.8 (Stumm 1992), and charge neutralisation of kaolin clay was observed at pH 7.8 (Ching, et al. 1994), indicating that the charge neutralisation is not negligible. Another possibility is the electrostatic patch model (Gregory 1976, 1988), which may explain the destabilisation or coagulation.

It should be noticed that all above discussion is for the case of Fe$^{3+}$, not Al$^{3+}$. Due to different characteristics of charged hydrolysis species as a function of pH between the two metal ions, the conditions of destabilisation of colloids are not the same at these values of pH. However, similarities exist. It was found by Black and Chen (1967) that, at pH 3.0 the destabilisation of kaolinite suspension by aluminium sulphate was caused by double layer compression by nonhydrolyzed Al ($H_2O)_6^{3+}$. Compared to pH 3, at pH 5, destabilisation and restabilisation of kaolinite occur due to adsorption of positively charged polynuclear aluminium hydrolysis products (Sullivan and Singly 1968). At pH 8.0, near the IEP of the Al(OH)$_3$(am) (Hayden and Rubin1974), the destabilisation mechanism is either the adsorption of the aluminium hydrolysis species onto the surfaces of particles, or enmeshment of particles by Al(OH)$_3$(am) species depending on the concentration of aluminium.
2.5.4.4 Effect of solution chemistry

As discussed in 2.4.3.2, solution chemistry has considerable influence on aluminium precipitation. So, it is obvious that the solution chemistries also influence the coagulation by these metal ions. This influence is generally dependent on how strongly anions can co-ordinate with aluminium in terms of replacement of hydroxyl ion (Marion and Thomas 1946; or see 2.4.3.2).

It has been found that nitrates have very little tendency to co-ordinate with metal ions and, therefore, do not have an evident influence on destabilisation with metal coagulants. However, anions such as the bicarbonate ion, chlorides, sulphate ions, etc. have considerable effects on coagulation by aluminium salts.

The effects of the bicarbonate ion on coagulation of kaolin particles by aluminium have been studied by several researchers (Hanna & Rubin 1970; Letterman et. al.1979). The traditional view of the significance of the bicarbonate ion in the coagulation or flocculation of suspensions using hydrolysing coagulants has been associated with its contribution to the alkalinity (buffer capacity) of the water. The reaction between aluminium and the bicarbonate ion is given in simplified form by

\[ \text{Al}^{3+} + 3\text{HCO}_3^- \rightarrow \text{Al(OH)}_3(\text{am}) + 3\text{CO}_2 \]

Here, the importance of maintaining a buffered solution is related to the chemical characteristics of precipitates of Al\(^{3+}\), because, if the suspension does not contain sufficient alkalinity, addition of the hydrolysing metal salt may depress the pH to a value where no precipitate could be formed. In addition, results from studies on the effect of anions on flocculation (Letterman et al. 1979) suggest that the significance of the bicarbonate ion is also related to its ability to alter the chemical and physical characteristics of the metal hydroxide precipitate. Generally, this ion and others such as sulphate and chlorides have little or no effect on the range of pH values corresponding to the precipitation of aluminium hydroxide and cannot prevent the precipitation, but might exert great effect on the range of
pH values where the precipitate aggregates and form settleable floc (Marion and Thomas 1946; Hayden and Rubin 1974; Black et al. 1963). Black and co-workers showed that at alum concentrations of 35 mg L\(^{-1}\), alum floc is settleable between pH range around 6.8 and 7.8, whereas addition of SO\(_4\) up to 125 mg L\(^{-1}\), the alum floc becomes settleable in the range of pH from 4.5 to 7.5. It is also postulated (Letterman et. al. 1979; Ames 1976) that the effect of a particular anion depends on its ability to complex aluminium, and may be due to the ability to enhance floc formation by increasing the cross-linking of insoluble positively charged Al\(^{3+}\) species that would otherwise form a stable, positively charged sol.

Sulphate is a moderately strong co-ordinator with aluminium, and the presence of sulphate ion extends the pH zone of destabilisation towards the acid side, as a result, broadening the whole coagulation range of pH for aluminium (Hanna and Rubin 1970; Letterman and Vanderbrook 1983). In explaining the effects of the adsorbed aluminium hydrolysis products and the specific adsorption of sulphate on particle surface charge, a schematic diagram is proposed by Letterman and Vanderbrook(1983) shown in Figure 2.12. In this diagram, the negative charge of the kaolin particles is assumed due to the dissociation of silanol groups, =SiO\(^-\) and the charge on the surface precipitated aluminium hydroxide is assumed to be due to ionizable, surface-complex-forming sites denoted by =AlOH\(^2+\). In regard to the function of sulphate in solution, Letterman and Vanderbrook (1983) pointed out that near to the isoelectric pH of freshly precipitated aluminium hydroxide, destabilisation of particles is due to the coating of the inherently unstable aluminium hydroxide possibly resulting from ionisation of the precipitate surface or adsorption of sulphate anions and simple double layer compression by indifferent electrolytes.

Hohl et al. (1978) also have proposed the following ionisation and complex formation reactions for hydrous aluminium oxide to explain the sulphate effects on coagulation:

\[
\begin{align*}
\text{AlOH}_2^+ + \text{OH}^- & \leftrightarrow \text{AlOH} + \text{H}_2\text{O}, \quad (1) \\
\text{AlOH} + \text{OH}^- & \leftrightarrow \text{AlO}^- + \text{H}_2\text{O}, \quad (2) \\
\text{AlOH} + \text{SO}_4^{2-} & \leftrightarrow \text{AlSO}_4^- + \text{OH}^-, \quad (3) \\
2(\equiv \text{AlOH}) + \text{SO}_4^{2-} & \leftrightarrow \equiv \text{Al}_2\text{SO}_4 + 2\text{OH}^- \quad (4)
\end{align*}
\]
According to these reactions, increasing the pH and/or the sulphate concentration means increasing the number of neutral (≡AlOH and ≡Al₂SO₄) and negative (≡AlO⁻ and ≡AlSO₄⁻) surface groups, as a result, decreasing the charge of the aluminium hydroxide surface. However, this series of reactions may only possess indicative meaning, for the aluminium hydrolysis reactions are actually much more complicated than these, not to mention the adsorption process onto the particle surfaces.

Having a weak co-ordinating capacity with metal ions, chloride has been reported to shift the optimum pH slightly to the acid side if the concentration is high enough, whereas phosphate anions can shift the optimum pH range to the acid side markedly.

**Figure 2.12** Schematic diagram of the aluminium treated particle surface for “zone 1 to 4”.
CHAPTER THREE

INTERACTIONS BETWEEN METAL IONS AND DISSOLVED SILICA

In this study, properties of dissolved silica and the interaction between Al\(^{3+}\) (and Fe\(^{3+}\)) and soluble silica are greatly concerned. To get a better understanding of these aspects, silica chemistry has to be involved to some extent. The chemistry of silica generally covers a variety of aspects, for example, solubility, polymerization, colloid and surface properties, etc. However, here only the closely relevant aspects such as definitions, solubility of amorphous silica, and sodium silicate solutions, will be given, so that basic concepts can be established. In addition, interactions between soluble silica and aluminium (and iron(III)) in aqueous solution will be briefly reviewed with interest in modification of properties of aluminium hydrolysis products such as solubility and electrical charge. Apart from these two aspects, one related area is the role of polymerised or activated silica on coagulation by aluminium salts. Activated silica has been used as a coagulant aid when aluminium salts are used as coagulants, the mechanism of its action is different from that of dissolved silica. A brief review of the studies of activated silica on coagulation may provide a base to which the role of dissolved silica can be compared.

3.1 The Chemistry of Silica

3.1.1 Terminology

In silica chemistry, *silica* is generally used as a short designation for *silicon dioxide* in all its crystalline, amorphous, and hydrated or hydroxylate forms (Iler, 1979). In analysis, the term *silica* indicates that the silicon content is expressed in terms of weight of SiO\(_2\), regardless of the actual form in which it is present. *Soluble silica* is defined as the form of silica that is monomeric, containing only one silicon atom and generally formulated as Si(OH)\(_4\). This is
often called monosilicic acid or orthosilicic acid. For convenience, this terminology will be applied in this study.

### 3.1.2 Solubility of amorphous silica and silicate solution

#### 3.1.2.1. Solubility of amorphous silica

The solubility of amorphous silica has been studied by many researchers and reported values vary somewhat among these studies, possibly due to differing size of the solid phase and different bases used. It has been reported by many investigators (Alexander et al. 1954, Baumann 1955, Krauskopf 1956, Stoeber 1967) that, up to pH values of approximately 9, the solubility is 100 to 150 mg/L as SiO$_2$ (1.67 to 2.5×10$^{-3}$M) at 25 °C, the soluble species being in the form of Si(OH)$_4$. The solubility of amorphous silica increases greatly when solution pH increases above about 9. Due to the discrepancy between the equilibria, it is difficult to establish a solubility diagram that would be unanimously accepted. However, if we could neglect those minor differences, a fairly precise sketch of the solubility diagram could be made. In **Figure 3.1**, the solubility of amorphous silica for the entire pH range is presented together with the relative concentration of the species that are in equilibrium with amorphous silica (SiO$_2$(am)) (constants from Lagerstrom 1959, see **Table 3.1**). From the diagram, one can see that solubility remains constant from pH 1 to 8, and increases as pH further increases, especially after pH 9; For example, at pH 11, the solubility is more than 5×10$^{-1}$M (30000 mg/L as SiO$_2$). It worth noting that below pH 8, only the soluble silicic acid exists, but at high pH some anions may exist.

The solubility can be affected by several factors, such as the particle size of the solid phase, electrolytes, the presence of impurities, etc. It is worth noting that the addition of polyvalent metal cations such as iron, aluminium, and other metals, to a solution of soluble silicate results in the formation of colloidal silicate with a much lower solubility with respect to monosilicic acid. In this precipitate, silicate ions are presumably linked together by the metal ions to form an insoluble network. Iler has reported that soluble aluminium reduces
Figure 3.1 Solubility diagram of silica: species in equilibrium with amorphous silica. (adapted from Stumm et. al. 1967; data see Table 3.1). (Note: mononuclear wall denotes lower concentration limit below which multinuclear silica species are not stable).

Table 3.1 Silicate equilibria

<table>
<thead>
<tr>
<th>Reactions</th>
<th>log k (25°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $\text{SiO}_2$(am) + 2$\text{H}_2\text{O}$ = $\text{Si(OH)}_4$</td>
<td>-2.7</td>
</tr>
<tr>
<td>2 $\text{Si(OH)}_4$ = $\text{H}_2\text{SiO}_4^- + \text{H}^+$</td>
<td>-9.46</td>
</tr>
<tr>
<td>3 $\text{H}_2\text{SiO}_4^-$ = $\text{H}_2\text{SiO}_4^{2-} + \text{H}^+$</td>
<td>-12.56</td>
</tr>
<tr>
<td>4 $\text{Si(OH)}_4$ = $\text{Si}_4\text{O}_6(\text{OH})_6^{2-} + 2\text{H}^+ + 4\text{H}_2\text{O}$</td>
<td>-12.57</td>
</tr>
</tbody>
</table>

Note: Data of log k for reaction 1 vary between -2.5 and -2.85. Data for reactions 2 - 4 are taken from those by Lagerstrom (1959), valid for a 0.5 M $\text{NaClO}_4$. 
the solubility of amorphous silica from about 110 to less than 10 mg/L (Iler, 1973, 1979). This may be due to the formation of hydroxyaluminosilicate (HAS) in solution, because silicic acid may interact with soluble aluminium (Farmer and Lumsdon 1994, Browne and Driscoll 1992).

3.1.2.2. Nature of silicate solution

Nature of silicate solution generally concerns with many aspects, and here we only discuss one of the important aspects, the species in silicate solutions. In a silicate solution, if silica concentration is below the solubility, monomeric silicic acid \((\text{Si(OH)}_4)\) is the dominant species in the acidic and neutral pH region. This can be seen in the solubility diagram (Figure 3.1). Apart from the monomeric silicic acid, there are some other forms of species existed. The equilibria listed in Table 3.1, and some other proposed reactions are in the efforts to describe the nature of silicate solution. Iler (1979), in his book, also gave some fundamental equilibria, which had been proposed up to that time.

\[
\begin{align*}
\text{SiO}_2 + 2\text{H}_2\text{O} &= \text{Si(OH)}_4 \\
\text{Si(OH)}_4 + \text{OH}^- &= \text{HSiO}_3^- + 2\text{H}_2\text{O} \\
2\text{HSiO}_3^- &= \text{Si}_2\text{O}_5^{2-} + \text{H}_2\text{O} \\
\text{HSiO}_3^- + \text{OH}^- &= \text{SiO}_3^{2-} + \text{H}_2\text{O}
\end{align*}
\]

For the above equations at 25 °C:

\[
\begin{align*}
[H^+] [\text{HSiO}_3^-] / [\text{Si(OH)}_4] &= 10^{-9.8} \\
[H^+] [\text{SiO}_3^{2-}] / [\text{HSiO}_3^-] &= 10^{-12.16} \\
[H^+] [\text{Si}_2\text{O}_5^{2-}] / [\text{HSiO}_3^-] &= 10^{-9.8} \\
[H^+] [\text{HSi}_2\text{O}_6^{3-}] / [\text{Si}_2\text{O}_5^{2-}] &= 10^{-12.8} \\
[\text{Si}_2\text{O}_5^{2-}] / [\text{HSiO}_3^-]^2 &= 2200
\end{align*}
\]
These constants were measured by Roller and Ervin (1940) in a system involving calcium as the base. There is some doubt on formation of disilicate ions in sodium silicate solution; from Iler’s observation, only HSiO$_3^-$ and SiO$_2^{2-}$ are in equilibrium with Si(OH)$_4$ and OH$^-$ ions in the presence of colloidal particles and at very low sodium ion concentration. Even for concentrated solutions of sodium (or potassium) silicate with (SiO$_2$:M$_2$O) molar ratios of 1:1, silica exists as SiO$_2^{2-}$ and HSiO$_3^-$ ions (Iler 1979). The disilicate ions might be only formed in calcium silicate system.

From the equilibria above, one can see that anions only exist at high pH values, while at low pH silicic acid will be dominant. This general observation is consistent among results from Lagerstrom (1959), and Roller and Ervin (1940). From these results, it is quite clear that despite disputes about the forms of species in silicate solution, there is an agreement about the dominant species, the monomeric silicic acid, below the solubility and value of pH around 9.

### 3.2 Interactions between Aluminium and Dissolved Silica

Interactions between aluminium and silicic acid or dissolved silica have been studied for many years. The formation of hydroxyaluminosilicate (HAS) species in aqueous systems has been reported in the range of aluminium concentration 5 μM up to 0.1 M and with the range of dissolved silica 0.1 to 2 mM (6-120 mg/L as SiO$_2$). Factors that influence the interactions include: concentration of silicic acid, concentration of aluminium and solution pH. The solubility, stability and charge of aluminium species in aqueous solution or suspension may be affected due to these interactions. Although there has not been studied, this process might be affected by presence of certain anions. The chemical reactions between aluminium species and silicic acid remain quite vague, possibly because of complication with speciation of aluminium hydroxyl species in aqueous solution.
Chapter 3 Interactions between metal ions and dissolved silica

There is great difficulty in summarising the results of previous works in this aspect. This is because the experimental systems employed by these authors and the field of application of these studies vary greatly. Consequently, the results may be different and even contradicted sometimes. However, in this section, we would like to do our great endeavour to try to give a brief review of some aspects, which are supposed to be important and relevant to this study. These aspects include: chemical reactions between silicic acid and aluminium, effects of these interactions on stability and electrical charge of aluminium. Finally, a general conclusion will be followed.

3.2.1 Chemical interactions between silicic acid and aluminium

Some proposed reactions are listed below.

\[
pAl^{3+} + q Si(OH)_4 + rH_2O = Al_p(OH)_(r)(OSi(OH))_q ^{3p-q+r} + (q+r)H^+ \quad (3.1)
\]

when \( p = 1, q = 1 \) and \( r = 0 \), Equation 3.1 becomes

\[
Al^{2+} + Si(OH)_4 \rightarrow AlOSi(OH)_{3}^{2+} + H^+ \quad (3.2)
\]

The equation 3.1 was proposed by Browne and Driscoll (1992). The significance and thermodynamic stability of a 1:1:0 Al: Si:OH complex and of 2:2:2 and 2:1:2 HAS species was characterised in their work. In addition, an assessment of the mononuclear species, AlOSi(OH)_3^{2+}, can be found in the work of Farmer et al. (1994). Apart from these equations, another equation proposed in Iler’s early work (Iler 1955) is given in equation 3.3.

Note that all these reactions only delineate the reaction between the simple \( Al^{3+} \) and silicic acid. Since aluminium ion undergoes hydrolysis reactions, interactions between silicic acid and the hydrolysis species may exist. However, there has been no proposed reaction equations to describe it up to present time.
Chapter 3 Interactions between metal ions and dissolved silica

3.2.2 Effects on stability and electrical charge of aluminium

Brace and Matijivic (1977) examined the precipitation of *alumino-silicates* from ionic solutions, to identify the solubility boundaries, and characteristics of the sols in terms of their colloidal stability and particle charge. In their study, aluminium nitrate \( \text{Al(NO}_3\text{)}_3 \) and *meta-silicate* (\( \text{Na}_2\text{O}:\text{SiO}_2 = 1:1 \)) were used as reagents and the reactions were performed by mixing aluminium nitrate solutions of low pH with silicate (\( \text{SiO}_3^{2-} \)) at high pH. Acid (\( \text{HNO}_3 \)) or base (\( \text{NaOH} \)) was used for pH adjustment. Light scattering measurements of suspensions after mixing of the two reagents and measurements of volumes of the precipitates were made for the determination of solubility and stability of the sols. An electro-osmosis apparatus allowed electrokinetic mobilities of various dispersions to be determined. The results indicated that with
mobilities of various dispersions to be determined. The results indicated that with concentration ranges \((1\times10^{-1} \text{ to } 5\times10^{-4} \text{ M } \text{Al(NO}_3\text{)}_3; 1\times10^{-1} \text{ to } 1\times10^{-4} \text{ M } \text{Na}_2\text{SiO}_3)\), the solubility of aluminium was not affected significantly in the employed aluminium concentrations. However, the colloidal characteristics, such as stability and electrical charge, may be affected evidently within aluminium precipitation region. As shown in Figure 3.2, within the aluminium precipitation region, with presence of dissolved silica, three zones with different types of precipitate exist: on the acidic side, zone VI, is positively charged sol, on the alkaline side, zone V, is negatively charged sol; and between them, zone III, is the unstable precipitate region, in which the aggregates settled readily. These three colloidal stability domains change when the silicate concentration becomes greater than \(5\times10^{-4} \text{ M} \) (30 mg/L SiO\(_2\)). These results seem in line with the observations made by Hayden and Rubin (1974) (see also 2.4.3.2): aluminium precipitate with different electrical charges can be stable or unstable depending on solution pH. The presence of dissolved silica seems to alter the characteristics of aluminium precipitates. From Figure 3.2, one can see that presence of dissolved silica shifts and narrows the unstable precipitate region to more acidic pH values.

From the work of Brace and Matijevic, it seems that in the presence of dissolved silica at concentrations less than \(2\times10^{-3} \text{ M} \) (or 120 mg/L as SiO\(_2\)), the precipitation boundaries of aluminium may not change. However, when the silicate concentration is greater than around \(2\times10^{-3} \text{ M} \) the pH range for precipitation become wider. Assuming the concentration \(2\times10^{-3} \text{ M} \) be the solubility of amorphous silica, in a silicate solution below this concentration, only monosilicic acid exit. So, it is concluded by the authors that Al\(^{3+}\) ions and soluble silicic acid do not react to produce precipitate.

By the way, the effects of presence of aluminium salts on electrical charge and stability of colloidal silica was also demonstrated by Matijevic and co-worker (Matijevic et al. 1971). It was reported that effective flotation of silica with presence of alumina is in the region where the systems consist of unstable, low charged precipitates.
Figure 3.2 Stability domains of aluminium hydroxide precipitate in presence of silica: (a) $1 \times 10^{-4}$ M, and (b) $1 \times 10^{-3}$ M Na$_2$SiO$_3$. I and II denote the regions of no solids; III represent the region of unstable precipitates; VI and V denote the regions of stable sols of positive and negative charge respectively. The region III of unstable precipitates is narrowed and shifted to the more acidic side with increasing the concentration of silicate.
In regard to the solubility of aluminium in presence of dissolved silica, Birchall (1990) reported that interaction between aluminium and silicic acid seems make aluminium more soluble at low aluminium concentration \((10^{-4} \text{ M})\) and soluble silica concentration \((0.5 \times 10^{-3} \text{ M})\). This result is very different from others which generally indicate lower solubility of aluminosilicate. In his study of bioavailability and toxicity of aluminium, using a system: \(10^{-4} \text{ M } \text{AlCl}_3\) with and without \(0.5 \times 10^{-3} \text{ M } \text{Si(OH)}_3\) (or 30 mg/L as SiO₂), Birchall (1990) demonstrated that the solubility of aluminium appears to be enhanced by the presence of silica. For in the system without silica, less than 10 % Al could pass through a 0.2 μm membrane in pH range around 6.5-7.5; in contrast, with silica present nearly 100 % passed through the same pore size membrane in the same pH range (note: prepared solutions stand for 20 hours before filtration). Also, in the same chemical system, retainability of aluminium on certain functional resins was reduced by the presence of silicic acid due to formation of hydroxyaluminosilicate (HAS) in the pH range around 7-8.5, with great difference at around pH 8. From this result, it seems that the presence of silicic acid may make aluminium more soluble and reduce aluminium uptake by the resins. However, it seems that more experiments would need before a conclusion can be made about this point. Besides, we would like to note that, presence of anion Cl might have some profound effects on solubility of aluminium in the system, for strong effects of some anions on aluminium solubility have been reported (Reiber et. al. 1995). Reiber and co-worders proposed that, in the system of floride, sulphate and silicate, solubility of aluminium can be greatly affected. Fluoride can form a series of strong complexes that compete with hydroxo complexes to bind aluminium, so does sulphate but less strongly. As a result, formation of these dissolved complexes enhances the solubility of aluminium. This enhancement of aluminium solubility is observed at pH around 6 from their study.

Formation of hydroxyaluminosilicate (HAS) was further studied in very low concentration of aluminium and silicic acid \((4 \mu \text{M } \text{Al(NO}_3)_3; 0-500 \mu \text{M Si(OH)}_4)\) using the techniques of membrane filtration \((0.04 \mu \text{m membrane filter})\) and ion exchange as well as dialysis (Exley and Birchall 1992). At this aluminium concentration,
precipitation may not be expected (see aluminium solubility in Table 2.2 or Figure 2.4). So, the interactions should occur between dissolved aluminium hydrolysis species and silicic acid. The experimental results indicate that HAS can be formed in solutions of such low total aluminium concentration, and that the identification of these HAS species is dependent upon pH, silicic acid concentration, and preparation method. The mechanism of HAS formation was suggested as inhibition of aluminium hydroxide polymerization by silicic acid. Silicic acid may retard the growth of aluminium species to a filterable size. The stability and charge associated with such species were also dependent upon both solution pH and silicic acid concentration. Based on their experimental results, the authors claimed that the general effect of increasing the silicic acid concentration seems to be the shift of the pH of minimum aluminium solubility towards more acidic pH.

The membrane filtration method was also used to investigate the mechanism of HAS formation by determining the size distribution profile of aluminium particles against pH in the same aluminium concentration (4μM added as Al(NO₃)₃), but in rather broadened range of silicic acid concentration 0-2000μM (Exley and Birchall 1993). Although at lower silicic acid concentration, formation of HAS was not identified by membrane filtration as in their previously study, at higher concentration of silicic acid (>500μM or 30 mg/L as SiO₂) results showed that presence of silicic acid affects the aluminium particle size distribution profile. Based on the observed results, a similar mechanism of HAS formation was proposed: silicic acid may block growth sites on aluminium hydroxide lattices resulting in inhibition of the nucleation of aluminium hydroxide. The rate of HAS formation was dependent upon both the solution pH and the silicic acid concentration. At high silicic acid concentration, the effect on the nucleation of aluminium hydroxide was a strong inhibition.

Formation of hydroxyaluminosilicate (HAS) between soluble aluminium and silicic acid is also supported by the result of Browne and Driscoll (1992). Using a fluorescence probe technique, Browne and Driscoll (1992) showed that Al-Si complexes account for up to 95% of the total inorganic mononuclear Al in natural
waters. With this technique, the estimated value of $pK_{i,1.0}$ for $\text{AlOSi(OH)}_3^{2+}$ is $1.07 \pm 0.06$, values of $pK_{i,2.2}$ and $pK_{i,2.1.2}$ for 2:1:2 and 2:2:2 Al:Si:OH species are $1.9 \times 10^{-7}$ and $7.7 \times 10^{-6}$ respectively at pH 5.5. These results indicate that mononuclear species predominate over polynuclear species under the experimental conditions (note the concentration ranges of samples: 0.1-0.26 mM $\text{H}_4\text{SiO}_4$, 0.26 -10.3 $\mu$M Al).

However, Farmer and Lumsdon (1994) have quite different view from the above. Through a measurement of the shift in pH between solutions containing $\text{Al(CIO}_4)_3$, $\text{HClO}_4$, and $\text{NaClO}_4$ with and without addition of silicic acid at pH around 4, the extent of the reaction $\text{Al}^{3+} + \text{Si(OH)}_4 \rightarrow \text{AlOSi(OH)}_3^{2+} + \text{H}^+$ had been assessed by Farmer and Lumsdon (1994). From their results, with silicic acid concentration in the range 30-100 $\mu$M (1.8-6 mg/L as SiO$_2$) and aluminium concentration in the range before saturation with respect to amorphous Al(OH)$_3$, the concentration of aluminosilicate species can be neglected in such solution. The reason for this great discrepancy of the results between Farmer and Lumsdon, and Browne and Driscoll is not clear. One possible answer may possibly be due to the different methods used.

The formation of HAS complexes in aqueous solution at pH 8 was examined, with concentration of: $[\text{Al}]$ 5 mg/L; $[\text{SiO}_2]$ 0, 100 mg/L (Yokoyama 1987). The results showed that the complexes are anions other than $\text{Al(OH)}_4^-$ having a higher charge than that of sulphate. It is stated that the species with Al-O-Si bonds form and the negative charge appears to be due to dissociation of protons from silanol groups of silicic acid bonded to aluminium.

### 3.2.3 Conclusions

There is no intention here to present all the research works in this area here. From the literature quoted above, although the identification of formation of HAS may vary from one author to the other, maybe due to different chemical systems used and/or
different techniques or preparation methods employed, some general conclusion could be drawn as follows.

a) Firstly, the interactions between aluminium and silicic acid might occur at very low concentration of aluminium, e.g. 4µM, before saturation with respect to amorphous aluminium. At low silicic acid concentration, mononuclear HAS complex may be dominant in solution at certain pH. The interaction may inhibit the aluminium polymerisation and alter the electrical charge of aluminium hydrolysis species, especially when the silicic acid concentration become high.

b) Secondly, at high aluminium concentration, interactions between aluminium and dissolved silica become evident. Although there are no proposed reaction equations to describe these HAS species, the observed change of aluminium precipitates in their colloidal characteristics, such as stability and charge, is evident. The interactions are dependent upon the concentration of aluminium and concentration of silicic acid, solution pH, as well as preparation methods.

c) At high concentration of dissolved silica (e.g., ≥ 10^{-3.5} M), solubility of aluminium may be affected by the presence of dissolved silica. In addition, within the precipitation area, the properties of aluminium precipitate may change by the presence of dissolved silica depending concentration of dissolved silica and solution pH. However, at medium concentration of dissolved silica, the solubility of aluminium may not affected, whereas the properties of precipitates will still be altered. The interactions may reduce the high electrical charge of aluminium precipitates and promote the growth of the precipitates under certain conditions; on the other hand, the interactions may result in inhibition of the formation of aluminium hydroxide precipitate, or it may prevent growth of precipitate, reduce the size of precipitate significantly.

d) The interactions can alter electrical properties of aluminium hydrolysis products, hence the colloidal state of precipitates.
3.3 Interaction between Fe(III) and Dissolved Silica

Interaction between iron and dissolved silica were suggested in some early works (Hazel et. al. 1949, Yedava and Ghosh 1957). Interaction between Fe(III) and dissolved silica was studied by Weber and Stumm (1965). Under the experimental conditions (pH < 3.5 and at 25 °C), formation of a silicato-iron (III) complex was delineated as:

\[ \text{Fe}^{3+} + \text{Si(OH)}_4 + \text{H}_2\text{O} \leftrightarrow \text{FeSiO(OH)}_3^{2+} + \text{H}_3\text{O} \quad (3.4) \]

The equation 3.4 only describe the reaction between free ferric iron and silicic acid. Since ferric iron undergoes hydrolysis reactions in aqueous solution under appropriate pH and concentration. It may be expected that the hydrolysis reaction would be affected by the interaction between dissolved silica and ferric iron.

Schenk and Weber (1968) examined the effect of the interactions between ferric iron and dissolved silica on hydrolysis reaction. In their study, they measured the absorbance of the sample as an indication of the degree of colour developed as a result of hydrolysis product formation, and the iron concentration in filtrate of the samples after a 0.45 μm membrane filter, with iron concentration range 0.01-1 mM (0.56-56 mg/L) and silica concentration range below 2 mM (120 mg/L as SiO₂). The experimental results suggest that the hydrolysis reaction is hindered by silica, possibly due to the competition of the silicic acid with water and hydroxide for co-ordination sites on the iron. The results also indicate that formation of complex between iron and silica reduces the extent of formation of hydrolysis products to the degree that can pass the 0.45 μm filter. This modification of colloidal state of hydrolysed Fe(III) was also reported by Mayer and Jarrell (1996). It is also reported that adsorption of H₄SiO₄ species on Fe(OH)₃ reduces the surface sites available to other sorbates and decreases the surface potential of the Fe(OH)₃ (Meng and Letterman 1993, 1996).
3.4 Silicate as a Coagulant Aid

Silica used in water treatment as a coagulant aid is *activated silica*, which can be prepared using sodium silicate. There are several kinds of sodium silicate which can be expressed conveniently in the form of NaO\(_2\)\(\times\)SiO\(_2\), in which \(x\) ranges 1.65 to 4. In water treatment, the neutral grades (\(x:3.2-3.3\)) are considered suitable. The sodium silicates are activated normally by an acid before use, such as sulphuric acid or aluminium sulphate, etc. No matter which activator is used, the silica undergoes polymerisation. So the activated silica implies a suspension containing negatively charged colloidal particles, with a size approximately 1-10 nm (Iler 1979, Perrin 1973).

Aluminium sulphate is a widely used coagulant in water treatment, and there are several ways for prepared silica to be used as a coagulant aid with respect to aluminium sulphate. In his study, using either sulphuric acid or hydrochloric acid as activator, Packham (1966) found that: when the activated silica was added in advance of aluminium sulphate, a low dose of activated silica can enhance the coagulation (destabilisation and aggregation) markedly between pH 5.5 and 6.7; on the other hand, if the activated silica was added after aluminium sulphate, it can promote flocculation (strengthening growth of flocs) over the whole pH range from 5 to 9. Compared with this, when aluminium sulphate was used as activator and prepared with concentrated sodium silicate solution with final pH 6, using the complex as coagulant, the coagulation with clays was also enhanced significantly (Perrin 1973).

Based on the coagulation effects, it was proposed that the action of activated silica as a coagulant aid was due to the rapid precipitation and flocculation of hydrolysis products of aluminium over a wider pH range in the presence of colloidal silica, the effect being similar to that of anions (Packham 1966). The effect on flocculation was suggested to be due to a particle-bridging mechanism, the type of floc formed being related to the percentage of the particle surface covered with adsorbed polymerised silica. Complete coverage resulted in inhibition of coagulation. However, these proposed mechanisms have not been examined thoroughly.
Stumm et al. (1967) delineated conditions of polysilicate formation and provided a method for evaluating the coagulative properties of polysilicates. In their study, they demonstrated that adsorption of polysilicate from dilute solution onto colloidal particles can influence the properties of positively charged $\text{Al}_2\text{O}_3$ and AgBr sol. This adsorption leads to a charge reversal of the colloids and a restabilisation of the sol. This adsorption of polysilicate on surfaces is also observed in negative AgBr sols. The fact that negatively charged colloids can be flocculated by anionic polysilicates, may indicate that the energy of interaction due to sorption may outweigh purely electrostatic effects, although effects due to electrostatic interaction are also recognisable.

It appears that, no systematic work has been done on the interaction between aluminium and polysilicate, and its effects on coagulative behaviour of aluminium in a hydrophobic colloid system.

However, from the results of Stumm et al. (1967), it is reasonable to think that when polysilicates are employed to act as a coagulant aid with respect to aluminium salts, the interaction between them will modify the physico-chemical properties of the so-called alumino-polysilicate in terms of its capacity for charge neutralisation, hence, determining the performance of the product in coagulation with negatively charged hydrophobic colloids. Interaction between aluminium and polysilicate may increase molecular weight or size of these species so that coagulation could be promoted. Also, the interactions between aluminium and polysilicate will most likely change the charge of the aluminium hydrolysis products, thus influence the mechanism of coagulation by aluminium in aqueous solution.

### 3.5 Conclusions

It is fairly clear from discussion above that, interaction between aluminium and soluble silica occurs even at very low aluminium concentration. The interactions at low aluminium concentration may inhibit polymerisation of aluminium hydrolysis species; and at high
aluminium concentration, the interactions tend to change the properties of aluminium precipitates. This change may lies in two aspects: sizes and electrical charge. It may inhibit precipitate formation or growth and shift isoelectric point to more acidic side. It also appear that the similar interaction between iron(III) and dissolved silica may exist. Therefore, it most likely that the coagulative properties of aluminium and ferric salts will be influenced.

Although interactions between activated silica and aluminium are not fully understood, activated silica as a coagulant aid had been studied, and the performance of it in coagulation is rather clear. It seems that interactions between that of soluble silica and aluminium, and that of activated silica and aluminium may share some similarities and difference, so maybe the coagulative properties.

Hydrolysing metal salts such as aluminium sulphate and ferric chloride are commonly used coagulants. Since the presence of soluble or dissolved silica in natural waters is universal, it would be very interesting and important to examine the influence of dissolved silica on the coagulation by the hydrolysing metal salts.
CHAPTER FOUR

EXPERIMENTAL METHODS

4.1 General

As is mentioned before (see 1.1), the objective of present study is to examine the influence of dissolved silica on flocculation of kaolin particles by the hydrolysing salts, aluminium sulphate and ferric chloride. In order to delineate the influence of dissolved silica on the coagulation, several experimental aspects are involved. These include:

1) Monitoring the flocculation process kinetically.
2) Examining charge effects on coagulation/flocculation, especially in the case of presence of dissolved silica.
3) Monitoring aggregation of the primary aluminium precipitates in the absence and presence of dissolved silica.
4) Examining "solubility" of aluminium hydroxide in the absence and presence of dissolved silica.

In doing these, several instrumental techniques are involved. These are:

1) Photometric dispersion analyser (PDA) (monitoring flocculation kinetically);
2) Particle monitor (PM) (monitoring precipitation kinetically);
3) Particle electrophoresis apparatus (for measurement of mobility of particles);
4) Atomic absorption spectrometer (AAS) (for measurement of residual aluminium).

In this chapter, the principles of the main instruments, PDA and PM, will be reviewed; the instrumentation for electrophoresis and atomic adsorption will be briefly introduced. Then all the experimental procedure will be presented, including main set-up, experimental methods and preparation of materials and chemicals.
4.2 Experimental techniques

4.2.1 Photometric dispersion analyser

The technique of measuring turbidity fluctuations was proposed by Gregory and
Nelson (1984, 1986); and its theoretical background has been fully described by
Gregory (1985). This technique made it possible that the information about relative
sizes of aggregates can be recorded during the whole process, rather than only final
floc properties are determined as in the case of conventional jar tests. As a result, the
kinetics of coagulation can be discussed based on the recorded information. In this
work, this technique has been used for monitoring the kinetic flocculation. In this
section, a theoretical review will be made briefly, while the experimental set-up will be
given later.

When a suspension is flowing through an illuminated light beam, the intensity of
transmitted light fluctuates randomly about the mean value (see Figure 4.1) (Gregory
1985). This random variation is due to the random variation of particle numbers in a
defined volume; and extent of this variation will depend on particle size and
concentration of suspended particles.

The intensity of a beam of light passing through a suspension can be taken the form:

\[
\frac{I}{I_o} = \frac{V}{V_o} = \exp(-NCL)
\]  

where \(I\) is the intensity of transmitted light; \(I_o\) is the incident light intensity; \(N\) is number
concentration of particles; \(C\) is scattering cross section of the suspended particles; \(L\) is
the optical path length. In practice, the light intensity at the detector is converted to a
voltage for monitoring purpose; and the measured voltage can be made linearly
proportional to the light intensity, so \(\frac{I}{I_o} = \frac{V}{V_o}\).
Figure 4.1 The principle of photometric dispersion analyser (PDA): The light intensity or output voltage fluctuation in a flowing suspension.

The equation 4.1 can be applied to a flowing suspension of particles illuminated by a light beam. If the optical path length is L and the effective cross-section area of the light beam is A, then the average number of particles in the beam is given by:

\[ n = NAL \]  \hspace{1cm} 4.2

where \( N \) is the average number of particles per unit volume. And in this case, \( I \) and \( V \) in equation 4.1 represent the mean values corresponding to the average number of particle and can be rewritten as \( \bar{I} \) and \( \bar{V} \) conveniently. Equation 4.1 is known as the Lambert-Beer law (Kerker 1969).
The actual number of particles contained in a illuminated volume will undergo random change about the mean value \( n \) when a flowing suspension is passing through the defined volume. This is because the sample is continually renewed by the flow in such a situation. The variation in the number of particles follows the Poisson distribution, so that the standard deviation about the mean value \( (n) \) can be expressed as \( n^{1/2} \) (Gregory 1985).

The random variation of numbers of particles of flowing suspensions in the light beam will cause corresponding fluctuations in the transmitted light intensity. The frequency of the fluctuations will depend on the rate of flow (Gregory 1985). It is shown by Gregory (1985) that the standard deviation of the intensity about the mean value, or the standard deviation of voltage \( (V_{\text{rms}}) \) about the mean value \( (\bar{V}) \) can be derived as follows based on the Poisson distribution in variation of particle numbers:

\[
V_{\text{rms}} = \bar{V} \sinh(n^{1/2} \frac{C}{A}) = \bar{V} \sinh \left( \left( \frac{L}{A} \right)^{1/2} N^{1/2} C \right)
\]

Assuming \( ((L/A)^{1/2} N^{1/2} C) << 1 \), the above equation can be further simplified to

\[
\frac{V_{\text{rms}}}{\bar{V}} = \left( \frac{L}{A} \right)^{1/2} N^{1/2} C
\]

where the left term is called ratio value symbolised by \( R \), i.e. \( R = \frac{V_{\text{rms}}}{\bar{V}} \). For a given apparatus, the term \( L/A \) is constant. So, the equation 4.4 shows that the fluctuating signal or the ratio value depends on the square root of the particle concentration and on the first power of the scattering cross section, which is dependent on the size and shape of the suspended particles at a given wavelength.

For a heterodisperse suspension, the ratio value is given by (Gregory and Nelson 1986):
where \( N_i \) and \( C_i \) are the number concentration and scattering cross section of particles of size \( i \), respectively. The equation 4.5 states that the ratio values in this case still depends on the square root of the particle concentration and on the first power of the scattering cross section.

It is shown that, in the term \( \left( \sum N_i C_i^2 \right)^{1/2} \) smaller particles have negligible effect on \( R \), and in a suspension undergoing flocculation, the larger aggregates have a dramatic influence on \( R \) (Gregory and Nelson 1986). This indicates that in a flocculation process, the ratio value \( R \) increases as the particle size increases. Therefore, the ratio value can be used to indicate the growth of aggregate size or the degree of aggregation during the whole flocculation process and detect the stability of colloids in respect to aggregation (i.e. no change of ratio value will indicate no aggregation). In this case, large \( R \) values may imply large aggregate size, and this has been observed in studies on flocculation (Ching et. al. 1994, Kang and Cleasby 1995). This ratio value will be used as the “flocculation index value” (FI) in this study. A commercial instrument, photometric dispersion analyser (PDA2000), is available based on these principles.

### 4.2.2 Particle monitor (PM)

The principle of Particle Monitor (PM) is basically the same as that of PDA, both are based on the phenomenon of turbidity fluctuations in flowing suspensions (Gregory 1985, 1994). However, the sensitivity of PM is high and the dc value is maintained constant by a feedback technique, and it is very sensitive to particles about 1 \( \mu \text{m} \) in size or greater (Gregory 1990, 1994). It has been shown that turbidity fluctuation technique is much more sensitive than turbidity measurements for particles greater than a certain
size, which depends on the refractive index. For particles a few microns in size, the fluctuation method can detect concentrations 100-1000 times lower than by turbidity measurements (less than 1 ppb by volume) (Gregory 1994). Therefore, with the Particle Monitor, it is possible to measure particle formation (such as precipitation) in a solution when size of particles is coming up around 1 μm or greater in size.

Since the sensitivity of PM is different from that of PDA, the rms output of PM is not compatible with that of PDA. In order to emphasize this difference, the ratio value of PM is reported as Particle Index (PI), other than Flocculation Index (FI).

When aluminium salts is added into water, if the concentration is supersaturated with respect to the solubility of aluminium hydroxide, primary crystallites or primary precipitates may be formed within seconds in solution with size scale of several nm. If these primary precipitates are colloidally unstable, they will undergo an aggregation process to form the amorphous precipitates with larger size (assuming a few μm or more). In this case, the PI versus time will provide the information on the aggregation process.
4.3 Preparation of Materials

4.3.1 Deionised water and ST-water

The deionised water is made by ELGASTAT OPTION3. The conductivity of it is below 1.5 μS/cm (WAYNE KERR Autobalance Universal Bridge B642). The content of silica is much less than 1 mg/L as SiO₂ based on analysis using ammonium molybdate standard method (Clesceri et al. 1989) carried out about every two weeks. Contents of some other chemicals are shown in table 4.1.

Table 4.1 Chemical analysis for the deionized water

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Fe</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.1</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

The synthetic test-water (ST-water) is the deionised water, in which 1 mM Na₂CO₃ was added to give alkalinity (8 mL of 0.1N Na₂CO₃ stock solution added in 800 mL deionised water), the pH was adjusted with HNO₃ (0.1 or 1N stock solution) to designated points such as 6, 7 and 8 depending the target pH at which experiment was conducted.

4.3.2 Kaolin suspension

Dry kaolin (BDH Ltd., Poole, UK) has been used in this experimental study. The high concentration of kaolin suspension was made for stock suspension, the stock suspension will be further diluted in the flocculation test. The preparation methods are as follows:
Stock kaolin suspension:

Dry kaolin power around 200 gram was dispersed in deionised water by a high speed laboratory blender for about half an hour. Then the kaolin dispersion was further diluted to a volume 1 litre, the pH was adjusted to 7.5 by addition of NaOH solution to give complete dispersion. The dispersion was allowed to stand in a 1 litre measuring cylinder overnight, then the upper 500 mL was carefully decanted and retained and further diluted to around 800 mL as a stock suspension (adjusted pH again to 7.5). The suspension was found to have a solid content of 52.7 g/L. Particle size analysis by the particle counter (ELZONE 280 pc) using orifice 30 \( \mu \)m show that 99.7% of the population of kaolin particles is below 2.7 \( \mu \)m in diameter and the geometric mean size of the particle in the suspension is 1.4 \( \mu \)m. The particles were negatively charged, the electrophoretic mobility of the suspended particles range from -0.8 at pH 3 to -2.5 (\( \mu \)m s\(^{-1}\) V\(^{-1}\) cm) at pH 10.

Experiment kaolin suspension

For the flocculation experiment, a 760 mL volume of sample of this stock suspension (52.7 g/L) is added in ST-water 800 mL to give a final clay concentration of 50 mg/L, corresponding to a turbidity of around 65 NTU. Temperature is between 20-25 °C.

4.3.3 Other chemicals

Aluminium sulphate (alum):

A BDH product of aluminium sulphate \((\text{Al}_2(\text{SO}_4)_3\cdot16\text{H}_2\text{O}), \text{MW 630.38}\) in analytical grade (BDH AnalaR) has been used throughout this work. Stock solution of alum with concentration 0.1M is prepared by dissolving the reagent in deionised water (e.g. 31.52g of \(\text{Al}_2(\text{SO}_4)_3\cdot16\text{H}_2\text{O}\) dissolved in deionised water to 500 mL). To prevent ageing effect, a fresh stock solution was prepared for a sequence of experiments or
renewed every two weeks; the stock solution is kept in a refrigerator at 5 °C. In this study, in most case the alum concentration will be reported as micro molar (μM). So, 1μM alum is equivalent to 2 μM aluminium, or 53.96×10^{-3} mg/L aluminium. The stock is directly pipetted in kaolin suspension in the flocculation experiments without dilution.

*Sodium silicate:*

A BDH technical grade sodium metasilicate Na$_2$SiO$_3$ (Na$_2$O:SiO$_2$, 1:1) has been used in this study when the presence of dissolved silica in solution/suspension is needed. A stock solution of sodium silicate was prepared from the sodium metasilicate using deionised-distilled water, the concentration of silica in the solution is 1 g/L as SiO$_2$ with solution pH 11.5. For convenience, the dissolved silica will be reported in mg/L as the weight of SiO$_2$ throughout this work.

*Ferric chloride:*

Ferric chloride used in this study is the BDH laboratory reagents FeCl$_3$•6H$_2$O (MW 270.30). Stock solution of concentration 0.1 M was made by dissolving the solid ferric chloride in deionised water (e.g. 6.76 g of (FeCl$_3$•6H$_2$O) was dissolved to a volume 250 mL). The stock was kept in refrigerator at 5 °C and renewed every two weeks to avoid ageing effect. This stock is directly used in the flocculation experiments without dilution.
Calcium nitrate:

A stock solution of calcium nitrate (\(\text{Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}\), MW 236.15, BDH AnalaR) was prepared using deionised water for use. The concentration is 0.2 M (e.g. 47.23 g dissolved to a solution of volume 1000 mL).

Sodium hydroxide and nitric acid:

Stock solutions of sodium hydroxide (0.1 M and 1 M) were prepared by using BDH AnalaR grade (NaOH) and deionised water. Nitric acid is BDH laboratory reagent solution with further dilution to 0.1 or 1 N(M). These two chemical solution are used for pH adjustment.

4.4 Experimental Methods

4.4.1 Monitoring flocculation by PDA

Experimental set-up:

The flocculation monitoring system, the PDA set-up, is shown schematically in Figure 4.2. The system is mainly composed of a Photometric Dispersion Analyser (PDA 2000, Rank Bros Ltd., Cambridge, UK), a flocculator (Flocculator 90; Kemira, Helsingborg, Sweden) and a computer auto-recording unit. The flocculator is a semi-automatic device, which allows a pre-set of flocculation conditions. In present work the conditions are: one minute of rapid mixing at 350 rpm, 15 minutes of slow stirring at 50 rpm and 20 minutes settling time.

The flocculating suspension was conveyed through PVC tubing of 1.5 mm internal diameter, by means of a peristaltic pump at a rate about 2.0 mL/min (G: 67 s\(^{-1}\)). The sample continuously passes through the detector of PDA and the measurements are
carried out directly in the transparent tubing and the results are recorded in terms of ratio values or *Flocculation Index* values. The absolute output of the ratio or index values depends on instrument settings both for rms and dc. The setting (rms 50, dc 3 for deionised water) is chosen so that aggregation of kaolin suspension at early stage can be detected. Note that at this setting, the output value for kaolin suspension made in deionised water at pH 7.5 is 0.01 and kept the same during 10 minute stirring. It was also seen that the ratio value for kaolin suspension made in tap water is 0.14 at the rms setting 50 (Table 4.2 provide output values at four RMS settings for kaolin suspension made in tap water). Since tap water induces a small amount of aggregation, because of presence of calcium ions, the ratio reading is higher than that for kaolin in deionised water. A gain setting of 50 units provides good sensitivity for flocculation by hydrolysing salts.

<table>
<thead>
<tr>
<th>RMS Scale</th>
<th>10</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio Value</td>
<td>0.01→0.02</td>
<td>0.14</td>
<td>0.25</td>
<td>0.50</td>
</tr>
</tbody>
</table>

note: dc value for the above table is 3 for deionised water.

Under the condition used, the sample takes about 10 seconds to pass from the flocculation vessel to the detector, so that a rapid indication of the effect of an additive can be obtained. The output from the PDA 2000 is converted to digital form and the data are stored in a personal computer spreadsheet for subsequent analysis. The output response is also logged by a chart recorder.

The flocculation vessel is a 1000 mL Pyrex beaker, mixed by a rectangular blade (700×250mm), and positioned 45 mm above the base of the beaker. A detector of pH metre (HANNA Instrument HI 931402 Microprocessor pH meter) is inserted in the suspension during the whole flocculation test. The pH meter was calibrated every day with standard buffer solutions (RUSSELL pH Limited).
Flocculation test procedure:

Firstly, 800 mL ST-water was prepared in a 1000 mL Pyrex beaker with designated pH. Then, 760 µL of stock kaolin suspension (52.7 g/L) was added in the ST-water and mixed at 350 rpm for 30 seconds. Next, a certain volume of alum (0.1M) (or ferric chloride 0.1M) stock solution and a corresponding pre-determined volume of NaOH solution were pipetted in through holes in the cover with NaOH around one second in advance. Immediately after these additions, one minute rapid fast mixing (350 rpm) period of the Flocculator 90 was initiated. At this point of time, around 15mL of the suspension was taken by a 20 mL syringe for electrophoretic mobility measurements (4.4.3). Then 15 minute slow mixing (50 rpm) and 20 minute sedimentation were followed. During the mixing time (fast and slow), the readings of the Flocculation Index (FI) were logged every 10 seconds for analysis.

If presence of dissolved silica is required, before addition of kaolin stock solution into the ST-water, either a certain volume of stock sodium silicate (1 g/L as SiO₂) was added if required concentration of dissolved silica is 20 mg/L or below, or certain amount of solid sodium metasilicate was directly added in the ST-water if the required concentration is higher than 20 mg/L, and stirred for one minute and left to stay for around 15 minutes (no differences were observed in flocculation tests under the same flocculation condition between such solutions of 15 minutes and overnight stay). Then a predetermined volume of HNO₃ (0.1 or 1 N) solution to bring the pH to the target value, such as 6, 7 or 8.
4.4.2 Monitoring aggregation of the primary precipitates by PM

Experimental set-up:

The experimental set-up is shown schematically in Fig 4.3. A Pyrex beaker 500 mL is used for the solution preparation, which is equipped with a glass blade paddle stirrer (two each side). A particle monitor (PM) is used to monitor the precipitation formation from aluminium sulphate (principle see 4.2.2). The solution was sampled to the flow-through sensor of the PM through PVC tubing of 1.5 mm internal diameter, by means of a peristaltic pump at a rate of 5.2 mL/min, and monitored continuously by it. Measurements are carried out directly in the transparent tubing and the results, the rms value, are reported in terms of a Particle Index (PI). The output from the PM is converted to digital form and the data are stored in a personal computer spreadsheet for subsequent analysis. The monitor signal is also logged by a chart recorder. A pH electrode is inserted in the solution/suspension during the whole process to see whether the target pH is achieved.

Precipitation test procedure:

400 mL ST-water was prepared in a 500 mL Pyrex beaker with a target pH. If presence of dissolved silica in solution is required, sodium silicate will be added. In this case, if concentration of dissolved silica in solution is ≤ 20mg/L, certain volume of stock silica solution (1 g/L as SiO₂) is added in; if concentration of dissolved silica in solution is >20mg/L, certain amount of sodium metasilicate solid will be added into the ST-water. The solution pH is returned to the target value by addition of a certain volume of HNO₃ solution (0.1 or 1N) and left to stay for about 15 minutes before further addition of chemicals. Then, a certain volume of alum stock solution together with pre-determined amount of NaOH solution will be pipetted at different surface position in the ST-water or the dissolved silica solution depending on whether presence of dissolved silica is required.
Figure 4.2 Experimental set-up of photometric dispersion analyser (PDA) for monitoring flocculation of kaolin suspensions.
Figure 4.3 Experimental set-up of particle monitor (PM) for monitoring aggregation of primary aluminium hydroxide precipitate.
Addition of NaOH is around one second in advance of addition of alum each time and the target pH is obtained. Immediately after addition of alum and NaOH, 35 second fast stirring (140 rpm) is initiated and followed by 15 minute slow stirring (45 rpm). During all these stirring time, the readings of the Particle Index were logged every 10 seconds for subsequent analysis.

4.4.3 Electrophoresis measurements

**Instrumentation:**

The principle of particle electrophoresis was briefly sketched in 2.1.3.2. This technique has been extensively used in coagulation/flocculation study (Black and Chen 1965, Williams 1978, Letterman et. al. 1982). The purpose of electrophoretic mobility measurements is to provide the information about the surface charge of particles aggregated or to be aggregated. This is because surface charge is important in explaining aggregation process in most condition. From the DLVO theory (see 2.2), the stability of colloids can be related to the surface potential ($\zeta$).

In this study, measurement of electrophoretic mobility of kaolin particles under different conditions was carried out by using a Particle Micro-electrophoresis Apparatus (Mark II, RANK BROTHERS, Cambridge, ENGLAND). In this study, a rectangular cross section cell (flat cell) is used; some parameters are: $H/d = 20$, $s/d = 0.202$, $d = 79\mu m$, $s = 16\mu m$ (see Figure 4.4).

The electrode is platinum (blacked), and the field strength can simply expressed: $E = V/L$ (where V is the potential difference applied to the electrode (50 V is selected in the experiment)). The electrophoretic mobility ($U$) can be taken as:

$$ U = \frac{\nu}{E} $$
where $v$ is the particle velocity ($\mu$m s$^{-1}$) and $E$ is the electric field strength (V/cm). So, the standard unit of the mobility can be taken the from: $\mu$m s$^{-1}$ V$^{-1}$ cm. This unit will be used throughout this study.

![Diagram](image)

**Figure 4.4** Flat cell cross section: the stationary level position is seen to depend on the ratio $L/d$.

**Measurement procedure:**

After addition of coagulants such as alum or ferric chloride and one minute fast stirring, around 15 mL samples were taken by a 20 mL syringe. These samples were pumped into the cell directly without dilution. Timing of particles was carried out using a microcomputer keyboard as a "stopwatch". Typically, 10 particles were timed in each direction and at the two stationary level, and the mean mobility was computed directly from the 40 readings. Standard deviations were usually around 5 % of the mobility, or less.
4.4.4 Measurement of residual aluminium by AAS

Principle:

In atomic absorption spectrometry, a sample is firstly aspirated into a flame and atomised like in flame emission photometry. Then a light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomised element in the flame. Since each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used, so that the measurement is relatively free from spectral or radiation interference. The amount of energy absorbed in the flame at the characteristic wavelength is directly proportional to the concentration of the element in the sample. In this way, the concentration of element in the sample can be determined (Clesceri et al. 1989).

Measurement procedures:

The measurement of residual aluminium was carried out in the following way. Aluminium sulphate (40 µM) and a predetermined amount of NaOH solution (for pH adjustment) were added to ST-water, with and without dissolved silica. After stirring for about five minutes, 20 mL of the solution was filtered through a 0.45 µm Millipore membrane. The filtrate was acidified with 2 mL of concentrated (1:1) HCl solution and allowed to age for 48 hour. Finally, the aluminium content of the samples was measured using a Unicam model 939 atomic absorption spectroscope.
CHAPTER FIVE

EXPERIMENTAL RESULTS

All the experimental results will be presented in this chapter. The results include several aspects. Firstly, presented in 5.1 are the results of flocculation of kaolin suspensions by aluminium sulphate (alum). Second, in 5.2 are the results showing influences of dissolved silica on the coagulation in terms of kinetics of aggregation and electrical charge of particles surfaces. Third, kinetics of aggregation of primary aluminium precipitates will be presented in 5.3. Then, in 5.4 is the influence of dissolved silica on aluminium precipitation. After that, in 5.5 is the results of residual aluminium measurements of solutions after membrane filtration with and without presence of dissolved silica. Further, in 5.6, the effect of calcium on the coagulation is examined especially when the presence of dissolved silica prevents the coagulation. Finally, the influences of dissolved silica on coagulation of kaolin by ferric chloride will be presented in 5.7.

Results in 5.1 will allow the coagulation stages (or zones) to be defined depending on the coagulant dosage and solution pH. Based on it, with the results in 5.2, the influence of dissolved silica on flocculation in terms of kinetics of aggregation, EM of particles and supernatant turbidity can be discussed. The information in 5.3, 5.4 on aggregation of primary aluminium precipitates will provide new and useful information on the coagulation mechanism, and hence for discussing the dissolved silica effects on the coagulation. The influence of dissolved silica on solubility of aluminium will be provided in 5.5, which would be useful in discussing the effect of dissolved silica on the coagulation. Based on all these experimental evidence, the mechanism of flocculation and the influence of dissolved silica on it will be discussed in chapter 6.
5.1 Coagulation of Kaolin Suspension by Aluminium Sulphate

Coagulation of clay suspensions by aluminium sulphate (alum) has been shown to be dependent on concentration of clay, concentration of alum and solution pH. One of the objectives of the experiments in this section is to define the coagulation system of alum with kaolin clay in absence of silica, so as to identify several stages of coagulation at which the influence of dissolved silica on coagulation will be examined. This identification is important, because the mechanism of coagulation may vary greatly between different stages (see 2.5.4), and so may the influence of dissolved silica at the different stages. Moreover, these experiments together with those on kinetics of alum precipitation (see in 5.3) are intended to provide some new information on the mechanism of coagulation by alum, which could allow the influence of dissolved silica on coagulation to be discussed from a new angle as can be seen later (see 6.1, 6.2).

Here, the coagulative behaviour of alum will be demonstrated in two aspects: coagulation and kinetics of flocculation; altering of surface charge of particles after addition of alum. First, the destabilisation of suspensions and rate of aggregation (growth rate of aggregates' size) as a function of mixing time, will be presented by the flocculation index value (FI) as a function of mixing time. The FI is measured by the Photometric Dispersion Analyser (PDA). As stated before, the FI values can indicate coagulation and kinetics of flocculation of a clay suspension (see 4.2.1). That is, in simple terms, a constant low FI value signifies a stable colloidal suspension and no destabilisation and subsequent aggregation occur; an increasing of the FI value indicates occurrence of aggregation; at the same time, FI values can give comparative size of aggregates as a function of mixing time under given physical and chemical condition of flocculation (see 4.2.1). Second, the surface charge of particles after addition of the coagulants will be investigated by the electrophoretic mobility (EM) measurements by the Particle Microelectrophoresis Apparatus. This will provide information on the effects of alum addition on surface charge of particle in suspensions, allowing examination of the charge effect on coagulation. In addition,
supernatant turbidities of suspensions after coagulation, flocculation and sedimentation are also examined for a conventional consideration.

5.1.1 Coagulation by alum at pH 6

5.1.1.1 Coagulation at low concentration of alum at pH 6

In Figure 5.1.a, the index value is shown as a function of mixing time (including one minute fast mixing) at seven low dosages of alum (Al$_2$(SO$_4$)$_3$ • 16H$_2$O) (1, 2, 3, 4, 5, 7, 10µM). It is seen that, when the dosage of alum increases from 0 to 4 µM, FI values as a function of time increase faster and to a higher final value. At 0 and 1 µM dosage of alum, there is no increase of FI values, indicating no occurrence of colloid aggregation; this is in the zone 1 of insufficient coagulant dosages. In comparison, at an alum dosage of 4 µM, the rate of increase of FI value as a function of mixing time becomes largest and the final index value reaches its maximum value. This means that coagulation proceeds very well under this condition. In contrast, further increasing alum dose from 4 µM, the rate of increase of FI values becomes lower. For example, at 5 µM of alum, no evident increase of index values was observed until 5 minutes mixing. Moreover, at 7 and 10 µM of alum, no increase of FI values was seen during the whole mixing time, indicating no occurrence of flocculation of suspended particles.

The electrophoretic mobility (EM, µm s$^{-1}$ V$^{-1}$ cm; note: from now on all EM results are given in the standard units) particles after addition of alum and one minute fast mixing; and the supernatant turbidity (NTU) of suspensions after standard mixing conditions, and sedimentation corresponding to the system in Figure 5.1.a is presented in Figure 5.1.b. As seen in Figure 5.1.b, the negative surface charge of kaolin particles is reduced as the dosage of alum is increased from zero to 4 µM.
Figure 5.1.a Kinetics of flocculation of kaolin suspensions by addition of alum, expressed in the flocculation index (FI) value against mixing time, at low dosages of alum at pH 6±0.05. The system consists of: ST-water, $\text{Al}_2(\text{SO}_4)_3$ (µM as shown in the key), and kaolin (50 mg/L).

Figure 5.1.b Electrophoretic mobility (µm s$^{-1}$ V$^{-1}$ cm) of kaolin particles after addition of alum; supernatant turbidity of the suspensions after the standard procedure against alum dose in the same system as Figure 5.1.a.
Figure 5.2.a Kinetics of flocculation of kaolin suspensions by addition of alum, expressed in the flocculation index (FI) value against mixing time, at high dosages of alum at pH 6±0.05. The system consists of: ST-water, Al$_2$(SO$_4$)$_3$ (μM as shown in the key), and kaolin (50 mg/L).

Figure 5.2.b Electrophoretic mobility (EM) (μm s$^{-1}$ V$^{-1}$ cm) of kaolin particles after addition of alum; supernatant turbidity of the suspensions after the standard procedure against alum dose in the same system as Figure 5.2.a.
For example, at the alum dosage of 4 μM, the negative surface charge of kaolin particles is completely neutralised and the EM of particles becomes zero (from equation 2.10, when $U = 0$, $\zeta = 0$, so this is an isoelectric point) at this dosage. Further increasing the dosage of alum causes a charge reversal of the particles. For example, at a dosage of 5 μM, the particles become slightly positively charged (around 0.2 unit), whereas at dosages of 7 and 10 μM the particles are strongly positively charged with EM around 1.2 and 1.6 standard unit.

The supernatant turbidity (NTU) in the same coagulation system as a function of alum is also shown in Figure 5.1.b. It is seen that the lowest turbidity is at the alum dose of 4 μM, which corresponds to the isoelectric point (see Figure 5.1.b). Highest increase rate and final index value in this stage of flocculation is also observed at this point.

From all the results above, the coagulation zones can be defined. The coagulation by alum in the system at the given pH 6, when in the dosage range of 2 to 5 μM, is in zone 2 coagulation, for the negative surface charge of the particles is neutralised and aggregation occurs. However, at alum dosage 7 and 10 μM, the coagulant dosage is in zone 3 of restabilisation of the colloids, for the surface charge of particles is reversed from original negative to a high level of positive and there is no occurrence of coagulation.

5.1.1.2 Coagulation at high concentration of alum at pH 6

The kinetics of flocculation by alum at high concentration (10 to 100 μM), indicated by the FI values as a function of mixing time, is shown in Figure 5.2.a. The index value does not increase at 20 and 40 μM during the whole mixing time; but it slightly increases with a long lag time around 13 minutes at an alum dose of 80 μM and increases significantly at alum dose of 100 μM with approximately 7 minutes lag time after addition of alum. (Note also that the highest final FI values reaches much higher values than those in Zone 2 shown in Figure 5.1.a).
The EM of particles after addition of alum at high concentration and corresponding supernatant turbidity of the suspensions is shown in Figure 5.2.b. As can be seen, the EM of particles decreases slightly from 1.7 at alum dose of 20 µM to 1.5 at alum dose of 40 µM, but decreases significantly from 1.5 to 1.05 (standard unit) at alum dose of 100 µM. The supernatant turbidity does not decrease until the alum dosage reaches 100 µM.

A comparison between the FI value in Figure 5.2.a and the EM, and supernatant turbidity in Figure 5.2.b shows that when the index value increases significantly at an alum dose 100 µM, the supernatant turbidity decreases correspondingly. One interesting fact is that, as the alum dose increases, the reversed surface charge of particles is reduced to a low level (from +1.7 to 1.05 standard unit). From a traditional view, if substantial decrease of supernatant turbidity is achieved after charge reversal of colloids, the coagulation will be categorically put in zone four flocculation, in which a mechanism of enmeshment of colloidal particles by massive precipitates is indicated (sweep flocculation). However, massive precipitate enmeshment of colloidal particles should indicate an immediate and a rapid aggregation process. This is contradicted to the phenomenon observed at the alum dose of 100 µM (see Figure 5.2.a.), where a lag time around 6 minutes was observed after addition of coagulant. This kinetic phenomenon of flocculation may be important both in coagulation by alum and influence of solution chemistry on it, which will be discussed later in our study (see 6.1).
5.1.2 Coagulation by alum at pH 7

5.1.2.1 Coagulation at low concentration of alum at pH 7

In Figure 5.3.a, the FI value as a function of mixing time is presented at six low dosages of alum: (2, 3, 4, 5, 8, 9 μM). It is seen that, when the dosage of alum is very low, at 2 or 3 μM, index values do not increase with mixing time, indicating no occurrence of colloid aggregation. In comparison, at a dosage of 4 or 5 μM, the FI value increases evidently with higher final index value at the dose of 5 μM. However, further increasing the dosage of alum to 8 μM, the increase of FI values is depressed to a low level compared with those at the dose of 4 and 5 μM. Moreover, when the dosage becomes 9 or 10 μM, only slight increase of the index value is observed after 10 minutes mixing, indicating the particles are nearly restabilised in this case.

The EM of particles after addition of alum and one minute fast mixing; and the supernatant turbidity of suspensions after standard mixing and sedimentation conditions, corresponding to the system in Figure 5.3.a is presented in Figure 5.3.b. In Figure 5.3.b, the negative surface charge of particles is reduced as the dosage of alum is increased from 0 to 8 μM. At the dosage of 8 μM, the negative surface charge of kaolin particles is completely neutralised and isoelectric point is achieved at this dosage. Further increasing the dosage of aluminium, a charge reversal of the particles occurs. At alum dosages of 9 or 10 μM, the particles become positively charged (0.5 standard unit).

From the results above, the zones of coagulant can be defined. At alum dosages of 2 and 3 μM is in zone 1 of insufficient coagulant. In the alum dose range of 4 to 8 μM, is in zone two, for charge neutralisation is observed. At the dose of 9 and 10 μM, the system is in zone 3 of restabilisation for charge reversal.
Figure 5.3.a Kinetics of flocculation of kaolin suspensions by addition of alum, expressed in the flocculation index (FI) value against mixing time, at low dosages of alum, at pH 7±0.05. The system is composed of: ST-water, kaolin (50mg/L), and alum (Al$_2$(SO$_4$)$_3$·16H$_2$O μM as shown in the key).

Figure 5.3.b Electrophoretic mobility (μm s$^{-1}$V$^{-1}$ cm) of kaolin particles after addition of alum; supernatant turbidity (NTU) of suspensions after the standard procedure against alum dose in the same system as in Figure 5.3.a.
Figure 5.4.a Kinetics of flocculation of kaolin suspensions by addition of alum, expressed in the flocculation index (FI) value against mixing time, at higher dosages of alum, at pH 7±0.05. The system is composed of: ST-water, kaolin (50mg/L), and alum (Al$_2$(SO$_4$)$_3$·16H$_2$O µM as shown in the key).

Figure 5.4.b Electrophoretic mobility (µm s$^{-1}$V$^{-1}$cm) of kaolin particles after addition of alum; supernatant turbidity (NTU) of the suspensions after the standard procedure against alum dose in the same system as Figure 5.4.a.
The supernatant turbidity in the same coagulation system as a function of alum is also shown in Figure 5.3.b. It is seen that the lowest turbidity is not at the alum dose of 8 μM, which corresponds to isoelectric point (IEP) (see Figure 5.3.b).

Comparing the results at low dosages at pH 6 (see Figure 5.1a and Figure 5.1b) and the results at pH 7 (see Figure 5.3.a and Figure 5.3.b), one interesting fact is that, unlike at pH 6, the best aggregate growth rate (indicated by the index values in Figure 5.3.a) and lower turbidity at pH 7 did not occur at the isoelectric point (IEP) in the zone two coagulation.

5.1.2.2 Coagulation at high concentration of alum at pH 7

The kinetics of flocculation by alum at high concentration (10 to 100 μM), indicated by the FI values as a function of mixing time, is shown in Figure 5.4.a. It is seen that, as alum dose increases from 10 μM to a higher level the index value begins to increase progressively. It begin with a fairly long lag time, then the lag time becomes shorter and shorter as the alum dose increases to high level; For instance, the index value almost does not increase at alum dosages of 10 and 20 μM; but at alum dose 30 μM, it begins to increase but with a lag time 5 minutes and then goes up sharply. Further increasing alum dose to 80 or 100 μM, the FI value begins increasing greatly even during the one minute fast mixing.

The EM of particles after addition of alum at high dose and corresponding supernatant turbidity of the suspensions is shown in Figure 5.4.b. As can be seen, the EM of particles increases from 0.5 at alum dose of 10 μM to 0.9 at alum 20μM, and further to 1.0 standard unit at the dose 30 μM; and then decreases gradually down to 0.77 standard unit at the dose of 100 μM. This reduction of reversed positive EM as the increase of alum dose is also seen at pH 6.
A comparison between the index value in Figure 5.4.a and EM as well as turbidity in Figure 5.4.b shows that when the FI value increases significantly at an alum dose of 30μM, the supernatant turbidity decreases greatly. The charge effect would be profound to the coagulation process, since it is seen that the reversed positive EM of particles is higher at dose of 30 μM than that at dose of 20 μM, while flocculation at 30 μM is much greater than that at 20 μM. Conventionally, the coagulation at this stage may be defined as zone 4 sweep flocculation. However, as in the case at pH 6 and at dose of 100 μM, one should be aware that the coagulation may not be caused by massive precipitate enmeshment of particles, whereas it may be controlled dynamically by the aluminium precipitation. This kinetic feature of flocculation will be discussed with the aggregation of primary aluminium hydroxide precipitates in 6.1.

5.1.3 Coagulation by alum at pH 8

Coagulation of kaolin suspensions by alum at pH 8 shows different characteristics from those at pH 6 and pH 7. One major difference is that no charge reversal and restabilisation of the colloids occurs.

The kinetics of aggregate formation, indicated by the increase of FI values as a function of mixing time, is shown in Figure 5.5.a. It is seen that the increase of FI values with mixing time is accelerated as the increase of alum dose. At alum dose of 10 μM, there is only a slight increase of FI values with time; but at dose of 20 μM, an evident increase of index value is observed. At dosage of 30 μM, a sharp increase of index values is seen even during one minute fast mixing and the FI value reaches a plateau after only three minute mixing. With further increase of dosage from 30 μM to 40 μM, the slope of index value is nearly the same, but it rises to a higher value (2 at 40, and 1.5 at 30 μM). However, on increasing dosage of alum from 40 μM to 60 μM, no much difference in the index values as a function of mixing time is seen.
The corresponding EM of particles after addition of alum at all these concentrations and supernatant turbidity of the suspensions is shown in Figure 5.5.b. As can be seen, the negative EM of particles decreases as alum dose increases and at the dose of 30 μM, the surface charge of particles become zero (IEP). Moreover, with further increasing dosage of alum up to 60 μM, the EM of particles (or zeta potential (ζ)) remains zero. So, further increase of alum dose does not lead to charge reversal of particles at pH 8, as it does at pH 6 or 7.

In Figure 5.5.b, it is also seen that, the supernatant turbidity after coagulation, flocculation and sedimentation has a slight decrease at a dosage of 10 μM, but has a great decrease at dose of 30 μM.

A comparison of the index values as function of mixing time at doses of alum 10, 20, 30 μM and the EM at these dosages in Figure 5.5.a and Figure 5.5.b, shows that coagulation at these dosages of alum is in the zone two, or at a high dose, for example, greater than 30μM, coagulation is in the overlap of zones 2 and 4. So, the mechanism of coagulation will be different: at low dose of alum, the destabilisation is caused by the adsorption through surface complex formation of aluminium hydrolysis species; while at high alum dose, destabilisation may caused by surface precipitation of alum (see 2.3). At even higher concentration of alum, deposition of alum precipitates formed in bulk solution onto particle surface, or heterocoagulation between alum precipitates in bulk solution and colloidal particles may become important.
Figure 5.5.a Kinetics of flocculation of kaolin suspensions by addition of alum, expressed in the flocculation index (FI) value versus mixing time at varying dosages of alum at pH 8±0.05. The system consists of: ST-water, Al₂(SO₄)₃ (µM as shown in the key), and kaolin (50 mg/L).

Figure 5.5.b Electrophoretic mobility (EM) (µm s⁻¹ V⁻¹ cm) of kaolin particles after addition of alum; supernatant turbidity of the suspensions after the standard procedure against alum dose in the same system as Figure 5.5.a.
Chapter 5 Experimental results

**Figure 5.6.a** Kinetics of flocculation of kaolin suspensions by addition of alum, expressed in the flocculation index (FI) values versus mixing time at values of pH. The system consists of: ST-water, Al$_2$(SO$_4$)$_3$ (40μM), and kaolin (50 mg/L).

**Figure 5.6.b** Electrophoretic mobility (EM) (μm s$^{-1}$V$^{-1}$cm) of kaolin particles in suspensions after addition of alum (Al$_2$(SO$_4$)$_3$ 40μM); supernatant turbidity of the suspensions after the standard procedure against pH in the same system as Figure 5.6.a. Coagulation occurs between pH 6.76 and 8.44.
5.1.4 Coagulation by alum at 40 \( \mu \text{M} \) as a function of solution pH

The kinetics of coagulation of kaolin suspension by alum at concentration 40\( \mu \text{M} \), indicated by the FI values versus mixing time at different values of pH, is shown in Figure 5.6.a. As shown in Figure 5.6.a, the index value does not increase at this dosage at pH 6 and pH 6.5, indicating that there is no occurrence of coagulation at these pH values. However, at pH 6.76, the index value increases but with a fairly long lag time of 10 minutes. As pH increased to around 7, the lag time is shortened to around 5 min; but when pH is at 7.5, the lag time nearly disappears, for the FI value began increasing noticeably within the one minute fast mixing period. At pH around 8, the index value also began increasing within one minute fast mixing, but the final value is suppressed compared with those at lower pH such as 7 and 7.5. With further increase of pH values to 8.3 and 8.4, the increase of the index values with mixing time is greatly depressed; while at pH 8.6 and over, no increase of index value is observed.

The EM of particles after addition of 40\( \mu \text{M} \) alum at different pH, and corresponding supernatant turbidity is shown in Figure 5.6.b. As can be seen, IEP is at pH 8. Above this point, EM of particles decreases as the solution pH increases. That is, from pH 6 to pH 8, the EM of particles decrease gradually from 1.52 to around zero at pH 8. Below the IEP, EM of particles plummeted to a low negative value, -1.36 standard unit at pH 8.32. It is seen that when EM of particles larger than around 1 standard unit due to a charge reversal, and EM of particles lower than -1.5 standard unit, no increase of index value was seen indicating no coagulation.

The supernatant turbidity (NTU) of suspensions is fairly low between pH 6.76 and 8.44, and with lower values between pH 7 to 8, which corresponds the coagulation region indicated by the index values.

One interesting feature of the results above is that the lag time can be considerably reduced as the pH increases to around 8, where the EM (or zeta potential) is around
zero. This may indicate that the kinetics of flocculation is related to the charge of aluminium hydroxide precipitates. That is, aggregation of particles may be strongly affected or even controlled by the aggregation of primary aluminium hydroxide precipitates. A detailed discussion on this will be carried out in chapter 6.

5.1.5 Conclusion

From the results above, some noteworthy points are summarised below:

(1) at pH 6, the IEP of kaolin particles is at alum dosage of 4 μM, and good coagulation is observed at this point in the zone two coagulation (2-6 μM). At this pH, zone four coagulation can be initialised with high alum dosage up to 80 - 100 μM. The coagulation in the zone four is much better than those in zone two in terms of aggregate size and turbidity removal.

(2) at pH 7, the IEP of kaolin particles is at alum dosage of 8 μM, and good coagulation occurred before this point in the zone two coagulation (4-8 μM). At this pH, zone four coagulation began to occur at a lower alum dosage (30 μM), compared with that at pH 6. Again, the coagulation in zone four is much better than in zone two.

(3) at pH 8, the IEP of kaolin particles was found at alum dose of 30 μM, and with further increasing the dosage to 60μM, the EM of the particles remain constant at a value of about zero.

(4) at the constant alum dosage 40 μM, the coagulation of kaolin suspension by alum is characterised by pH. On acidic or neutral pH side, a slow kinetic aggregation process is observed with a long lag time. While at around pH 8, where the zeta potential of particles is at zero, a fast aggregation process is seen.
5.2 Influence of Dissolved Silica on Alum Coagulation

Influence of dissolved silica on coagulation of kaolin suspension by alum has been examined at several pH values 6, 7, 8 with varying concentrations of dissolved silica. The influences are also examined as a function of pH at alum dosage 40 μM and at two concentrations of dissolved silica (20, 50 mg/L). It will be demonstrated that presence of dissolved silica can promote or prevent the coagulation in the given coagulation system depending on pH, alum dose and silica concentration.

5.2.1 Influence on alum coagulation at pH 6

Alum coagulation with kaolin is shown in Figure 5.1.a&b and Figure 5.2.a&b. The influence of dissolved silica on coagulation with kaolin is examined at an alum dose of 40 μM, which is in the zone three restabilisation. As shown in Figure 5.7, the FI value has no change (or no increase) in presence of 50 mg/L dissolved silica, as in case of no dissolved silica (Figure 5.1). That is, FI value remained very low throughout the mixing time.

The EM of particles after addition of alum 40 μM and with presence of dissolved silica 50 mg/L at pH 6 is 1.15 standard unit, compared with the EM value of 1.52 at pH 6 in absence of dissolved silica. Thus dissolved silica reduced the reversed positive charge. Since no aggregation occurs, the supernatant turbidity shows no change at this dissolved silica level.
Figure 5.7 Kinetics of flocculation of kaolin suspensions by addition of alum at pH 6, with and without presence of dissolved silica expressed in the flocculation index (FI) value; inserted small figure: electrophoretic mobility (EM) of kaolin particles in the same system.
5.2.2 Influence on alum coagulation at pH 7

Experiments on the influence of dissolved silica on coagulation by alum have been conducted in two ranges of coagulant dose: zone two and zone four. The results are presented separately in 5.2.2.1 and 5.2.2.2.

5.2.2.1 Influence on zone two alum coagulation at pH 7

It is clear from Figure 5.3.a that, at an alum dose 8 μM the zeta potential of particles is at the zero point; and that the system is in zone two coagulation due to charge neutralisation.

At this alum dosage (8 μM), influence of dissolved silica at several different concentrations 5, 10, 20, 30, 40 mg/L was examined. This examination includes kinetics of flocculation reflected by the FI value against time and the changing of EM of particles, in the presence of dissolved silica in the given coagulation system. Supernatant turbidities of suspensions are also measured to give a conventional reference. The results are shown in Figure 5.8.a and Figure 5.8.b.

From the Figure 5.8.a, when 5 mg/L dissolved silica is present in solution, no much difference in the index value is seen compared with that in absence of dissolved silica. However, as the concentration of dissolved silica increased to 10 and 20 mg/L (as SiO₂), there is a considerable improvement in increasing of FI values with mixing time. The index value starts increasing much earlier than that in absence of dissolved silica, for example, the lag time is only around 2 minutes at dissolved silica 10 and 20 mg/L, whereas it is around 5 minutes at zero and 5 mg/L. Nevertheless, with further increasing concentration of dissolved silica to 30 mg/L, the FI value as a function of mixing time is greatly depressed as shown by a slower increase of the FI value against mixing time and lower final index value. Moreover, there is no increase of FI value at dissolved silica 40 mg/L. From these results, it is clear that the presence of dissolved
silica can improve, suppress or even prevent completely the coagulation; and these effects at this pH will depend the concentration of dissolved silica in solution under the given coagulation situation (zone two coagulant dosage).

The EM of particles after addition of alum 8 μM and with presence of dissolved silica 5, 10, 20, 30, 40 mg/L at pH 7 is shown in Figure 5.8.b. It is seen that at alum dose 8 μM, the EM of particles is at zero; with presence of dissolved silica, the EM of particles at this alum dose decrease as the concentration of dissolved silica increases. At dissolved silica 10 mg/L the EM of particles is decreased to -0.15, at dissolved silica 40 mg/L the EM of particles is descended to -1.74 standard unit.

Comparing Figure 5.8.a with Figure 5.8.b, one can see that as the EM of particles decreased from 0 to -0.15 and -0.75 by the presence of dissolved silica 10 and 20 mg/L, the flocculation is improved as indicated by the FI value. Accordingly, the supernatant turbidity of suspensions showed a minimum value at the dissolved silica concentration 20 mg/L.

Interestingly, this improvement of flocculation due to reduction of particle EM from zero point of EM caused by presence of dissolved silica is in accordance with what is observed in absence of dissolved silica (Figure 5.3.a&b). Since it is seen that the better coagulation occurs before the IEP of particles after addition of alum. That is, with slightly negative EM, coagulation is better than at the IEP at pH 7. The reason for this will be discussed later.
Figure 5.8.a  Kinetics of flocculation of kaolin suspensions by addition of alum expressed in the flocculation index (FI) value versus mixing time in presence of dissolved silica (mg/L as SiO₂ as shown in the key), at pH 7±0.05. The system consists of: ST-water, Al₂(SO₄)₃ 8μM, and kaolin (50 mg/L), and Na₂SiO₃ (mg/L as SiO₂).

Figure 5.8.b  Electrophoretic mobility (μm s⁻¹V⁻¹cm) of kaolin particles in suspensions after addition of alum (Al₂(SO₄)₃ 8μM), in presence of dissolved silica (mg/L); Supernatant turbidity of the suspensions after the standard procedure against dissolved silica (mg/L as SiO₂) in the same system as Figure 5.8.a.
5.2.2.2 Influence on zone four alum coagulation at pH 7

The influence of dissolved silica on zone four alum coagulation is carried out at two dose level of alum 30 and 100 μM. As seen before (see 5.1.2 and Figure 5.4.a&b), the zone four coagulation could extended over a quite wide range of coagulant concentration; the mechanism of coagulation may vary greatly over this concentration range. In this case, at alum dose 30 μM, the coagulation is in primary stage of zone four coagulation, in which kinetics of coagulation may be strongly dependent on the slow kinetic aggregation of primary aluminium hydroxide precipitation (see 6.1); on the other hand, at a dose of 100 μM, a fast aggregation of the primary aluminium hydroxide precipitates with high number concentration may result in an enmeshment of particles by the massive precipitates. Therefore, the influence of dissolved silica on coagulation can be examined at these two different coagulation conditions.

(1) at dosage of alum 30 μM

As showed before, the coagulation of kaolin suspension by alum at 30 μM at pH 7 is in the beginning of the zone four coagulation (5.1.2 and Figure 5.4.a and Figure 5.4.b). At this alum dosage, the effects of influences of dissolved silica on coagulation, at varying dissolved silica concentrations, 10, 20, 30, 40, 50, 80, 100 mg/L, are shown in Figure 5.9.a.

As is seen in Figure 5.9.a, at lower concentrations, presence of dissolved silica can promote the coagulation kinetically. Nevertheless, as the concentration of dissolved silica increases, this kind of promotion would be diminished; Moreover, at even higher dissolved silica concentration, prevention of coagulation was observed.
Figure 5.9.a Kinetics of flocculation of kaolin suspensions by addition of alum expressed in the flocculation index (FI) value versus mixing time in presence of dissolved silica (mg/L as shown in the key), at pH 7±0.05. The system consists of: ST-water, Al$_2$(SO$_4$)$_3$ 30μM, kaolin (50 mg/L), and Na$_2$SiO$_3$ (mg/L as SiO$_2$).

Figure 5.9.b Electrophoretic mobility (EM) (μm s$^{-1}$V$^{-1}$cm) of kaolin particles in suspensions after addition of alum (Al$_2$(SO$_4$)$_3$ 30μM) in presence of dissolved silica (mg/L); Supernatant turbidity of suspensions after the standard procedure against dissolved silica (mg/L as SiO$_2$) in the same system as Fig. 5.9.a.
At 10 and 20 mg/L, the FI value begin increasing within the one minute fast mixing time, in contrast to a long lag time of around five minutes in absence of dissolved silica; in addition, the final plateau value of FI reaches the highest at 20 mg/L. Further increasing concentrations of dissolved silica, for example, 30, 40, and 50 mg/L, the increase of FI value and the final plateau value are depressed compared with that at 20 mg/L, although the FI values still begin increasing within one minute mixing and the plateau value maintains fairly high values. However, at a concentration of 80 mg/L, despite the FI value begin increasing within one minute mixing, it is greatly depressed to a very low value compared with those at lower concentration of dissolved silica, such as 20 mg/L. Furthermore, at even high concentration of dissolved silica (e.g. 100 mg/L), the FI value does not increase with time.

The EM of particles at the alum dose 30 μM in the presence of dissolved silica is seen to decrease as concentration of dissolved silica increases. At 20 and 30 mg/L of dissolved silica, the EM of particles decreased from 1.0 to about zero. With further increasing concentration of dissolved silica to 50 mg/L, the EM of particles dropped to -0.8. When the concentration of dissolved silica increases to 100 mg/L, the EM becomes very low, -1.5 standard unit.

A comparison between Figure 5.9.a and Figure 5.9.b shows that the presence of dissolved silica can neutralise the reversed positive surface charge of particles and lead to a promotion of coagulation. For example, at 20 mg/L of dissolved silica, the EM of particles is reduced from 1.01 to zero, and the FI values against time show a fastest increase and highest plateau values. When the EM of particles reaches a low negative value (e.g. -1.2), due to presence of high concentration of dissolved silica (e.g. 80 mg/L), the FI values is greatly suppressed both in the terms of rate and final plateau value (e.g. FI value only around 0.75 at dissolved silica 80 mg/L, in contrast to FI value around 4 at dissolved silica 20 mg/L). When the EM of particles is further decreased by presence of dissolved silica to a very low value (e.g. -1.5 standard unit), the index value is completely suppressed to values near zero (e.g. at dissolved silica 100 mg/L).
The supernatant turbidity of suspensions in the same system is shown in Figure 5.9.b. Comparing the FI values versus mixing time, with EM of particles at concentrations of dissolved silica, one can see that the lowest supernatant turbidity of suspensions occurred in highest increase rate and final value of FI, which corresponds to the IEP in this case. It is seen that, at the alum dosage 30 µM, presence of dissolved silica 10, 20 mg/L can reduce the supernatant turbidity compared with that in absence of dissolved silica. At higher dissolved silica concentration 30, 40, 50 mg/L, the supernatant turbidity is lower than that without dissolved silica, but is higher than those with dissolved silica at lower concentrations 10 and 20 mg/L. However, with dissolved silica concentration up to 80 mg/L, the supernatant turbidity increases significantly to a higher value around 25 NTU; moreover, with dissolved silica at 100 mg/L, no decrease of supernatant turbidity was seen.

In conclusion, the presence of dissolved silica can promote, suppress, or prevent the coagulation of kaolin suspensions by alum at this primary stage of zone four coagulation at alum dose 30µM at pH 7. Which of these effects will occur, depends on the concentration of dissolved silica present. A concentration of dissolved silica below 30 mg/L may greatly promote the coagulation kinetically, whereas very high concentration can prevent the coagulation completely. This effect is related to the influence on surface charge of particles by presence of dissolved silica in the coagulation system. Presence of dissolved silica in the coagulation system can reduce the reversed positive charge by alum alone to zero and further to negative values if the dissolved silica concentration is high. The mechanism of the influence will be discussed later (see chapter 6).
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Fig. 5.10.a Kinetics of flocculation of kaolin suspensions by addition of alum expressed in the flocculation index (FI) values versus mixing time at concentrations of dissolved silica at pH 7±0.05. The system consists of: ST-water, kaolin 50 mg/L, Al₂(SO₄)₃ 100μM, and Na₂SiO₃ (mg/L as SiO₂ as shown in the key).

Fig. 5.10.b Electrophoretic mobility (μm s⁻¹V⁻¹cm) of kaolin particles after addition of alum (Al₂(SO₄)₃ 100μM) and supernatant turbidity of the suspensions after the standard procedure against dissolved silica (mg/L as SiO₂) in the same system as Fig. 5.10.a.
(2) at dosage of alum 100 \( \mu \text{M} \)

Above, we showed the results of influence of dissolved silica on alum coagulation at dosage 30 \( \mu \text{M} \) in the primary stage of zone four coagulation. In this section, the results of the influences of dissolved silica on the zone four coagulation will be presented at a high dosage of alum 100 \( \mu \text{M} \) with varying concentrations of dissolved silica. This will give the information on the influence of dissolved silica on flocculation in case of sweep flocculation, which is of great importance in the water treatment process under certain circumstances.

Results showing the influence of dissolved silica on the coagulation at alum dosage 100 \( \mu \text{M} \) are given in Figure 5.10.a and Figure 5.10.b. It is seen in Figure 5.10.a that, at alum dose 100 \( \mu \text{M} \), dissolved silica at 30 and 50 mg/L can enhance the coagulation kinetically. For at these concentrations of dissolved silica, the rise rate of FI value and the final plateau value are greater than those in the absence of dissolved silica. However, at a higher concentration of dissolved silica (80 mg/L), the growth rate and the final value of FI are decreased compared with those at 30 and 50 mg/L. That is, the coagulation is suppressed by high levels of dissolved silica. With further increasing dissolved silica to 100 mg/L, the index values remain very low, near zero, indicating that the coagulation is prevented completely under the given condition.

The EM of particles at alum dose 100 \( \mu \text{M} \) in presence of dissolved silica 30, 50, 80, 100 mg/L is shown in Figure 5.10.b. It is seen that presence of dissolved silica reduces the surface charge of particles in such suspensions at alum dose 100 \( \mu \text{M} \). At dissolved silica concentration 30 mg/L, the EM of particles is reduced from 0.77 to -0.33; the EM of particles is further reduced to -0.67 at dissolved silica 50 mg/L. With higher concentrations of dissolved silica, the EM of particles drops even lower. For example, at dissolved silica concentration 80 and 100 mg/L, the EM of particles are -1.18 and -1.48 standard unit respectively.
The supernatant turbidity of the suspensions at the same system is shown in Figure 5.10.b. At concentrations of dissolved silica 30 and 50 mg/L, the supernatant turbidities are slightly lower than those without presence of dissolved silica. However, at concentration of dissolved silica 80 mg/L, the supernatant turbidity rises above 10 NTU. Moreover, at 100 mg/L dissolved silica concentration the supernatant turbidity of suspension remained the same as that of the original clay suspension.

Comparing Figure 5.10.a and Figure 5.10.b, at pH 7 and alum 100 μM, several points can be drawn. First, presence of dissolved silica at lower concentrations can improve the coagulation kinetically. In this case, presence of dissolved silica can reduce the reversed positive surface charge of particles by alum to zero (EM), or further to a negative value above -1.0, as in the case of dissolved silica at 30 and 50 mg/L. Second, presence of dissolved silica at higher concentration depresses the coagulation kinetically. In this situation, the surface charge of particles may be decreased to a more negative value below -1.0 as in the case of dissolved silica 80 mg/L. Finally, dissolved silica in solution at very high concentration can prohibit the coagulation completely, and in this case, the surface charge of particles may be reduced to near -1.5 or even lower.

Comparing the influence of dissolved silica on coagulation at 30 and 100 μM, there are some similarities and differences. Firstly, the presence of dissolved silica can enhance coagulation at lower contents of dissolved silica at both these alum dosages; in these cases, the EM of particles may be reduced from the reversed positive value to zero or below. Next, the presence of dissolved silica at high concentration, e.g. 100 mg/L, can prevent coagulation completely in both cases, the EM of particles may be brought to more negative values. However, these influences of promotion or prevention at particular concentration of dissolved silica may show some difference. For example, at dissolved silica 80 mg/L, the coagulation is strongly inhibited at alum dose 30 μM, whilst is only depressed at alum dose 100 μM. This difference can be explained by the mechanisms of coagulation in these cases.
5.2.3 Influence on alum coagulation at pH 8

The influence of dissolved silica on alum coagulation with kaolin suspensions at pH 8 has been examined at alum dose 30 μM in presence of dissolved silica 0, 5, 10, 15 mg/L, as shown in Figure 5.11.a and Figure 5.11.b. At this dosage of alum, the coagulation proceeds in zone two, or in the range between zone two and zone four (see Figure 5.5.a&b). A general trend, from promotion to prevention of coagulation has been observed when increasing the concentration of dissolved silica. However, the concentration of dissolved silica needed to prevent coagulation is much lower than that at pH 7.

As shown in Figure 5.11.a, presence of dissolved silica at a low concentration, 5 mg/L, can promote increase of FI values both in terms of increase rate and final plateau value. However, at a higher concentration of dissolved silica, 10 mg/L, the FI value versus mixing time is considerably reduced, since only a slight increase of FI values is observed during five minute mixing and only a low final value around 1 unit is achieved. Further increasing dissolved silica concentration to 15 mg/L, causes the FI values to be depressed to values near zero, and no increase of the value is observed in this case.

The EM of particles in the same system is given in Figure 5.11.b. It can be seen that, at 30 μM of alum and in absence of dissolved silica the EM of particles is at the zero point at pH 8. Presence of dissolved silica can reduce the EM of particles to a negative value and the degree of this reduction depends on the concentration of dissolved silica. For example, at dissolved silica 5 mg/L, the EM of particles is around -1.1; at dissolved silica 10 mg/L, the EM of particles is at around -1.8; at dissolved silica 15 mg/L, the EM of particles is at an even more negative value of -2.1.
The supernatant turbidity of suspension after the standard procedure is also shown in Figure 5.11.b. It can be seen that at dissolved silica 5 mg/L, the supernatant turbidity of suspension is slightly reduced compared to that without dissolved silica. However, at dissolved silica 10 mg/L, the supernatant turbidity becomes high (around 48 NTU). Furthermore, at dissolved silica concentration 15 mg/L, no reduction of supernatant turbidity is seen.

A comparison between Figure 5.11.a and Figure 5.11.b shows three important aspects of the influence of dissolved silica on coagulation at the pH 8. First, at dissolved silica 5 mg/L, the growth rate of index value and final plateau index value is largest; and this corresponds a lowest supernatant turbidity. So, the coagulation of kaolin by alum (30 μM) is improved at this concentration of dissolved silica. This improvement of coagulation cannot be explained in terms of the charge effect, for the EM of particles is reduced by this amount of dissolved silica from zero to a negative value (around -1.1 unit). This is very different from what was seen at pH 7, for coagulation is depressed greatly when the EM of particles is around -1 unit (see 5.2.2.2). This great difference between pH 7 and 8 will be discussed later (see Chapter 6). Secondly, at dissolved silica concentration 10 mg/L, the growth rate of FI value and final plateau value are greatly reduced; the supernatant turbidity of suspension reaches a correspondingly high value. The coagulation is inhibited by this amount of dissolved silica, and the EM of particles is more negative (around -1.8 unit) in this case. Finally, at dissolved silica 15 mg/L, there is no increase of FI value with time and the supernatant turbidity is the same as that of the original kaolin suspension; the EM of particles is still more negative (-2.1 unit). In this case, there is no coagulation.
Figure 5.11.a Kinetics of flocculation of kaolin suspensions by addition of alum expressed in the flocculation index (FI) values against mixing time in presence of dissolved silica (mg/L as shown in the key), at pH 8±0.05. The system consists of: ST-water, Al₂(SO₄)₃ 30μM, and kaolin (50 mg/L), and Na₂SiO₃ (mg/L as SiO₂).

Figure 5.11.b Electrophoretic mobility (μm s⁻¹ V⁻¹ cm) of kaolin particles in suspensions after addition of alum (Al₂(SO₄)₃ 30μM) and in presence of dissolved silica (mg/L); Supernatant turbidity of the suspensions after the standard procedure as a function of dissolved silica (mg/L), at pH 8±0.05, in the same system as Fig. 5.11.a.
5.2.4 Influence on alum coagulation as a function of pH

The influence of dissolved silica on coagulation of kaolin suspension by alum at dosage of 40 μM and dissolved silica at 20 and 50 mg/L (as SiO₂) were examined as a function of solution pH. The results are shown in Figure 5.12.a and Figure 5.12.b, Figure 5.13.a and Figure 5.13.b.

The purpose of these experiments is to show the influence of dissolved silica at a medium and a higher level on the optimum range of solution pH for coagulation of kaolin suspension by alum at a dosage in the optimum range. 40 μM alum is chosen as an optimum dosage in the system. The reason for choosing this dosage as an optimum dosage can be seen from Figure 5.4.a&b, and Figure 5.5.a&b. In these two figures it is seen that at alum dose 40 μM, at pH 7 and 8, the rate of coagulation indicated by the FI value is at the highest and supernatant turbidity is in the lowest.

5.2.4.1 At dissolved silica concentration 20 mg/L

The influence of dissolved silica on coagulation of kaolin suspensions by alum at values of solution pH at dosage of 40 μM at dissolved silica 20 mg/L (as SiO₂) is shown in Figure 5.12.a and Figure 5.12.b.

In Figure 5.12.a, the influences of dissolved silica on kinetics of coagulation are given. It is seen that FI value increases with time between pH 6.47 and 7.69. That is, below pH 6.5 and above pH 7.8, there is no coagulation. Compared with the coagulation in absence of dissolved silica (see Figure 5.6.a&b), presence of dissolved silica 20 mg/L slightly shifts the coagulation to acidic side, at the same time narrows this pH range for coagulation from between 6.76 and 8.44 to the present range of pH.
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Figure 5.12.a Kinetics of flocculation of kaolin suspensions by addition of alum expressed in the flocculation index (FI) value versus mixing time at varying values of pH (as shown in the key) in presence of dissolved silica (20mg/L). The system consists of: ST-water, Al₂(SO₄)₃ 40μM, kaolin (50 mg/L), and Na₂SiO₃ (20 mg/L as SiO₂).

Figure 5.12.b Electrophoretic mobility (µm s⁻¹/V cm) of kaolin particles in suspensions after addition of alum (Al₂(SO₄)₃ 40μM) and in presence of dissolved silica (20 mg/L as SiO₂); Supernatant turbidity of the suspensions after standard procedure versus pH in the same system as Fig.5.12.a.
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The EM and supernatant turbidity corresponding to the system in Figure 5.12.a is shown in Figure 5.12.b. The EM of particles showed decreasing as pH increasing; the EM corresponding the coagulation range is from 0.89 to -1.31 unit. In addition, there is clear indication that the EM of particles decreases more quickly in presence of dissolved silica. The supernatant turbidity agrees well with the kinetics of coagulation reflected by the FI value.

5.2.4.2 At dissolved silica concentration 50 mg/L

The influence of dissolved silica on coagulation of kaolin suspensions by alum at values of solution pH at 40 μM alum dose at dissolved silica 50 mg/L (as SiO₂) is shown in Figure 5.13.a and Figure 5.13.b.

The influences of dissolved silica on kinetics of coagulation is shown in Figure 5.13.a. One can see that the coagulation region indicated by FI value is between pH 6.18 to 7.32. That is, there is no coagulation occurring below pH 6.2 and above 7.45. So, the coagulation range of pH shifts further to the acidic side compared with the previous case.

The EM and supernatant turbidity in the same system (Figure 5.13.a) is shown in Figure 5.13.b. The EM of particles decreases with pH more quickly than for 20 mg/L dissolved (see Figure 5.12.b). The EM of particles corresponding to the coagulation range is approximately 0.69 to -1.55 unit. The supernatant turbidity shows better than 90 % removal is in the pH range from 6.33 to 7.19, which agreed well with the kinetics of coagulation indicated by the FI values.

The results in Figure 5.6.b, Figure 5.12.b and Figure 5.13.b are also presented together in Figure 5.14. One can see that the shift of coagulation region corresponds the decrease of EM as a function of pH in presence of dissolved silica 20, 50 mg/L.
Figure 5.13.a Kinetics of flocculation of kaolin suspensions by addition of alum, expressed in the flocculation index (FI) value versus mixing time at varying values of pH (as shown in the key) in presence of dissolved silica (50 mg/L). The system consists of: ST-water, Al₂(SO₄)₃ (40μM), kaolin (50 mg/L), and Na₂SiO₃ (50 mg/L as SiO₂).
Figure 5.13.b  *Electrophoretic mobility* (EM) (μm s⁻¹ V⁻¹ cm) of kaolin particles after addition of alum; supernatant turbidity of the suspensions after the standard procedure versus pH in the same system as Figure 5.13.a.
Figure 5.14 *Electrophoretic mobility* (EM) (µm s⁻¹ V⁻¹ cm) of kaolin particles versus pH under conditions: (1) Kaolin particles in suspensions made with ST-water; (2) Kaolin particles in suspensions after addition of alum (Al₂(SO₄)₃ 40 µM), in presence of dissolved silica (50mg/L as SiO₂); (3) Kaolin particles in suspensions after addition of alum (Al₂(SO₄)₃ 40 µM), in presence of dissolved silica (20mg/L as SiO₂); (4) Kaolin particles in suspensions after addition of alum (Al₂(SO₄)₃ 40 µM) without presence of dissolved silica. It is seen that presence of dissolved silica can reduce the reversed positive charge of kaolin particles after addition of alum, or make the particles more negative. Note: D-silica, dissolved silica; pH adjustment, NaOH/HNO₃ (0.1(N)M).
5.2.5 Conclusion

All above, the influence of dissolved silica on flocculation of kaolin suspension by alum can be summarised below:

(1) At the low alum dose, the zone 2 coagulation, presence of dissolved silica can make the surface charge of particles after addition of alum more negative; hence, the coagulation can be affected accordingly.

(2) At high alum dose, the zone 4 coagulation, presence of dissolved silica can improve or prevent the coagulation depending on the content of dissolved silica and solution pH. At lower dosage of alum in this zone where coagulation by alum proceeds with a long lag time, presence of dissolved silica at around 15-20 mg/L can greatly enhance the coagulation by shortening the lag time (e.g. at pH 7). In this case, presence of dissolved silica brought the EM of particles to around zero. At higher dosage of alum in this zone, where there is no lag time in the coagulation, presence of dissolved silica at 30-50 mg/L can also improve the coagulation evidently. However, in this case, the EM of particles was brought to negative values. In both cases, when content of dissolved silica becomes high, the coagulation can be hindered or prevented when the EM of particles goes down around -1.5 unit by presence of dissolved silica. One noticeable fact is that, the presence of dissolved silica can even prevent coagulation in the sweep flocculation stage.

(3) The degree of the effect of dissolved silica on coagulation can be different depending on pH. At pH 8, where EM of particles is at the IEP after addition of alum, strong effect is observed at comparatively low concentration of dissolved silica. It is seen that at only 15 mg/L dissolved silica, the coagulation can be prevented completely, where the EM of particles is brought to around -2.
(4) Presence of dissolved silica can shift and narrow the coagulation region of pH to acidic side. The shift of coagulation region is closely related to the charge effect of dissolved silica on particles. At alum 40 μM, the EM range for coagulation with or without dissolved silica is approximately between 1 to - 1.5 unit.

5.3 Aluminium Precipitation

Study of aluminium precipitation has been experimentally focused on the stability of the precipitate (Rubin and Hayden 1974) or the factors which affect the precipitation (Clark and Srivastava 1993). These methods cannot give the information on growth of the primary precipitates as a function of time. Little is known about the significance of the growth of the primary precipitates to the kinetics of aggregation of kaolin particles when hydrolysing metal salts are used. Here, using a simple technique, aggregation of primary alum precipitates as a function of mixing time is demonstrated under several conditions. The implications of these measurements to the aggregate formation will be discussed together with the aggregation of kaolin particles by alum as detected by PDA.

5.3.1 Aluminium precipitation at different solution pH

Aggregation of primary aluminium precipitate at values of pH are examined at an alum (Al$_2$(SO$_4$)$_3$) dose 40 μM. The kinetic process of the precipitation has been detected by a particle monitor (PM) under given conditions. Detailed experimental procedure and principles of the measurement were given before in 4.4.2. The results at pH 6.00, 6.78, 7.07, 7.61, 8.03 are shown in Figure 5.15.
Figure 5.15 Kinetics of aluminium precipitation expressed in particle index (PI) values versus mixing time, at varying pH values (as shown in the key). The system consists of: ST-water, $\text{Al}_2(\text{SO}_4)_3$, 40µM.
From Figure 5.15, it can be seen that, in the chosen pH range from 6 to 8, aggregation of primary aluminium precipitates is enhanced strongly as the solution pH increases. At solution pH 6, there is no increase of the PI value during the 15 minute mixing time. At pH 6.78, the PI value shows an increase with a long lag time around 12 minutes. However, at pH 7, the index value increases with a short lag time around 5 minutes. Furthermore, at pH 7.61 and pH 8, the PI value increase almost immediately after fast mixing without lag time.

5.3.2 Aluminium precipitation at different alum concentrations

Aggregation of primary aluminium precipitates against time at different alum concentrations is examined at alum concentrations 40, 100 μM, at pH 7. The results are shown in Figure 5.16. One can see from this figure that aggregation of primary aluminium precipitates is promoted as the concentration of alum is increased. At alum concentration 40 μM the PI value shows an increase with a lag time around 5 minutes and reaches a relatively low plateau around 1 unit; whereas at alum concentration 100 μM, the PI value increases immediately after fast mixing and achieves a higher plateau value. This indicates that aggregation of primary precipitates begins soon after fast mixing at alum concentration 100 μM and the size of aggregates can reach a higher value than that of aggregate at alum concentration 40 μM (note that the increased number concentration of precipitates would also cause a small increase in the PI values (see Equation 4.4)).

5.3.3 Conclusion

The results of 5.3.1 and 5.3.2, for the particle index versus time, indicate particle aggregation process. It is not clear from the results at what size of particles, the PI value begins to show an evident increase. However, it might be reasonable to think that this increase begins with an aggregation of primary aluminium precipitates after formation of crystallites in solution. This is because although the crystal growth (or
formation) can be a slow kinetic process in case of minerals such as CaCO$_3$ or Mg(OH)$_2$ (Nancollas and Reddy 1974), crystal formation in case of aluminium (Al(OH)$_3$) may be very fast. That is, it may finish within seconds. These crystallites may be colloidally stable and difficult to grow, or colloidally unstable and ready to aggregate. Therefore, the result may indicate that crystallites formed at acidic pH values such as pH 6 are very small and colloidally stable, whereas those formed at neutral and alkaline pH may be colloidally metal-stable or unstable. Due to this reason, the crystallites formed at alkaline side can aggregate quickly into larger aggregates. Obviously, this kinetic characteristics of aggregation of the crystallites will exert distinctive effect on flocculation. In the past, this kinetics process and its effect on coagulation is unknown and completely neglected due to the limitation of experimental instrumentation.

Therefore, from the results, one can see that the aggregation of the primary aluminium precipitate is strongly related to the pH. Its implication to flocculation will be discussed later.
Figure 5.16 Kinetics of aluminium precipitation expressed in the particle index (PI) values versus time at two alum concentrations. Aluminium precipitation can be dynamically promoted as the concentration increasing. The system consists of: ST-water, Al$_2$(SO$_4$)$_3$·16H$_2$O (40μM; 100 μM as shown in the key). The final solution pH is 7±0.05.
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5.4 Influence of Dissolved Silica on Aluminium Precipitation

From the results in 5.3, it is known that aggregation of primary aluminium hydroxide precipitate is dependent on solution pH and concentration of aluminium. Since coagulation by aluminium is closely related to aluminium precipitation at certain stage, kinetics of aggregation of the primary aluminium precipitate will exert great influence on the coagulation of kaolin suspension. Therefore, it is quite possible that the influence of dissolved silica on aluminium coagulation in such stage may be related to its influence of dissolved silica on aluminium precipitation. Examination of this influence could shed some light on the influence of dissolved silica on aluminium coagulation.

Using a particle monitor (PM), the influence of dissolved silica on aluminium precipitation has been examined in this study. Detailed experimental procedure and principle is given in 4.4.2. The influence of dissolved silica on alum precipitation is carried out at pH 7 and 8; the results are presented below.

5.4.1 Influence of dissolved silica at pH 7

The results for influence of dissolved silica on aluminium (alum) precipitation at pH 7 are shown in Figure 5.17. The experiment is carried out at alum dosage 40 μM and three concentrations of dissolved silica: 20, 50, 100 mg/L.

As can be seen, the PI value at alum dose 40 μM in absence of dissolved silica begins to increase with a lag time around seven minutes and with a plateau value around 0.9 unit. However, with presence of dissolved silica 20 mg/L, the PI value shows an increase nearly immediately after addition of alum, and reaches a higher maximum value around 1.2 unit. The situation at dissolved silica 50 mg/L is very similar to that at dissolved silica 20 mg/L. In contrast, at dissolved silica 100 mg/L,
Figure 5.17  kinetics of aluminium precipitation expressed in the particle index (PI) value versus mixing time without and with presence of dissolved silica at pH 7. The system consists of: ST-water, $\text{Al}_2(\text{SO}_4)_3$ 40$\mu$M, Na$_2$SiO$_3$ (mg/L as SiO$_2$ as shown in the key). 

there is no increase of the PI value throughout mixing time.

From these results, it is seen that the precipitation at the dosage 40 \( \mu \text{M} \) alum is promoted by the presence of dissolved silica at 20 and 50 mg/L. This indicates that, with these amounts of dissolved silica present in solution, aggregation of primary aluminium precipitates begins soon after addition of alum, other than after a long lag time as in absence of dissolved silica. However, presence of dissolved silica at concentration 100 mg/L can prevent the aggregation process of the primary the precipitates. In this case, with presence of dissolved silica at such high content, the crystallites of aluminium formed in solution may be very small and colloiddally stable. So that, no aggregation of particles could occur and no aggregation could be detected by the PM. One could say that presence of dissolved silica may even prevent the formation of the small crystallites of aluminium hydroxide, there would be unlikely. For in such case, the initial values of the PI indicate that there are very small particles in the such solution and this is confirmed by the turbidity measurement of such solution.

**5.4.2 Influence at pH 8**

The results for influence of dissolved silica on aluminium precipitation at pH 8 are shown in Figure 5.18. The experiment is carried out at alum dosage 40 \( \mu \text{M} \) and concentrations of dissolved silica: 5, 10, 15 mg/L.

From Figure 5.18, the PI value at alum dose 40 \( \mu \text{M} \) and pH 8 in absence of dissolved silica increases nearly immediately after addition of alum. With presence of dissolved silica 5 mg/L, the PI value shows an improvement compared with that with alum alone. For the PI values increase faster and with a higher final value. However, at dissolved silica 10 mg/L, increase of PI value is considerably depressed and the plateau value becomes lower. Furthermore, at dissolved silica concentration 15 mg/L, there is no increase of PI value throughout time.
Figure 5.18 Kinetics of aluminium precipitation expressed in the particle index (PI) values versus time with and without presence of dissolved silica at pH 8±0.05. The system consists of: ST-water, Al$_2$(SO$_4$)$_3$ 40μM, and Na$_2$SiO$_3$ (mg/L as SiO$_2$ as shown in the key).
From this result, it seems that aggregation of primary precipitates at the dosage 40 μM and pH 8 can be promoted by the presence of dissolved silica at 5 mg/L. However, presence of dissolved silica at concentration only 10 mg/L, the aggregation process can be suppressed considerably. Moreover, at concentration of 15 mg/L dissolved silica can prevent aggregation of primary precipitates.

A comparison between the results at pH 7 and pH 8, two distinctive features are observed. Firstly, at pH 8, the influence of dissolved silica on aluminium precipitation is more sensitive. Secondly, the presence of dissolved silica can promote, or prevent aggregation of primary aluminium hydroxide precipitates depending solution pH and contents of dissolved silica.

5.5 Solubility of Aluminium in Presence of Dissolved Silica

The solubility of aluminium has been examined by the residual aluminium measurements in this study. The purpose of this experiment is to check whether aluminium is more soluble in presence of dissolved silica. The experiment was conducted at alum concentration 40 μM (or aluminium 80μM). Detailed experimentation is given 4.4.4.

The results of measurements of residual aluminium at initial alum concentration of 40 μM in absence of dissolved silica and with presence of dissolved silica 20 mg/L is presented in Figure 5.19 as a function of pH. In presence of silica (20 mg/L as SiO₂) there is an appreciable increase in the free aluminium concentration over most of the pH range. In the region around 6, corresponding to the minimum in soluble aluminium species, the increase is of order of fivefold or more (Figure 5.19.a). This may indicate that complex formation prevent the formation of insoluble species or presence of silicic acid may release some aluminium from precipitate, although it has to be recognised that around neutral pH there is very little residual aluminium, even in the presence of silica.
**Fig. 5.19.a** Residual aluminium in solutions as a function of pH after membrane filtration (pore size 0.45 μm) without and with presence of dissolved silica (mg/L as SiO₂ as shown in the key). Aluminium sulphate (Al₂(SO₄)₃, 40μM) is added in ST-water and NaOH/HNO₃ for pH adjustment (for preparation, see 4.4.4).

**Figure 5.19.b** As Figure 5.19.a but with logarithmic scale.
At solution pH 8, there is a considerable increase of free aluminium in presence of dissolved silica, indicating that at this pH interaction between aluminium and dissolved silica has more influence on the solubility of aluminium. Considering the membrane pore size is fairly large, it is also possible that, the presence of dissolved silica does not make aluminium completely soluble, but only reduces the size of precipitates. Therefore, interactions between aluminium and silicic acid may enhance the solubility of aluminium or simply reduce the size of precipitates.

From this result, one can see that presence of dissolved silica 20 mg/L has little effect on solubility of aluminium at pH 7; but has more effect on solubility of aluminium at pH 8. The implication of this result to alum coagulation will be discussed later (see Chapter 6).

5.6 The Effect of Calcium in the Coagulation System

In this section, the effects of calcium on coagulation of kaolin suspension in the alum dissolved silica system will be given.

Calcium commonly exists in water environments in high levels from 50 to 250 mg/L as CaCO$_3$ or more (Faust and Aly 1983). When the coagulation by aluminium is affected by solution chemistry, such as presence of soluble silica, the role of the simple ion Ca$^{++}$ may be important. In this section, we will examine the role of calcium ion in the coagulation system, especially when presence of dissolved silica prevent alum coagulation with kaolin suspension.
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5.00
Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} 40\textmu M; dissolved silica 50 mg/L as SiO\textsubscript{2}
Ca(NO\textsubscript{3})\textsubscript{2} mM
pH 7.5

Figure 5.20.a Kinetics of flocculation of kaolin suspensions by addition of alum expressed in the FI value versus mixing time in presence of dissolved silica (50 mg/L), at varying amounts of calcium (Ca(NO\textsubscript{3})\textsubscript{2} mM) (as shown in the key), at pH 7.5±0.05. Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} (40\textmu M,), Na\textsubscript{2}SiO\textsubscript{4} (50 mg/L as SiO\textsubscript{2}), kaolin (50 mg/L).

Figure 5.20.b Electrophoretic mobility (EM) (\mu m s\textsuperscript{-1}V\textsuperscript{-1} cm) of kaolin particles in suspensions after addition of alum (Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} 40\textmu M) in presence of dissolved silica (50 mg/L), and calcium (Ca(NO\textsubscript{3})\textsubscript{2} mM); Supernatant turbidity of the suspensions after standard procedure as a function of Calcium (Ca(NO\textsubscript{3})\textsubscript{2} (mM) in the same coagulation system as Figure 5.20.a.
5.6.1 Effect of calcium concentrations at pH 7.5

The effects of Ca\(^{++}\) is examined at pH 7.5 with increasing its concentration, at concentration of dissolved silica 50 mg/L, alum dosage 40 \(\mu\)M, and concentration of kaolin 50 mg/L. The calcium is added as Ca(NO\(_3\))\(_2\) (mM). The results are shown in Figure 5.20.a and Figure 5.20.b.

The kinetic effect of Ca\(^{++}\) on the coagulation is examined by using PDA and the results are presented in Figure 5.20.a. One important observation is that Ca\(^{++}\) with relatively low concentration can restore the coagulation by alum when it is prevented by dissolved silica. As is seen in Figure 5.20.a (also see Figure 5.13.a&b), at pH 7.5, presence of dissolved silica 50 mg/L prevents completely the coagulation of kaolin suspension by alum (40 \(\mu\)M). At concentration of calcium (Ca(NO\(_3\))\(_2\)) 0.10 and 0.25 mM, there is no increasing of FI values versus mixing time. However, at concentration of Ca\(^{++}\) 0.50 mM, the FI values increase gradually with a lag time around 2 minutes indicating the suspension is destabilised and coagulation occurs at a low level. Moreover, at Ca\(^{++}\) 1.00 mM, the FI value increases greatly with time, indicating a good coagulation. With even higher concentration of Ca\(^{++}\), such as 2 and 3 mM, the coagulation even more improved, for a short lag time around 30 seconds and higher plateau values is observed.

The EM of particles and supernatant turbidity of the suspensions in the corresponding system are presented in Figure 5.20.b. The negative EM of particles decreases as concentrations of calcium increases. At concentrations of Ca\(^{++}\) 0.10 and 0.25 mM, the negative EM of particles decreases from -1.97 to -1.61 and -1.33 unit respectively. At Ca\(^{++}\) 0.50 mM, the negative EM of particles further decreased to -1.06, where the FI values indicate a weak coagulation. When concentration of Ca\(^{++}\) reaches 1.00 mM and more, the decreasing rate of the negative EM of particles slows down with a final value around -0.70.
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Figure 5.21.a Kinetics of flocculation of kaolin suspensions by addition of alum expressed in the FI values versus mixing time in presence of dissolved silica (50 mg/L) and calcium (Ca(NO$_3$)$_2$ 1mM), at values of pH (as shown in the key). The system consists of: ST-water, Al$_2$(SO$_4$)$_3$ (40μM), kaolin (50 mg/L), Na$_2$SiO$_3$ (50 mg/L as SiO$_2$), and Ca(NO$_3$)$_2$ (1mM).

Figure 5.21.b Electrophoretic mobility (EM) (μm s$^{-1}$V$^{-1}$ cm) of kaolin particles in suspensions after addition of alum (Al$_2$(SO$_4$)$_3$ 40μM), in presence of dissolved silica (50 mg/L as SiO$_2$) and Calcium (Ca(NO$_3$)$_2$ 1mM); Supernatant turbidity of the suspensions after the standard procedure as a function of pH in the same system as Figure 5.21.a.
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The supernatant turbidity of suspensions agree well with the results of EM and FI above. The supernatant turbidity begins to decrease at 0.5 mM Ca$^{2+}$; and at 1.00 mM and more, a substantial decrease of supernatant turbidity was seen.

A comparison between Figure 5.20.a and Figure 5.20.b shows that addition of calcium in the coagulation system (dissolved silica, alum, and kaolin) can reduce the negative surface charge of particles. When the EM of particles is reduced to around -1.0, coagulation of particles occurs; when the EM of particles is further reduced to -0.8, coagulation of kaolin is strongly promoted, for the FI value versus time is restored to the level generated by alum (40 μM) at pH 7.5 in absence of dissolved silica.

However, with addition of calcium 1 mM or more in such suspensions the EM of particles does not restore to the value found with the alum dose alone at this pH, (around + 0.47). For the EM of particles after addition of alum 40 μM with dissolved silica 50 mg/L is -1.97; after addition of calcium 1 and 3mM, the EM of particles is around -0.8 and -0.7.

5.6.2 Effect of calcium as a function of pH

The effect of calcium on coagulation of kaolin suspensions, in the coagulation system of alum and dissolved silica, as a function of pH is examined at concentration of 1 mM Ca$^{2+}$ (Ca(NO$_3$)$_2$), dissolved silica 50 mg/L and alum 40 μM. The results is shown in Figure 5.21.a and Figure 5.21.b.

The effect of calcium on coagulation in such system at values of pH are shown in Figure 5.21.a. It is seen that, FI value increases greatly with time in the pH range from around 7 and up to 10. Also, there is a fairly evident trend of increasing in plateau values as pH increases from around 7 to a higher value, with the highest value around pH 9. This result is extremely different from both the one obtained in the system with alum as a coagulant alone as shown in Figure 5.6.a, and the one in the system with
alum as a coagulant in presence of dissolved silica as shown in Figure 5.13.a., in both
cases no coagulation occur when value of pH is greater than around 8.5.

The EM of particles and supernatant turbidities of suspensions in the same system are
presented in Figure 5.21.b. As can be seen, the EM of particles decreases as pH
increases from pH 6 to 8. However, from pH 8 to 10, the EM of particle maintained
one level around -0.9 unit. This profile of EM versus pH is very different from that
observed in Figure 5.6.b and Figure 5.13.b, where the negative EM of particles will
increase to around -2 unit in the high pH range.

5.6.3 Conclusion

Based on the above results, some conclusions can be drawn as follows:

(1) Under conditions that the presence of dissolved silica prevent the coagulation/
flocculation of kaolin suspensions by alum, presence of calcium can counteract the
prevention effect of dissolved silica on coagulation. The flocculation can be restored to
the same or even higher level in terms of aggregate size or turbidity removal.

(2) Presence of calcium can even extend the range of pH for coagulation in such
system up to very high pH (e.g. > 10) with high level of aggregation or enhanced
turbidity removal.

(3) These effect indicate that the role of simple ion Ca^{2+} can be very important in the
coagulation by the hydrolysing metal salt when solution chemistry, such as presence of
anions, affects the coagulation. This would be very important to the water treatment
process. For, in natural waters, there often exist many chemicals or anions, which
would exert great influence on the coagulation otherwise.
5.7 Influence of Dissolved Silica on Coagulation by Iron(III)

In this section, the flocculation of kaolin suspension by ferric chloride will be examined by using the PDA and Particle Microelectrophoresis Apparatus. After that, the influence of dissolved silica on coagulation will be carried out at several stages of coagulation.

5.7.1 Characteristics of coagulation by ferric chloride

5.7.1.1 Coagulation by ferric chloride at pH 6

At low dosages

In Figure 5.22.a, the FI value is shown as a function of mixing time (including one minute fast mixing) at some low dosages of ferric chloride (FeCl₃ \( \mu \)M). It is seen that, when the dosage increases from 0 to 10 \( \mu \)M, FI values as a function of time increase faster and to a higher final value. At 0 and 2 \( \mu \)M dosages, there is no increase of FI values, indicating no occurrence of colloid aggregation. In contrast, at a dosage of 10 \( \mu \)M, the increase rate of FI value as a function of mixing time becomes largest and the final index value reaches its maximum value. This means that coagulation proceeds very well under this condition. However, further increasing the dosage from 10 \( \mu \)M, the rate of increase of FI values becomes lower. For example, at 20 \( \mu \)M, no evident increase of index values was observed indicating that the system is in the restabilisation region.
Figure 5.22.a Kinetics of flocculation of kaolin suspensions by addition of ferric chloride at low dosages, expressed in the *flocculation index* (FI) value against mixing time at pH 6±0.05. The system consists of: ST-water, FeCl₃ (μM as shown in the key), and kaolin (50 mg/L).

Figure 5.22.b *Electrophoretic mobility* (μm s⁻¹ V⁻¹ cm) of kaolin particles after addition of ferric chloride at low dosages; *supernatant turbidity* of the suspensions after the standard procedure against dose of ferric chloride in the same system as Figure 5.22.a.
Figure 5.23.a Kinetics of flocculation of kaolin suspensions by addition of ferric chloride at high dosages, expressed in the flocculation index (FI) value against mixing time at pH 6±0.05. The system consists of: ST-water, FeCl₃ (μM as shown in the key), and kaolin (50 mg/L).

Figure 5.23.b Electrophoretic mobility (μm s⁻¹ V⁻¹ cm) of kaolin particles after addition of ferric chloride at all dosages; supernatant turbidity of the suspensions after the standard procedure against dose of ferric chloride in the same system as Figure 5.23.a.

The electrophoretic mobility (EM, μm s⁻¹ V⁻¹ cm) of particles after addition of ferric chloride and one minute fast mixing; and the supernatant turbidity (NTU) of suspensions after standard mixing conditions, and sedimentation corresponding to the
system in Figure 5.22.a is presented in Figure 5.22.b. As seen in Figure 5.22.b, the negative surface charge of kaolin particles is neutralised as the dosage of the coagulant is increased to 10 μM. Further increasing the dosage of ferric chloride causes a charge reversal of the particles. For example, at a dosage of 20 μM, the particles become strongly positively charged with EM around 0.9 standard unit.

The supernatant turbidity (NTU) in the same coagulation system as a function of the coagulant dosage is also shown in Figure 5.22.b. It is seen that the lowest turbidity is at the isoelectric point. Highest increase rate and final index value in this stage of flocculation is also observed at this point.

From all the results above, the coagulation by ferric chloride in the system at pH 6, when in the dosage range of 3.5 to 15 μM, is in zone 2 coagulation, for the charge neutralising effects. However, at the dosage 20 and more (before very high dose like 100 μM), the coagulant dosage is in zone 3 of restabilisation of the colloids for the reason of surface charge reversal.

At high dosage

The kinetics of flocculation by ferric chloride at high concentration (20 to 200 μM), expressed by the FI values as a function of mixing time, is shown in Figure 5.23.a. There is no increase of the index value until the dosage reaches about 200 μM. Even at this dosage, around 10 minute lag time is seen before significant aggregation occurs.

The EM of particles after addition of the coagulant at high concentration and corresponding supernatant turbidity of the suspensions is shown in Figure 5.23.b. As can be seen, no significant decrease of the EM of particles is observed as the dosage increase.
From the comparison between the FI value in Figure 5.23.a and the EM as well as supernatant turbidity in Figure 5.23.b, one can see that when the index value increases significantly at the dose 200 μM, the supernatant turbidity decreases correspondingly. The aggregation is not at the sweep flocculation stage due to the slow kinetic characteristics. One noticeable fact is that, unlike in case of alum, there is no significant decrease of the particle EM as the dosage increase (see Figure 5.2.b, 5.4.b).

5.7.1.2 Coagulation by ferric chloride at pH 7

Coagulation of kaolin suspensions by ferric chloride at pH 7 exhibits different characteristics from those at pH 6. The main difference is that no charge reversal and restabilisation of the colloids occurs at this pH.

The kinetics of aggregation is shown in Figure 5.24.a. It is seen that the increase of FI values with mixing time is accelerated as the increase of the coagulant dose. The aggregation of the kaolin suspension can occur at low coagulant dose of 5 μM but fairly weakly. As the dosage increases, the aggregation of the suspension is strengthened indicated by the FI values with time. After the dose of 30 μM, further increasing the dosage, there is no significant increase of index value observed.

The corresponding EM of particles after addition of the coagulant and supernatant turbidity of the suspensions is shown in Figure 5.24.b. As can be seen, the negative EM of particles decreases as the coagulant dose increases. At the dose of 30 μM, the EM of particles become zero (IEP). Moreover, with further increasing dosage of coagulant, the EM of particles (or the zeta potential (ζ)) remains zero. So, increase of the dose does not change the surface charge of particles at this pH value.

In Figure 5.24.b, it is also seen that, the supernatant turbidity has great decrease at the dosage of 30 μM, and there is no significant decrease after this dosage.
A comparison of the index values and the EM at these dosages in Figure 5.24.a and Figure 5.24.b, shows that coagulation at the low dosages is in the zone two; at a high dose, for example, greater than 30μM, coagulation is in the overlap of zones 2 and 4.

5.7.1.3 Conclusion

From the results above, some noteworthy points are summarised below:

(1) at pH 6, the zone two coagulation can be seen at very low coagulant dosages (from 3.5 μM). As the dosage increase, the system enter the zone three restabilisation with wide dosage range, and the zone four coagulation can be initialised with very high coagulant dosage up to 200 μM. The coagulation in the zone four is much better than those in zone two in terms of FI values and turbidity removal.

(2) at pH 7, the IEP of kaolin particles was found at ferric chloride dose of 30 μM, and with further increasing the dosage, the EM of the particles remain constant at a value of about zero. The coagulation at low dosage is in the zone 2 and at high is in the zone 2+4 or 4.

(3) The EM of particles after adsorption of ferric chloride hydrolysis species is different from that of aluminium hydrolysis species.
Figure 5.24.a Kinetics of flocculation of kaolin suspensions by addition of ferric chloride, expressed in the flocculation index (FI) value against mixing time at pH 7±0.05. The system consists of: ST-water, FeCl₃ (µM as shown in the key), and kaolin (50 mg/L).

Figure 5.24.b Electrophoretic mobility (EM) (µm s⁻¹ V⁻¹ cm) of kaolin particles after addition of ferric chloride; supernatant turbidity of the suspensions after the standard procedure against dose of ferric chloride in the same system as Figure 5.24.a.
5.7.2 Influence of dissolved silica on coagulation by ferric chloride

5.7.2.1 Influence at pH 6

The influence of dissolved silica on coagulation by ferric chloride was examined at pH 6 at the dosage of 30 μM (FeCl₃). From 5.7.1.1, one can see that at this dosage the system is in the zone three restabilisation, in which only up to 200 μM of FeCl₃ coagulation can begin.

The result of kinetic influence of dissolved silica on coagulation at the dosage 30 μM is presented in Figure 5.25.a. As is seen, if 10 mg/L dissolved silica is present, coagulation begins after 10 minute lag time. As dissolved silica concentration increases, the flocculation is significantly improved so that coagulation can begin immediately after the fast mixing with a fast rate of aggregation at a concentration of 50 mg/L silica.

The EM of particles in the same system as above with presence of dissolved silica 10, 20, 50 mg/L at pH 6 is shown in Figure 5.25b. It is seen that, with presence of dissolved silica, the EM of particles decrease as the concentration of dissolved silica increases. At dissolved silica 20 mg/L, the EM of particles is decreased to 0.7; at dissolved silica 50 mg/L the EM of particles is descended to 0.2 standard unit.

Comparing Figure 5.25.a with Figure 5.25.b, one can see that as the EM of particles decreased from 1 unit to a low value by the presence of dissolved silica, the flocculation of the kaolin suspension is progressively improved.
Figure 5.25.a Kinetics of flocculation of kaolin suspensions by addition of ferric chloride expressed in the flocculation index (FI) value versus mixing time in presence of dissolved silica (mg/L as SiO$_2$ as shown in the key), at pH 6±0.05. The system consists of: ST-water, FeCl$_3$ 30μM, and kaolin (50 mg/L), and Na$_2$SiO$_3$ (mg/L as SiO$_2$).

Figure 5.25.b Electrophoretic mobility (μm s$^{-1}$V$^{-1}$cm) of kaolin particles in suspensions after addition of ferric chloride (FeCl$_3$ 30μM), in presence of dissolved silica (mg/L); Supernatant turbidity of the suspensions after the standard procedure against dissolved silica (mg/L as SiO$_2$) in the same system as Figure 5.25.a.
5.7.2.2 Influence at pH 7

The influence of dissolved silica on coagulation at pH 7 is carried out at two dose levels of ferric chloride 10, 30 μM. As seen before (see 5.7.1.2 and Figure 5.24.a&b), at 10 μM, the aggregation is at zone 2; while at 30μM, the aggregation is at zone 2+4, or 4.

The result at ferric chloride 10 μM is presented in Figure 5.26.a&b. From this Figure (a), one can see that the aggregation of suspension is decreased by the presence of dissolved silica. This kinetic decrease corresponds with the increase of the negative charge. For instance, at dissolved silica 30 mg/L, the aggregation of the kaolin suspension is greatly reduced, correspondingly the EM of particles is reduced to around -1.5. From this result, the dissolved silica at normal contents of waters can decrease the zone 2 flocculation evidently.

The result at dosage of ferric chloride 30 μM is presented in Figure 5.27.a&b. From Figure 5.27.a, it is seen that, aggregation is not affected or reduced significantly below concentration of dissolved silica 30 mg/L. However, up to 50 mg/L the aggregation is heavily affected, and at 80 mg/L the aggregation is prevented. From Figure 5.27.b, presence of dissolved silica can increase the negative charge of particles as in the other case. At 30 mg/L dissolved silica, the negative EM of particles is increased to -0.9; while at 80 mg/L, the negative EM is increased to -1.8 unit.

At all case, the supernatant turbidity responds reasonably the aggregation indicated by the FI value versus time, as is in case of alum.
Figure 5.26.a Kinetics of flocculation of kaolin suspensions by addition of ferric chloride expressed in the flocculation index (FI) value versus mixing time in presence of dissolved silica (mg/L as SiO₂ as shown in the key), at pH 7±0.05. The system consists of: ST-water, FeCl₃ 10μM, and kaolin (50 mg/L), and Na₂SiO₃ (mg/L as SiO₂).

Figure 5.26.b Electrophoretic mobility (μm s⁻¹V⁻¹cm) of kaolin particles in suspensions after addition of ferric chloride (FeCl₃ 10μM), in presence of dissolved silica (mg/L); Supernatant turbidity of the suspensions after the standard procedure against dissolved silica (mg/L as SiO₂) in the same system as Figure 5.26.a.
Figure 5.27.a  Kinetics of flocculation of kaolin suspensions by addition of ferric chloride expressed in the flocculation index (FI) value versus mixing time in presence of dissolved silica (mg/L as SiO₂ as shown in the key), at pH 7±0.05. The system consists of: ST-water, FeCl₃ 30μM, and kaolin (50 mg/L), and Na₂SiO₃ (mg/L as SiO₂).

Figure 5.27.b  Electrophoretic mobility (μm s⁻¹V⁻¹cm) of kaolin particles in suspensions after addition of ferric chloride (FeCl₃ 30μM), in presence of dissolved silica (mg/L); Supernatant turbidity of the suspensions after the standard procedure against dissolved silica (mg/L as SiO₂) in the same system as Figure 5.27.a.
5.7.3 Conclusion

The influence of dissolved silica on coagulation of kaolin suspension by ferric chloride is examined at pH 6 and 7. It is seen that at pH 6, at the dosage of zone 3 restabilisation, dissolved silica can promote the flocculation, in which the positive charge of particles can be reduced to near zero at concentration 50 mg/L. At pH 7, at low dosage of ferric chloride, the aggregation is affected or reduced evidently at low concentration of dissolved silica; while at high dosage of ferric chloride, at normal level of dissolved silica no evident influence is observed, only at high level of dissolved silica, the coagulation is prevented. In this case, the EM of particle is increased to a high negative value below -1.5 unit.
CHAPTER SIX

DISCUSSION

6.1 Characteristics of Alum Coagulation

As discussed in 2.4, 2.5 and 2.6, the mechanism of coagulation by alum is generally thought to be adsorption of aluminium hydrolysis species on particles and consequent charge neutralising effects at low doses of aluminium salts, and enmeshment of the particles by aluminium precipitates at high doses. The characteristic effects of the coagulant on coagulation are described by the four zone, depending solution pH, aluminium salt dose, and particle concentration. The adsorption process may involve surface complexation and surface precipitation or surface deposition of precipitate formed in bulk solution (see 2.4).

Despite these general explanation, there are still some uncertainties concerning the mechanisms of coagulation. In some case, the mechanisms are vaguely or even wrongly interpreted. Usually, there is no systematic elucidation to the mechanisms of coagulation/ flocculation of colloids by the hydrolysing metal salts. For example, the PCN model, which was supposed to gave a general model for coagulation control, can be only applied to a limited condition. From this model, the zone two coagulation is thought to be brought about by precipitation and charge neutralisation. However, this kind of coagulation can only occur at high pH (e.g., pH 8), where positive electrical charge is lower. For, even at around neutral pH, good coagulation can be brought about by a normal alum dosage, at which charge reversal is seen (see 5.1.2, Figure 5.4). Coagulation on this conditions can be important in the water treatment process. Conventionally, regeneration of coagulation after charge reversal is considered due to the enmeshment of colloids by great amount of precipitates, which is normally called sweep flocculation or zone 4 flocculation. As observed in our experiment, flocculation after charge reversal of colloids can be a slow process, especially before a very high
dosage of the coagulant is reached. Therefore, the mechanism of sweep flocculation may not be suitable for all this flocculation region. Moreover, although there is a general understanding of aluminium precipitation to aluminium coagulation, relationship between kinetics of coagulation and aggregation of primary precipitates remain unclear. Since in this study, the instrumentation has allowed us to examine the flocculation of kaolin suspensions kinetically, also the aggregation of primary aluminium precipitate can be monitored in such a time scale as in the flocculation experiment, the results reported in chapter 5 will allow a kinetic approach to discuss the mechanisms of flocculation by alum. This will undoubtedly lay a theoretical foundation for discussing the solution influence on alum coagulation.

In this section, based on the experimental results in Chapter 5, mechanisms of flocculation of kaolin suspension by alum will be discussed. This discussion will be divided into two sub-section: (1) mechanisms at low alum doses; (2) mechanisms at high alum doses.

6.1.1 Mechanism of coagulation at low doses at pH 6, 7 and 8

6.1.1.1 Charge characteristics of aluminium hydrolysis species

Electrical charge of aluminium hydrolysis product plays important part in the coagulation process. Here, the characteristics of the charge at pH 6, 7 and 8 will be discussed based on the experimental results.

The positive electrical charge of aluminium hydrolysis species is high at pH 6 and 7, and it is much higher at pH 6 than that at pH 7. There are strong evidence from the experiment results. First, at both pH 6 and 7, the IEP of particles in suspensions can be achieved at very low alum doses (5.1.1.1 and 5.1.2.1, Figure 5.1 and Figure 5.3). Second, from the experimental results (Figure 5.2.b and Figure 5.4.b), alum dosage at the IEP at pH 6 is only half of that at pH 7, with around 4 μM at pH 6 and 8 μM at
pH 7. These strong charge effects by the adsorption of aluminium poly or multinuclear species were also reported (Ching et. al. 1994, Hahn and Stumm 1968). This general observation of electrical charge of the dissolved species well agrees with the indicated charged species in the aluminium solubility diagram (Figure 2.4), which shows that highly charged aluminium hydrolysis species exist in the acidic side up to the neutral pH, and concentrations of these species diminish greatly as pH increases.

In contrast to the charges at pH 6 and 7, the charge of aluminium species is much weaker at pH 8. For, at this pH, there is no occurrence of charge reversal on the particle surface after addition of alum, and after higher alum dose, the EM or zeta potential can remain zero as alum dose increases.

It would be difficult to tell the electrical charge of the dissolved species directly from the experimental results. However, the electrical charge of aluminium hydroxide precipitate can be reflected by the surface charge of particles after a full surface adsorption. From the models of adsorption (see 2.4), particle surface can be fully coated by the adsorbed species through surface precipitation or deposition of precipitate formed in bulk solution (heterogeneous nucleation precipitation). In such case, surface charge of particle will be represented by the charge of adsorbed aluminium hydroxide precipitates. So, assuming at the highest reversed charge at pH 6 and 7, a full surface coverage is reached, then the values may represent the charge of aluminium precipitate. From the experimental results (Figure 5.2.b and Figure 5.4.b), at alum dosage 20 μM the EM of particles is highest at both pH 6 and 7, with a value around 1.7 at pH 6 and 1.0 at pH 7. This indicates that the charge of adsorbed aluminium species at pH 6 is significantly higher than that at pH 7.

It should be pointed out that, (1) these values may not be the true charge of aluminium species in solution, because during the adsorption process, through surface precipitation, the structures of aluminium precipitate might be altered in some ways; (2) this discussion can only be suitable in the case of hydrophobic colloids under the adsorption models in 2.4; (3) the positive reversed charge of particles after adsorption
decreases as dose of alum increases. The reason may be that as alum dose increases, sulphate will exert more influence on the aluminium hydrolysis products (Matijevic 1976, Matijevic et. al. 1971, Letterman et.al 1982, Letterman and Vanderbrook 1983).

6.1.1.2 Mechanism of coagulation at low alum doses

The mechanism of coagulation at the low dosage is generally linked with charge effects at pH 6 and 7 from the results. The experimental evidences suggest that it may involve the electrostatic patch interactions. These observed evidences include: (1) different coagulative behaviour at the IEP at pH 6 and 7 and (2) asymmetrical nature of particle surface charge for coagulation.

In the electrostatic patch theory, two things are essential in producing a good coagulation: highly charged polymer patches and uncoated areas of particle surfaces (Gregory 1973, 1976; or see 2.3.1). For if patches of polymers on particle surface with high positive charge can interact with negative areas of particle surface, attraction between them, can make particles stick together (Figure 2.3). In this case, attraction between particles, will be great, for not only is there no electrostatic repulsion between the two parts which is usually produced by two similar charged surface, but also there is an attraction through the two differently charged areas. In this case, the attraction energy is the sum of attraction energies from the electrostatic attraction and the Van der Waals attraction. This kind of aggregation of particles could also be taken as short bridge bonding (Bache 1996). However, as particle surface coverage increases, this interaction could be limited or prevented due to lack of uncoated areas. At the very case of full surface coverage by adsorbed polymer, this interaction will be totally prevented.

Therefore, in such case, one important feature may be that coagulation and flocculation will depend on conditions of patches and uncoated particle surface areas, rather than
the overall surface charge or zeta potential of particles. That is, the best coagulation may not necessarily happen at the IEP of particle after addition of coagulant.

**Coagulation at IEP at pH 6, 7**

One interesting observed phenomenon in the results is that coagulation of the particle suspensions show different kinetic features at the IEP at pH 6 and 7. This may indicate that coagulation does not follow simple charge neutralisation; instead, it follows the electrostatic patch model.

In 5.1.1.1 and 5.1.2.1 (Figure 5.1.a&b, 5.3.a&b), it is observed that, at pH 6, when the $\zeta$ potential of particles become zero with increasing alum dose, coagulation of the kaolin suspensions is optimal in terms of aggregation rate and aggregate size, as well as final supernatant turbidity. However, at pH 7, when the $\zeta$ potential approaches zero, coagulation become weaker. This can be explained by the mechanism of electrostatic patch model.

At pH 6, aluminium hydrolysis species are more highly charged as discussed in 6.1.1.1, the IEP can be achieved at low surface coverage of these adsorbed species. This leaves enough negatively-charged areas of particle surfaces for the positive patches to interact at the IEP. At this stage, further increasing the alum dose or adsorption of aluminium species may significantly reduce the uncoated areas on particle surfaces. As a result, aggregation will be hindered. In this way, aggregation proceeds best at the IEP. This coagulation could also explained by the simple non-patch neutralisation, however, uniform adsorption of aluminium species on particle surface would be unlikely at such low dose.

At pH 7, since charge of aluminium hydrolysis species is lower than that at pH 6, more aluminium species need to be adsorbed to achieve the IEP. This will lead to a higher surface coverage by the adsorbed positive species and less uncoated particle surface (note that the alum dose at pH 7 is twice as much as at pH 6 at the IEP). As a result, it
will limit the aggregation under the electrostatic patch manner and aggregation becomes less effectively.

Note that the coagulation was suggested as simple charge neutralisation (Ching et al. 1994, Dentel 1991). However, this speculation cannot explain the above observed phenomena.

**Asymmetrical nature of particle surface charge for coagulation**

Another evidence for the mechanism of electrostatic patches from this work is that the coagulation occurs at much high negative overall surface charge (EM around -1.4 unit at pH 6.7), but is stopped at comparatively lower reversed positive charge (EM around 1.0 and 0.5 unit at pH 6 and 7 respectively, see Figure 5.2 and Figure 5.4). That is, the particle surface charge for coagulation region is not symmetrical about the zero charge. If the surface charge of particles is evenly distributed around the whole surface, the EM of particles for the coagulation region should be symmetrical. That is, if one considers the particles with uniformly adsorbed charged species, application of DLVO theory will predict an approximately symmetrical surface charge region for coagulation in a weak electrolyte condition (as in this study only 1 mM Na$_2$CO$_3$).

Therefore, the reason for this asymmetrical nature is related to the electrostatic patch interaction. At low dosage, highly positively charged patches can be formed on particle surfaces. In this case, although the overall surface charge is low, coagulation can occur through attraction between highly charged positive patches and negative uncoated areas of surface. However, with increasing dosage of alum, adsorption of aluminium hydrolysis species may lead to a high surface coverage of these species and surface charge of particles is reversed. As the degree of surface coverage increases, the coagulation by electrostatic patchwise manner will be prevented due to lack of uncoated surface area. When the whole particle surface is covered by the aluminium hydrolysis species evenly, the electrical potential on particle interface follow the Stern model, and coagulation status can be predicted by the DLVO theory. In case of charge
reversal, coagulation can be prevented at some low positive surface charge, since only some weak anions may exist in suspension in most case.

*Mechanism of coagulation at pH 8 at low dosages*

As solution pH increases, the charge of aluminium species decreases. At low dosage of alum and high pH, the electrostatic patch mechanism may become weaker. At pH 8, the electrostatic patch mechanism become much weaker compared with at pH 6 and 7. This can be seen from the comparison of aggregation indicated by the FI values between Figure 5.1, 5.3 and 5.5. For at very low dosage at pH 6 and 7, the aggregation of the suspension is much better than that at pH 8 at higher dosage. This is because at this pH the charge of aluminium hydrolysis species is around zero, much lower than at pH 6 and 7. However, this mechanism may still exist between the very high negatively-charged areas of particle surface and the weakly positively-charged patches. This may be the reason that at a dose of alum 10 μM, weak coagulation can occur even at a very negative overall EM value -2 (ζ = 25mV); only at 20μM is the coagulation comparable to that at 3-4μM at pH 6, or at 5μM or more at pH 7 (Figure 5.1, 5.3, 5.5).

*6.1.2 Mechanism of coagulation at high alum doses*

The mechanism of flocculation at high dosage of alum cannot be explained simply by the charge effects or by the electrostatic patch theory. It is related to precipitation of aluminium hydroxide. The precipitation may influence the aggregation of colloids in several ways. Firstly, the adsorption of aluminium hydrolysis species on to particle surfaces will be characterised by the surface precipitation or deposition of precipitates on to the particles, as described by surface precipitation and/or heterogeneous nucleation precipitation (see 2.5.2), rather than the adsorption of only soluble species on particle surfaces like at low dosage of alum. Therefore, the surface property of kaolin particles in suspensions can be characterised by the adsorbed layer(s) of
aluminium hydroxide precipitate. As a result, all particles possess similar electrical charge in such suspensions. Furthermore, since the aggregation of primary aluminium hydroxide precipitates was observed to be a kinetic process depending on pH and concentration of aluminium (or alum) in this study, this kinetic characteristics of aggregation of primary aluminium precipitates will influence the whole aggregation process of the suspensions in some ways.

One striking characteristics of aggregation of primary aluminium hydroxide particles is the dependence on solution pH (Figure 5.15). This pH dependence suggests that aggregation between primary aluminium hydroxide precipitate be related to the electrical charge of these species, since the electrical charge varies according to solution pH. Although solubility of aluminium could give some contribution to this difference, this is not likely. It is likely that the electrical charge decides the energy barriers, which influence collision efficiency between these primary precipitates. The great influence of this kinetics of aggregation of aluminium hydroxide on aggregation of kaolin particles is strongly suggested by the similarity between the kinetics of aggregation of primary aluminium hydroxide precipitates and of kaolin particles.

Under the coagulation condition, the aggregation system involves two kind of particles and three kind of aggregations. The two kind of particles are primary aluminium hydroxide precipitates and kaolin particles; the three kind of aggregation processes are aggregation between the primary aluminium hydroxide precipitates, between these primary precipitates and kaolin particles, and between kaolin particles with adsorbed layer of the precipitates. Thus, the whole process will depend on the three processes.

It is most likely that the energy barrier will decide the collision efficiency between particles, which influence both the aggregation of primary aluminium hydroxide precipitate and the aggregation of kaolin particle with adsorbed layer. At pH 6, due to higher energy barrier, lower collision efficiency, aggregation will be difficult at a normal alum dosage employed in this study. At pH 7, due to lower energy barrier, higher collision efficiency, aggregation can proceed more easily than that at pH 6 at
these alum doses. At pH 8, due to non existence of energy barrier, and very high collision efficiency, aggregation can proceed very fast compared with those at pH 6 and 7. Below, the mechanisms will be discussed beginning with the situation at pH 6 and 7.

6.1.2.1 Characteristics of coagulation at high dosage at pH 6, 7

After charge reversal, higher alum doses promote effective coagulation (zone 4) (Figure 5.2 and Figure 5.4). It is observed that the coagulation begins with a long lag time, and then enhanced as alum is further increased. As a result, the lag time becomes shorter and shorter. Comparison between kinetics of coagulation at pH 6 and 7, shows that coagulation can be promoted at much lower alum dose at pH 7 than at pH 6 and that at the same dosage of alum, coagulation at pH 7 is much stronger than that at pH 6. For example, at alum dose 100 µM, coagulation begins within the one minute fast mixing period at pH 7, whereas there is a lag time of around seven minutes at pH 6. The mechanisms of coagulation in this stage have to be considered carefully.

From the conventional view, destabilisation and coagulation of suspensions after charge reversal is attributed to formation of aluminium (iron) hydroxide precipitates. This means that when enough precipitate is formed, the coagulation can be regenerated simply due to the massive precipitate enmeshment of the suspended particles. Under this general assumption, difference of coagulation at pH 6 and 7 at the same alum dose will be difficult to explain. This is because, this speculation neglects the important fact that within the precipitate region as illustrated in the solubility diagram (Figure 2.4), the colloidal properties of primary precipitate can be very different under different conditions, such as solution pH. That is, even if the same mass of solid phase is formed in the initial stage in solution/suspension, the difference in colloidal property may affect flocculation of kaolin suspension. For example, when the primary precipitate are colloidal stable, they will never grow up in size; when the primary precipitates are meta-stable, they may aggregate slowly; only when the primary precipitates are unstable, they can aggregate quickly. In such case, when the kaolin particles adsorb
these species, the colloidal property of kaolin particles will behave differently. This can help us to understand why the coagulation proceeds very differently at different solution pH, even when the solubility diagram predicts the formation of same amount of solid precipitates. Below, we will discuss the mechanisms of coagulation along these lines.

*General postulating of the coagulation system at this stage*

As is discussed above, in the coagulation system, when aluminium precipitation can occur in bulk solution, there is a kinetic process for the growth of primary precipitates. From the experimental results, it seems that very fine crystallites will first form, then grow up through an aggregation process. At the same time, adsorption can occur between the primary aluminium precipitates and kaolin particles. In this case, the coagulation system exists two kinds of particles, primary precipitate and the kaolin particle; and three kinetic aggregation process: between primary precipitates, between primary precipitate and kaolin particle, and between kaolin particles. This system can be schematically shown in Figure 6.1. The whole aggregation process will depend on these three aggregation processes. It would be difficult to analyse kinetics of the three process quantitatively, based on the experimental data. However, some important characteristics of aggregation can be discussed, which would be useful in understanding the whole aggregation process. Below, we will discuss the characteristics of the three process to explain the influence on the whole aggregation process of the suspensions.
Figure 6.1 The flocculation system of kaolin suspension after addition of aluminium salts and single layer adsorption of the primary precipitate. The system consist of two kinds of particles and three aggregation processes. The two kinds particle are: primary precipitate and kaolin particle with adsorbed layer. Three aggregation processes are: aggregation between primary precipitates, between the primary precipitate and kaolin particle with adsorbed layer, and between two kaolin particles with adsorbed layer.
Aggregation between primary precipitates

In this section, the number concentration of the primary precipitates will be estimated based on proposed size. On this basis, the collision frequencies between the particles can be calculated under the two mechanisms. The collision efficiency on the kinetic process will be discussed with the electrical charge of these precipitates. The implication for the whole aggregation process of suspension will be considered in next section.

Primary particles of aluminium hydroxide or ferric hydroxide are reported to be in the size range 2-4 nm (Bottero et al., 1982; Dousma and de Bruyn 1978). The number concentration of primary aluminium hydroxide particles can be estimated approximately based on the size range. Assuming that density of the primary particles is around 2 mg/mm$^3$ and solid phase be in the form of Al(OH)$_3$, taking 4 nm as the diameter, the equivalent number concentration for 10 μM alum precipitated is around $2.3\times10^{13}$ cm$^{-3}$. For 40 and 100 μM alum, the number concentration are $9\times10^{13}$ and $2.3\times10^{14}$ cm$^{-3}$ respectively.

As discussed in 2.3.2.4, collision between particles is transport limited and it is a function of radius and number concentration of particles. Two aggregation mechanisms exist: perikinetic and orthokinetic aggregation. For very small particles, perikinetic will be dominant; while as the particle size increases, orthokinetic aggregation will become important. This may mean that at the beginning of the aggregation process of the primary aluminium precipitates, perikinetic aggregation will be dominant. The preference of the two mechanisms can be seen from the collision constant as a function of size.

The collision constant is presented as a function of aggregate radius in Figure 6.2 and Figure 6.3. From Figure 6.2, in the size range of a few nanometers, the perikinetic collision constant is about $10^{17}$ m$^3$ s$^{-1}$ and the constant for orthokinetic collision is
Figure 6.2 Comparison of collision rate constants for the perikinetic and orthokinetic aggregation for two particles with equal radius varying from 1 to 1000 nm. (1) curves 1 for perikinetic transport mechanism; (2) curve 2 for orthokinetic transport mechanism.
Figure 6.3 Comparison of collision rate constants for the perikinetic and orthokinetic aggregation. (1) curves 1 and 2: taking one particle with a radius 2 nm and varying the other from 1 to 1000 nm (curve 1 for perikinetic; curve 2 for orthokinetic transport mechanism). (2) curves 3 and 4: taking one particle with a radius 700 nm and varying the other from 1 to 1000 nm (curve 3 for perikinetic; curve 4 for orthokinetic transport mechanism).
about $6 \times 10^{24} \text{ m}^3 \text{ s}^{-1}$. So, the perikinetic aggregation will overwhelmingly dominate the aggregation process at this size scale. Only when the radius of aggregates grows to around 250 nm, do the collision rate constants become about the same. This can also be clearly demonstrated by collisions between particles as listed in Table 6.1. It can be seen that the collision by perikinetic aggregation is much greater than that by orthokinetic aggregation. For instance, if 10 μM alum was precipitated into 4 nm small particles, the collision by perikinetic aggregation is more than $10^6$ times as high as that by orthokinetic aggregation.

<table>
<thead>
<tr>
<th>alum (μM)</th>
<th>10</th>
<th>40</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Number Conc. (cm$^{-3}$)</td>
<td>$2.3 \times 10^{13}$</td>
<td>$9 \times 10^{13}$</td>
<td>$2.3 \times 10^{14}$</td>
</tr>
<tr>
<td>Collisions for P.A. (cm$^3$ s$^{-1}$)</td>
<td>$5.3 \times 10^{15}$</td>
<td>$8.1 \times 10^{16}$</td>
<td>$5.3 \times 10^{17}$</td>
</tr>
<tr>
<td>Collisions for O.A.(cm$^3$ s$^{-1}$)</td>
<td>$3.2 \times 10^{9}$</td>
<td>$4.9 \times 10^{10}$</td>
<td>$3.2 \times 10^{11}$</td>
</tr>
</tbody>
</table>

Table 6.1 Collisions for perikinetic aggregation (P.A.) and orthokinetic aggregation (O.A.), assuming the amounts of alum are precipitated in the form of Al(OH)$_3$, at the very beginning of aggregation process of primary aluminium hydroxide particles (calculated from Equation 2.22 and 2.27).

In addition to collision frequency, collision efficiency is also important in kinetics of aggregation, because it decides the fraction of collisions which can lead to aggregate formation. Obviously, if collision frequencies are the same, the difference in collision efficiency will affect the kinetics of aggregation process. In case of perikinetic aggregation, the energy barrier is the most important factor which affects collision efficiency (2.3.3).

Now, kinetics of aggregation of primary aluminium hydroxide particle measured by the PI values versus time, presented in Figure 5.15 and Figure 5.16 can be analysed by means of collision frequency and collision efficiency. In the results, two important
observations are that the aggregation process for the primary aluminium hydroxide particles can be enhanced kinetically by increasing concentration of aluminium at a constant pH, and that the aggregation can show great differences kinetically at varying values of solution pH at the same added concentration of aluminium. From these figures, first, the increases of PI value versus mixing time can promoted as aluminium concentration increases (Figure 5.16); second, the growth of aluminium hydroxide aggregates begins almost immediately after addition of alum into solution at pH around 8, whereas at pH 7 and below aggregation does not begin until after a long lag time at the alum concentration 40 µM (Figure 5.15) (at pH 6, no aggregation of primary particle is observed at this dose of alum).

Firstly, the reason for promotion of aggregation of primary aluminium hydroxide particles by increasing alum concentration in solution may be attributed to the increased number concentration and increased collision efficiency due to decreased energy barrier between the particles when alum dose is increased.

The increase of number concentration of primary aluminium hydroxide particles as alum dose increases can be easily understood through the solubility. At a constant solution pH, the solubility of aluminium will be at a fixed value (see Figure 2.4 and Figure 2.5). When aluminium concentration exceeds the solubility, increasing aluminium concentration will mean more solid will form in solution. Basically, this would mean that, more crystallites will first form in solution (see 2.4.3). From the point of view of aggregation, the initial number concentration of particles will become greater.

The result of increasing the number concentration of primary aluminium hydroxide particles, can lead to an increase of collision frequency between the particles (see Table 6.1). This is because the collision rate is proportional to the square of number concentration (see Equation 2.18, 2.22, 2.27). Suppose the collision efficiency is constant, increasing collision can promote aggregation of particles or reduce the time for the formation of aggregates with certain size. Therefore, this is one of the reasons
that promotion of aggregation of primary aluminium hydroxide can occur when increasing aluminium concentration at a fixed pH.

Another important reason for the promotion of aggregation of primary aluminium hydroxide is the effect of charge of the precipitates on collision efficiency. For as the concentration of alum increases, the positive electrical charge of the precipitated species may decrease. When the electrical charge decreases, the energy barrier will decrease, and so the collision efficiency will increase. For example, at pH 7, at 100 μM alum, the EM of coated particle descend to 0.8 unit or (10 mV), at which the energy barrier is only half of that at 1 unit or (12.8 mV) at 30 μM (Figure 6.4). All these two may explain why, at pH 7, the kinetics of aggregation between primary aluminium hydroxide can enhanced by increased alum dose (Figure 5.16).

Secondly, the reason for the difference in kinetic aggregation of primary aluminium hydroxide particles at a constant aluminium concentration (e.g. 40 μM), at different pH may be caused by collision efficiency, which is affected by the energy barrier, thus the electrical charge.

Here there might be a difficulty in discussing the effect of the solubility on kinetics of aggregation of primary aluminium hydroxide particles at different pH, because of uncertainty about the solubility. This uncertainty arises for several reasons. The first has to do with the solubility diagram. Although the solubility of aluminium at different pH can be calculated from equilibrium data, these values might be questionable. This is because there has not been one solubility diagram or one set of equilibria universally accepted; different equilibria may produce different values of solubility limits. For instance, from solubility diagram shown in Figure 2.4, at pH 6, 7, and 8, the solubility of aluminium are 81, 5, and 34 μM respectively, but the solubility at pH 6 and 7.8 are also calculated using different equilibria to be 17 and 22 μM respectively (Ching et. al. 1994). Moreover, influence of sulphate or other anions on solubility of aluminium is not very clear; it is likely that when alum is used, the sulphate might exert some influence on the solubility. However, from these equilibria, one general conclusion may
be that the lowest solubility of aluminium hydroxide is around pH 6 to 7. This general conclusion is supported by the results of residual aluminium measurements in this study (Figure 5.19). It is found that the solubility at pH 6 and 7 may be below 5 \( \mu \text{M} \) with lowest at pH 6; the solubility at pH 8 is around 30 \( \mu \text{M} \). The enhancement of the solubility compared with predicted values by solubility diagrams may be attributed to the presence of sulphate.

The experiment results in Figure 5.15 show that there is no measured aggregation of primary aluminium hydroxide species at pH 6 at the alum dose 40 \( \mu \text{M} \); and aggregation begins when pH increases, to around 6.7-6.8. For, it is seen that at pH around 6.8, the aggregation proceeds with long lag time of around 11 minutes. As the pH goes up to 7, the lag time is significantly reduced; and at pH 8, aggregation begins almost immediately after addition of alum into the solution.

It would be difficult to say that the difference in kinetics of aggregation is caused by different amount of precipitates formed in solution/suspensions at the different pH and a constant added concentration of alum (e.g. Figure 5.15). Since the solubility of aluminium hydroxide is much lower at pH 6, 7 than pH 8, more solid should be formed at pH 6, 7 than at pH 8. Therefore, the question is, if more primary aluminium hydroxide particles can form at pH 6 and 7 than 8, why the fastest kinetic growth of aggregation of the primary aluminium hydroxide precipitate is at around pH 8.

The better or faster aggregation at higher pH is mostly likely due to the collision efficiency, which is affected by electrical charge of these particles. From the kinetic theory of particle aggregation, if the collision rate is the same, the difference in growth rate of aggregate size must be due to the collision efficiency. This most likely is the reason in this situation. For, as we discussed before, the charge of aluminium precipitate is a function of solution pH. The electrical charge of the precipitates at pH 6 is much high than that at pH 7, and at pH 8 the aluminium precipitate is at the IEP. Electrical charge of primary aluminium precipitate can decide the energy barrier in the same electrolyte solution; therefore, it decides the collision efficiency.
The relationship between electrical charge and energy barriers can be found through the DLVO theory, assuming that the adsorption of aluminium hydrolysis products on kaolin particle follow the Stern double layer model (see 2.1.2.2) and the concentration of free aluminium ion in solution is negligible. Figure 6.4 shows the relationship between zeta potential and energy barrier for two particles with radius 2 nm, electrolyte concentration 1.0 mM, \( z = 1 \). If the zeta potentials at pH 6 and 7 are taken as 21 mV (EM 1.5 unit) and 13 mV (EM 1 unit) respectively, the energy barrier for two fine particles at pH 6 is 0.55 kT, at pH 7 is 0.15 kT, the value at pH 6 is more than 3.5 times as much as that at pH 7 (Figure 6.4, line 1). And when zeta potential is below 6 mV (EM 0.5 unit), the energy barrier disappears. Obviously, the existence of energy barrier will tend to prevent particle to contact from each other. This will reduce the collision efficiency, as is discussed before (see 2.3.2.4).

Therefore, aggregation of the primary aluminium hydroxide particles must be correlated with the collision efficiency, which is affected by the zeta potential, and hence the energy barriers. At pH 6, the aggregation is prevented due to a high energy barrier. At pH 7, the reduced energy barrier allows low collision efficiency, which leads to an aggregation process with a long lag time. At pH 8, the energy barrier disappears and the collision efficiency is high, so the aggregation goes rapidly.

It should be pointed out that this collision efficiency limited aggregation process is important only at certain concentration of alum. For instance, in this experiment, the concentration of alum should be below 100 \( \mu \text{M} \); at around alum 40 \( \mu \text{M} \), this effect is observed very clearly. In the past, aluminium precipitation is only generally treated as solid phase formation indicated by the solubility diagram. No attention is paid to this kinetic growth of aluminium hydroxide precipitate, and its effect on the particle aggregation process when it is used as a coagulant. The kinetic influence of this alum precipitate formation on particle aggregation will discussed later in this section.
Aggregation between primary aluminium hydroxide particles and kaolin particles

Aggregation between primary aluminium hydroxide particles and the kaolin particles can be divided into two different stages. Firstly, the adsorption stage, in which the primary aluminium hydroxide particles aggregate with the kaolin particles leading to a single layer adsorption of these primary particle onto the kaolin particles. Secondly, the further aggregation between two kinds particles, in which multilayer adsorption may occur on the kaolin particle surfaces. The main difference between the two stages is that, in the former, aggregation occurs between two kinds of particles with opposite electrical charge; in the latter, aggregation proceeds between two particles with similar electrical charge. This would make a great difference in the kinetics between the two aggregation process. Below, the two processes will be discussed.

The single layer adsorption of polymer onto particle surface can be very fast, and this process can be tackled by using the Smoluchowski equation (see Equation 2.18 or 2.27). Assuming that polymer species in suspension are fine particles, and adsorption of polymer species can be treated as aggregation between polymer species and colloids, integration of Smoluchowski Equation 2.18 (or 2.27), gives the time for adsorption (Gregory 1988):

\[ t_A = -\ln(1-f)/k_{12} N_i \quad (6.1) \]

where \( k_{12} \) is expressed by Equation 2.23 and Equation 2.28 for perikinetic collision and orthokinetic collision respectively; \( f \) is the fraction of polymer adsorbed and \( N_i \) is the particle number concentration. For a single layer adsorption, there is no electrical repulsion between the two kinds of particle, so the collision efficiency is assumed to one. Therefore, the time for adsorption of aluminium species onto particles can be estimated. Assuming that, \( f = 0.95 \), particle radius \( a_i = 1 \mu m \), aluminium hydrolysis species radius \( a_2 = 2 \text{ nm} \), \( N_i = 10^7 \text{ cm}^{-3} \) (50 mg/L kaolin), mixing intensity \( G = 1000 \text{ s}^{-1} \) (for 350 rpm), the required times for adsorption are:
Perikinetic: $t_A = 0.04$ s  
Orthokinetic: $t_A = 0.02$ s.

From this, the adsorption of aluminium hydrolysis species can be completed much less than one second if it is generated either by orthokinetic aggregation, or by perikinetic aggregation. Adsorption by these two kinetic process does not show much difference, because of very small radius of aluminium hydrolysis species and high intensity mixing. Since these two processes occur simultaneously in a suspension, the adsorption for the single layer may be finished in less than one second. In our experiment, the EM of particles measured at 30 seconds, one minute and even five minute after addition of alum are the same, this may support this calculated results of the fast adsorption process.

After this single layer adsorption, the aggregation between aluminium hydroxide particles and kaolin particles will proceed between the primary precipitates and the kaolin particles with adsorbed the primary precipitates. In this case, the surface of these two particles will have similar charge property. So, this process can be treated as the aggregation process between one bigger and one smaller particle with same surface electrical property. From Figure 6.4, the energy barrier between a kaolin particle with adsorbed layer of aluminium hydrolysis species (bigger particle) and aluminium hydroxide precipitate (smaller particles) can be twice as high as that between two aluminium hydroxide precipitates (line 2) at pH 6 and 7. For the energy barrier at pH 6 is around 1.1 kT, at pH 7 is 0.3 kT. It may indicate that aggregation between aluminium hydroxide particles will be easier than between kaolin particle with the adsorbed layer and aluminium hydroxide particles.
Figure 6.4 Energy barriers for two particles as a function of zeta potential (mV) under conditions: electrolyte concentration 1.0 mM; \( z = 1 \); \( A/kT = 3 \). (1) Particle radius \( a_1 = a_2 = 2 \) nm; (2) \( a_1 = 2 \) nm, \( a_2 = 700 \) nm. Calculated by using equation 2.11, 2.13 and 2.15.
Figure 6.5 Energy barriers for two particles as a function of zeta potential ($\zeta$) (mV) under conditions: electrolyte concentration 1.0 mM; $z = 1$; particle radius $a_1 = a_2 = 700$ nm. (1) $A/kT = 2$; (2) $A/kT = 3$. Calculated by using equation 2.11, 2.13 and 2.15. It shows that the energy barrier disappear when $\zeta < 5$ mV (EM < 0.4); it increase greatly when $\zeta > 13$ mV (EM > 1).
Aggregation between kaolin particles

As indicated in Figure 6.1, the third kind of aggregation may occur between kaolin particles with adsorbed layer of aluminium hydroxide species. Compared with the former two cases, this case is between two bigger particles with similar electrical surface charge. As shown in Figure 6.5, energy barrier for the two bigger particles is much greater compared with that between the two smaller particles and between one bigger and one smaller particle. For instance, energy barrier is around 50 kT at zeta potential 13 mV (EM 1 unit) and around 200 kT at zeta potential 21 mV (EM 1.7), while for smaller particles is well below 2 kT. It seems that the aggregation would become more difficult between the bigger particles than between the smaller ones in terms of collision efficiency affected by the energy barrier in such case.

However, aggregation processes depend on not only the efficiency, but also the collision frequency, which can be related to both the kinetic mechanisms and particle number concentration. The collision frequency can become very high as the radius of particle increase in orthokinetic aggregation, this can be seen from Figure 6.2. For example, the collision constant for the small particle with radius less than around 250 nm will be $10^{-17} \text{ m}^3 \text{ s}^{-1}$, while the collision frequency for bigger particle with radius 1 \( \mu \text{m} \) and 10 \( \mu \text{m} \) will be around $10^{-15}$ and $10^{-12} \text{ m}^3 \text{ s}^{-1}$ respectively.

Mechanisms of coagulation at the high dose at pH 6 and 7

Based on the analysis above, the kinetics of aggregation at pH 6 and 7, will depend on aggregation between primary aluminium hydroxide particles or aggregates, between the primary aluminium hydroxide particles and kaolin particles, and between kaolin particles with adsorbed layer. Among them, the single layer adsorption of primary aluminium hydroxide species onto the kaolin particles can be very fast from the calculation based on transport limited aggregation and unit collision efficiency. These calculations agree with the many observations that the hydrolysing metal salt species can be adsorbed readily. In our experiment, we also found that the measured values of
zeta potential (or EM) of particles after addition of alum at constant solution pH does not depend on the sampling time, indicating that single layer adsorption is completed within less than 30 seconds. Under these conditions, the whole aggregation process will depend on the aggregation between primary aluminium hydroxide precipitates, the aggregation between the aggregates of primary aluminium hydroxide particles and kaolin particles with the adsorbed layer, and the aggregation between kaolin particles with adsorbed layer (Figure 6.1). One common characteristic of these aggregation processes is that all particles have the similar electrical charge.

Although it would be difficult to calculate the kinetics of these three aggregation processes separately, some kinetic analysis can be made, which may be useful in understanding the whole process. Obviously, among the three processes, the dominant one will be the one with higher collision frequency and efficiency.

The collision frequency between particles in such systems can be estimated. From Figure 6.2, for small particles in the size range from a few nanometer to 250 nm, the collision rate constant is at $10^{17} \text{m}^3\text{s}^{-1}$. Taking the number concentration as $10^{13} \text{cm}^{-3}$, the particle collision frequency is $10^{15} \text{cm}^3\text{s}^{-1}$. From Figure 6.3, for small particle size range radius in 50-200 nm, and big particle size range radius at 700 nm, collision frequency is at $5 \times 10^{17} \text{m}^3\text{s}^{-1}$ (by orthokinetic aggregation); taking number concentration for small and big particles as $10^{13}$ and $10^7 \text{cm}^{-3}$ respectively, the particle collision is $5 \times 10^9 \text{cm}^3\text{s}^{-1}$. For bigger particle size range radius in 700-1000, collision frequency is $5 \times 10^{16} \text{m}^3\text{s}^{-1}$; taking number concentration $10^7 \text{cm}^{-3}$, the particle collision $5 \times 10^4$. Therefore, the collision between small particles is much higher than that between big particles.

One important aspect of aggregation of the small primary aluminium hydroxide particles to the whole suspension is that at certain level of aggregation of these primary particles, they can form aggregates with large size and high volume. For example, if the small primary particle of $10^{13} \text{cm}^{-3}$ form 50000 fold aggregates, the number concentration is reduced $2 \times 10^8 \text{cm}^{-3}$; taking fractal dimension as 1.4-1.6, the radius of
aggregates would become 1.7-4.5 μm (Figure 6.6) and the volume become 700-38 cm³ (Figure 6.7). If large volumes of precipitate can form in suspension, aggregation can be enhanced through heteroaggregation or through enmeshment mechanism.

From the analysis above, in the suspension, after the single layer adsorption of the primary aluminium hydroxide precipitate, the aggregation between the small primary aluminium hydroxide particles may be dominant up-to certain size due to the higher collision frequency and efficiency. This may indicate that before the primary aluminium hydroxide precipitate grow up to certain size or volume, there is no substantial aggregation in the suspension. This may be the reason that the kinetics of aggregation between primary hydroxide precipitates and the suspension exhibit similarity in terms of the PI values and FI values versus time.

Therefore, in such aggregation system, the collision efficiency affected by the electrical charge can be decisive in the whole aggregation process. From the experimental results, there is a critical zeta potential for the aggregation process, above which the aggregation process will be much slower. In this experiment, this value is around 13 mV (EM 1 unit). Therefore, it is likely that, above this value, the aggregation between primary aluminium hydroxide particles (or solid hydrolysis species) is hindered, so is aggregation between kaolin particles with adsorbed layer of these species and the aggregation between aluminium hydroxide particle and the kaolin particles. The evidence of the prevention of aggregation between primary aluminium hydroxide particles at pH 6 at alum dose 40 μM can be seen in Figure 5.15 in the measurements of precipitate aggregation. The reason for this prevention is that the high energy barrier leads to very low collision efficiency near zero, thus no aggregation between primary precipitates could occur. In this case, although the aggregation between primary aluminium hydroxide particles and kaolin particles can occur for the single layer adsorption, multilayer adsorption or further aggregation between aggregates of the
Figure 6.6 Radius of fractal aggregates of aluminium hydroxide precipitate as a function of aggregation number. Assuming the primary radius is 2 nm, and the radius can be calculated by using Equation 2.31.
Figure 6.7 Volume of aluminium hydroxide precipitates as the fractal aggregates as function of aggregation number (k). Assuming 40 μM alum is added in water and all formed Al(OH)$_3$(s). The equivalent mass of the Al(OH)$_3$(s) is 6.24 mg. Taking the density of aluminium precipitate as 2 mg/mm$^3$, then the total volume of dry solid would be around 3 mm$^3$. The volume fraction of a k-aggregates can be expressed by Equation 2.31, so the total volume of the aluminium hydroxide precipitate for 40 μM alum can be expressed as in this figure. (Note: taking the radius of primary aluminium hydroxide particle as 2 nm, the total number concentration is about 9×10$^{13}$).
primary aluminium hydroxide precipitates and kaolin particles will be difficult, as will the aggregation between kaolin particles with adsorbed layer, because all these particles have high energy barrier. From Figure 6.4 and Figure 6.5, if the surface charge is the same, bigger particles will have much higher energy barrier. This is why when the aggregation of small primary aluminium hydroxide particles is prevented, the aggregation of the whole suspension is also prevented.

At or below this critical zeta potential, there is a range in which the energy barrier is still high and the collision efficiency is still limited greatly until the zeta potential goes down to a low level. It is seen that in this study, when the zeta potential is at around 13 mV (EM 1 unit), aggregation appear to proceed at certain level, like at alum dose 100 μM at pH 6 and alum dose 30 μM at pH 7. In this case, when aggregation between primary aluminium particle show certain kinetic characteristics, the aggregation of whole suspension show a similar characteristics. For instance, in Figure 5.15, at pH 7 and alum dose 40 μM, aggregation of primary aluminium hydroxide particle has around 5 minute lag time followed by a great increase, the similar pattern of aggregation of the whole suspension can be seen in Figure 5.4.a. This indicate that when the aggregation of the primary aluminium hydroxide particles is affected by collision efficiency, the whole aggregation process will also affected by it. This may suggest that in such aggregation system the collision efficiency is the controlling factor. At this stage of aggregation, an immediate enmeshment of kaolin particles by the massive precipitates will not be possible, because the aggregation of precipitates is controlled by the slow kinetic process.

At pH 6 or pH 7, if the dose of alum is very high, e.g. ≥ 100 μM at pH 7, the aggregation of kaolin suspension show an immediate fast increases. There are two mechanisms that could lead to this great and fast aggregation. First, as the greater amount of alum is added into the solution/suspension, more primary aluminium hydroxide particle should form, this can increase the collisions between the particles. As a result, the primary aluminium hydroxide precipitates can grow up quickly (see Figure 5.16), the whole aggregation processes can promoted fast. Secondly, increase
of alum dose, may lead to a decrease of electrical charge of aluminium hydroxide species, as indicated by the decreased zeta potential (or EM) of kaolin particles with adsorbed layer when alum dose increases (see Figure 5.2b and Figure 5.4b). This will decrease the energy barrier between aluminium hydroxide particles; as a result, the collision efficiency will increase. From experimental results of aggregation of aluminium precipitation shown in Figure 5.16, aggregation of the primary aluminium hydroxide particles is promoted greatly as alum dose increases. When fast aggregation of primary aluminium hydroxide is observed at certain alum dose, the similar fast aggregation of kaolin suspension is also observed (see Figure 5.16 and Figure 5.4.a at alum dose 100 μM). This supports the proposed mechanisms of aggregation above.

Therefore, it is clear that only when the alum dose is high enough, great amount of primary aluminium hydroxide particles can form, at the same time aggregation of the primary aluminium hydroxide precipitates can proceed quickly in solution, the mechanism of sweep flocculation can come into play immediately; whereas before the alum dose, a slow aggregation of primary aluminium hydroxide particles will occur, so does the aggregation of the whole suspension. This kinetic transitional phase of aggregation of clay suspension before the sweep flocculation by hydrolysing metal salts had not been observed and discussed before. One will see that this analysis on the characteristic aggregation is important in understanding the influence of dissolved silica on aggregation of the kaolin suspension. At the same time, understanding this is important to a practical water treatment process, as discussed later.

6.1.2.2 Characteristics of coagulation at high dosage at pH 8

At pH 8, the main characteristic of the aluminium hydroxide precipitates is that they are close to the IEP. That is, there is no energy barrier between the primary aluminium hydroxide particles, therefore, neither between kaolin particle with the adsorbed layer, nor between the primary aluminium hydroxide particles and the kaolin particles with the adsorbed layer. This make the collision efficiency very high between them.
Therefore, the aggregation of primary aluminium hydroxide particles proceed fast without lag time even before very high dose of alum like at pH 7, though the solubility of aluminium at this pH is high (at alum 40 µM, fast increase of PI values versus time is observed (Figure 5.15, pH 8.03)). Similarly, the aggregation of kaolin suspension showed the same character (Figure 5.5.a, alum 40 µM; Figure 5.6.a, pH 8.06). This indicates that at this pH, the whole three aggregation process can proceed very quickly. Because the primary aluminium hydroxide can aggregate quickly into large flocs, the sweep flocculation can come into effect before very high alum dose. This is the typical condition for coagulation described by the PCN model (Dentel 1988).

6.1.3 Conclusions

Mechanisms of flocculation of kaolin suspensions by alum has been observed to be dependent on alum dosage and solution pH. At low dosages of alum, the coagulation process based on charge neutralisation, which is called zone two coagulation conventionally, may follow the electrostatic theory. This speculation is supported by the two observed phenomena of kinetic aggregation of the kaolin suspensions: different behaviour of aggregation at the IEP at pH 6 and 7, asymmetrical nature of zeta potential about the zero value for the beginning and prevention of aggregation. This mechanism is characterised by uneven adsorption of the highly positively charged aluminium hydrolysis species on the surface of particles. It seems that fairly satisfactory explanation of the kinetic flocculation at the dosages of IEPs at pH 6 and 7, and at low dosages of alum at pH 8 can be made by this theory.

At high dosages of alum, or after the dose of charge reversal at around pH 6 and 7, kinetics of flocculation of kaolin suspensions has been found to be dependent on the kinetics of aggregation of primary aluminium hydroxide precipitates. It seems that the kinetics of aggregation at these two pH values may be largely controlled by the collision efficiency which may be affected by the electrical charges of the hydrolysis species or primary precipitates. In such a coagulation system, single layer adsorption of
aluminium hydrolysis products on kaolin particle surfaces could be finished within a fraction of one second, thereafter there are three kinds of aggregation process: between primary aluminium hydroxide precipitates, between the primary precipitates and kaolin particles with adsorbed layer of the primary precipitates, and between kaolin particles with the adsorbed layer. The whole process will depend on the three processes. Among them, the aggregation between the primary aluminium hydroxide particles may be more important to the aggregation of the whole suspension due to higher collision frequency and efficiency. At pH 8, these slow kinetic aggregation no longer exist. This may be due to that the zeta potential of aluminium hydrolysis species is around zero, there is no energy barrier between particles, and the collision efficiency is near unit. Thus, the all three aggregation processes can proceed quickly.

One important thing is that re-occurrence of flocculation of kaolin suspensions at pH 6 and 7, which is called zone 4 flocculation, can be a slow kinetic process depending pH and dosage of alum. This slow kinetic process may be caused by the slow kinetic aggregation of primary aluminium hydroxide. Only up to very high dosage of alum that aggregation of aluminium hydroxide primary particle can form very quickly, an immediate sweep flocculation or enmeshment of kaolin particles by massive precipitates can occur. Understanding this kinetic process can be important for discussion on the influence of dissolved silica on aggregation and for the water treatment process.

Based on the above discussion, the mechanisms of flocculation of the clay suspension by alum can be schematically presented as Figure 6.8.
Chapter 6 Discussion

I. at low dosage
aluminium hydrolysis
\[ \text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{Al}_x(\text{OH})_y^{(3x-y)+} \]
adsorption of positively charged hydrolysis species
→ electrostatic patch model (zone 2 coagulation)

II. increasing dosage

at low pH (e.g., 6,7)
adsorption of highly positively charged aluminium hydrolysis species or primary precipitate→ charge reversal and restabilisation

at high pH (e.g., 8)
adsorption of weakly positively charged aluminium hydrolysis species or primary precipitate→ charge neutralisation and coagulation (PCN model)

III. at high dosage

at low pH (e.g., 6,7)
slow kinetic aggregation of primary precipitate→ slow aggregation of particles (zone 4)

at high pH (e.g., 8)
similar charge effect and enhanced flocculation by increased precipitation (zone 2 and 4 overlap)

IV at very high dosage

fast and massive precipitation→ sweep flocculation (zone 4)

fast and massive precipitation→ sweep flocculation (cone 4)

Figure 6.8 A schematic representation of mechanisms of flocculation at different stages of aluminium dosage and characteristic solution pH.
6.2 Mechanisms of influence of dissolved silica on alum coagulation

Through the discussions above, the mechanisms of flocculation by alum is rather clear. In this section, the influence of dissolved silica on the coagulation will be discussed on that basis. This discussion will be based on three aspects of experiment results in chapter 5: (1) kinetics of aggregation; (2) charge effects; and (3) aggregation of alum precipitates in presence of dissolved silica. Through this discussion, the characteristics of the influence of dissolved silica on coagulation and the mechanisms of this influence will be given.

Below, the discussion will begin with the influence of dissolved silica on coagulation at the low alum dosage; then to the high alum dosage.

6.2.1 Mechanism of influence at low alum doses

Mechanisms of influence of dissolved silica on flocculation is related to the interactions between aluminium and dissolved silica. One important effect of the interactions may be the modification to the properties of aluminium hydrolysis species: presence of dissolved silica can reduce the electrical charge of aluminium hydrolysis species, or even can make the aluminium more soluble. This will affect the charge neutralising ability of the aluminium hydrolysis species, hence affect the aggregation process.

6.2.1.1 Charge effects of dissolved silica

The reduction of the electrical charge of aluminium hydrolysis species has been reflected in the measured EM (or zeta potential) of kaolin particles after addition of alum, in presence of dissolved silica.

As presented in Figure 5.8, at pH 7 and dosage of alum $8\mu$M without dissolved silica in solution, the zeta potential of kaolin particles is at the IEP. If certain amount of
dissolved silica is present in the system, the EM of the kaolin particles become negative after dosing the same amount of alum, and the negative potential increases when the concentration of dissolved silica increases.

At this aluminium concentration (16 $\mu$M Al), apart from the dissolved hydrolysis species, some fraction of aluminium hydroxide precipitates might form. The adsorption of these species may follow the surface complexation or surface precipitation. Since the change of kaolin particle surface charge is caused by adsorption of these species, any changing of the charge effect of these species on kaolin particles by dissolved silica can be made in two ways. First, reducing the electrical charge of aluminium hydrolysis species, i.e. lowering the positive charge or making it negative, so that when these species are adsorbed, the surface charge of particles is less positive than that in absence of dissolved silica. Second, making it more soluble thus less adsorbable, so that less aluminium species can be adsorbed.

These two actions might both exist in the discussed case. This is because it has been reported (Exley and Birchall 1992) that the interactions between aluminium and silicic acid may inhibit the nucleation of aluminium, or make aluminium more soluble at low aluminium concentrations and high silicic concentration (see chapter 3). If aluminium nucleation is hindered, the charge of aluminium hydrolysis species may reduced, if aluminium hydrolysis species become more soluble, it may become less adsorbable. From the literature (see Chapter 3), it is sure that the interaction between aluminium and silicic acid can occur at levels as low as a few $\mu$M aluminium and several mg/L dissolved silica and more. However, it is not very clear that which of the two functions will be important at such low level of concentrations of aluminium.
6.2.1.2 Mechanism of the influence on kinetics of coagulation

From above discussion, one can see that presence of dissolved silica can change the charge neutralising ability of aluminium. No doubt, this will affect the aggregation process by aluminium (or alum). It is seen that at pH 7, and the alum dose of IEP, aggregation of kaolin suspensions will be improved when the EM of kaolin become negative in the presence of dissolved silica (Figure 5.8). Further increasing dissolved silica concentration, the negative EM of particle become high, then the aggregation process is prevented.

Here, the aggregation improved when the zeta potential becomes negative from the IEP may be due to that the coagulation follow the electrostatic model as is described in 6.1. A comparison of aggregation of particles between Figure 5.3 and Figure 5.8 show similar surface charge effects on aggregation with and without presence of dissolved silica. With alum alone, the aggregation is seen better before the IEP than at the IEP. Similarly, when presence of dissolved silica shifts the zeta potential from 0 to negative (less than 1 unit of EM), the aggregation becomes better. This suggests that the aggregation does not depend on the simple overall charge effect, instead, it may follow the mechanism of electrostatic patches as before. However, when high concentration of dissolved silica is present, interactions between aluminium and dissolved silica may either reduce greatly the positive charge of aluminium hydroxide species to a very negative level, or make aluminium hydroxide species more soluble, so that the charge effects does not exist and the aggregation is prevented.

On the whole, at the low dosage of alum, influence of the presence of dissolved silica on coagulation by alum is due to the influence on the electrical charge of aluminium hydrolysis species. This influence is from the interaction between aluminium and dissolved silica. The interaction may reduce the positive electrical charge of aluminium hydrolysis products, or make them more soluble. The kinetics of aggregation of kaolin particles will be affected accordingly following the electrostatic patch theory. At lower
concentration of dissolved silica, aggregation may be improved or decreased depending on particle surface conditions for the electrostatic patch mechanism. At high concentration of dissolved silica, aggregation will be totally prevented due to the high negative charge and more soluble species.

6.2.2 Mechanism of influence at high alum doses

As is discussed in 6.1, the aggregation of kaolin particles at high doses of alum, after the dosage of charge reversal, can be strongly dominated by the aggregation of primary aluminium hydroxide precipitates. At pH 6 and 7 around, where the hydrolysing product possess high positive electrical charge, a slow aggregation process was observed. This slow aggregation is believed to be caused by the limited collision efficiency which is due to the existence of high energy barriers between particles to be aggregated. At pH 8, where the charge of aluminium precipitate may be around zero, aggregation does not show slow kinetic growth, indicating that the collision efficiency is high due to non-existence of energy barrier. However, at very high dosage of alum, the aggregation of primary aluminium hydroxide particles can become fast at pH 7. In such case, aggregation of particles can begin immediately after addition of alum into the kaolin suspensions due to two reasons: (1) increased concentration of primary aluminium hydroxide particles; (2) reduced electrical charge as the alum concentration increase. At this stage, a sweep flocculation can come into play.

Below, the mechanisms of influence of dissolved silica on flocculation will be discussed in these three conditions. That is, high and very high dosage of alum at pH 6 or 7, high dosage of alum at pH 8. Again, this discussion will be based on the charge effect, precipitation and kinetics of aggregation.
6.2.2.1 Mechanisms of influence at pH 6 and 7, at high dose of alum

General description

As discussed in 6.1.2.1, characteristics of aggregation of kaolin suspensions at this stage can be explained by the three aggregation processes. As soon as the single layer adsorption finishes, all particles possess the similar electrical charge. Before the primary aluminium hydroxide particles grow up to a certain size, aggregation of the particles will be important. In this aggregation process, one common feature is that all the three aggregation processes are affected by the limited collision efficiency due to the energy barrier of particles. Thus, the aggregation of suspension showed a slow process with some lag time.

From the experimental results presented in chapter 5, the presence of dissolved silica at a certain level can promote the aggregation process. That is, in the presence of dissolved silica, the aggregation process can begin immediately after addition of alum without lag time (see Figure 5.9.a, at 10-30 mg/L). However, further increase the concentration of dissolved silica, the aggregation is depressed or even prevented. These kinetic influence is observed to be related to the charge effects of dissolved silica on aggregated particles after addition of alum (see Figure 5.9.b). Below, the mechanism of the influence on aggregation will be discussed beginning with the effect of electrical charge.

Properties of precipitates and interaction between aluminium and silica

In chapter 3, the literature review shows the interactions between aluminium and dissolved silica and their influence on precipitates of aluminium hydroxide. The interactions can lead to the formation of hydroxyl aluminosilicate (HAS) precipitates, which modifies the colloidal property of aluminium hydroxide precipitates. This modification to the colloidal stability of the precipitates may be related to the
modification to electrical charge of the primary precipitates, which depend on the
solution pH, concentration of aluminium and dissolved silica. It was observed that, in
presence of dissolved silica, in the alkaline side, the HAS precipitates is colloidally
stable with negative electrical charge, and in the acidic side, the co-precipitates is also
colloidally stable but with positive electrical charge (Brace and Matijevic 1977). On the
contrary, between these two region is a colloidally unstable region. Increase
concentration of dissolved silica can shift the region to the acidic side. This shift must
be due to the effect of the influence on electrical charge of the precipitate. In addition
to the colloidal stability and the related electrical charge, the solubility of aluminium
hydroxide could be also affected.

The solubility of aluminium hydroxide was examined at alum concentration 40 µM,
and dissolved silica 20 mg/L, in this study (see 5.5). It is found that the solubility has
recognisable increase at pH 6, but nearly no change at pH 7; in contrast, there is
significant increase at pH 8 (see Figure 5.19). At pH 8, in the system of aluminium and
dissolved silica concentration, the aluminium hydroxide seems become more soluble.
This effect on solubility might also exist at neutral or acidic pH values at high
concentration of dissolved silica. Note that since pore size of membrane is fairly big in
the study (0.45 µm), it is quite possible that very small colloidal species may pass
through. Therefore, the results at pH 8 might just indicate that presence of dissolved
silica may reduce the precipitate size to a filterable size, rather than completely soluble
species.

There is no direct measurement of electrical charge of the HAS precipitate in this
study. However, from the surface adsorption model, the surface potential of kaolin
particles after a full or mutilayer surface adsorption should reflect the modified charge
of the co-precipitates of hydroxyl aluminosilicate. Therefore, from measured EM (or
zeta potential) of kaolin particles after addition of alum when dissolved silica is
presented in solution, the charge effects of dissolved silica on aluminium hydrolysis
products can be seen from Figure 5.9; 5.10; 5.11; 5.14. These results indicate that
presence of dissolved silica reduces the positive charge of aluminium hydroxide
precipitates or makes it more negative. Inevitably, the whole aggregation process will be affected by this charge effect.

*Influence on aggregation of primary aluminium hydroxide precipitate*

Since the charge effects of dissolved silica on aluminium hydrolysis products, aggregation of primary aluminium hydroxide precipitates can be influenced accordingly. Discussion of the kinetics of aggregation of the primary HAS precipitates, incorporated with the observed charge effect of dissolved silica would be very helpful in understanding the influence of dissolved silica on the aggregation of the whole suspension.

In Figure 5.17, the measurements of PI values as a function of mixing time showed that presence of dissolved silica 20 and 50 mg/L can promote the aggregation of aluminium hydroxide precipitates in terms of aggregate growth rate and size; while a high concentration of 100 mg/L can prevent the aggregation process. The mechanism of the aggregation can be discussed with the charge effects.

As promotion of an aggregation process can be made through two ways (see 6.1.2.1): (1) increasing collision frequency between particles, (2) increasing collision efficiency. Therefore, the observed promotion of aggregation in Figure 5.17 can be due to more primary precipitates produced resulting from the interactions between aluminium and dissolved silica, or by increased collision efficiency resulting from reduced or elimination of energy barrier.

Although it may be possible that under certain combination of concentration between aluminium and dissolved silica, the precipitation can be enhanced in terms of mass of precipitates produced, little is known in this aspect. On the contrary, the charge effect of dissolved silica on aluminium precipitate is evident both from this experiment results and from the literature (see chapter 3).
Collision efficiency is decided by the energy barrier, which is greatly affected by the electrical charge of colloids (see 6.1.2.1). Therefore, it would be reasonable to say that, the promoted aggregation of primary aluminium hydroxide particles in presence of dissolved silica (e.g. at alum 40 μM, silica 20 mg/L in Figure 5.17) is caused by the elimination of energy barrier, which in turn is caused by the reduction of positive charge of aluminium hydroxide particles in presence of dissolved silica. For one can see that, when dissolved silica concentration is 20 mg/L, the surface charge of adsorbed layer of kaolin particle is at IEP Figure 5.9.b. If the zeta potential is at zero, there is no energy barrier between particles. Therefore, the aggregation process can proceed fast without lag time.

**Mechanism of influence on aggregation of the kaolin suspension**

In the previous sections, we discussed the effect of dissolved silica on aluminium hydroxide precipitate and aggregation of the primary aluminium hydroxide precipitate in presence of dissolved silica. Here, the mechanism of influence of dissolved silica on the kaolin suspension can be discussed based on them.

As discussed in 6.1.2, the aggregation system of kaolin suspension after addition of alum consists of two kinds of particle and three aggregation process. Among them, the single layer adsorption of the primary aluminium hydroxide particles on kaolin particle surfaces will be within a fraction of one second. The importance of this single layer adsorption is that after this, all the particles in the system will have the similar electrical charge, which decides the collision efficiency between particles, hence influence the aggregation rate. Moreover, the aggregation of the primary aluminium hydroxide particles will be very important to the whole aggregation process, due to their characteristic kinetics of aggregation depending on alum concentration and solution pH, as well as the huge volumes of precipitates which may be eventually formed in suspension.
Therefore, when dissolved silica reduce the positive charge of primary aluminium hydroxide precipitate, firstly the aggregation between the primary aluminium precipitates will be promoted due to the reduced positive charge and improved collision efficiency. For the same reason, the aggregation between coated kaolin particles, as well as between the primary precipitates and coated kaolin particles will be also improved. As a result, the aggregation of the whole kaolin suspension is promoted.

However, when the dissolved silica concentration becomes very high, the electrical charge of primary aluminium hydroxide precipitates becomes very negative, so that the primary precipitates may colloidally stable and aggregation between them will not occur. Moreover, when kaolin particles adsorb these primary precipitates and they remain colloidally stable. As a result, aggregation of the whole kaolin suspension will be prevented.

Note that, apart from the charge effect of dissolved silica on aluminium hydrolysis precipitates, at some low level, inclusion of silica ion in the precipitate may strength the precipitate, which would be beneficial to the aggregation of suspension. This effect may be reflected in the PI values in Figure 5.17 and FI values and corresponding residual turbidity in Figure 5.9. For, in such case, high PI and FI values and lower residual turbidity can be observed.

6.2.2.2 Mechanisms of influence at pH 6 and 7, at very high dose of alum

In this section, aggregation of kaolin suspension is in the sweep flocculation, and not limited by slow kinetic aggregation of the primary aluminium hydroxide precipitates. The mechanism of this kind of aggregation has been discussed before (6.1.2). In this case, influence of dissolved silica is that at normal concentration of dissolved silica, the aggregation of the kaolin suspension can be improved significantly in terms of
aggregate size. However, at very high concentration of dissolved silica, the aggregation prevented (Figure 5.10.a and b).

Because the mechanism of aggregation is different from that in the previous section, the effect of dissolved silica show some differences. The charge effects are generally the same, in that, presence of dissolved silica reduces the electrical charge of aluminium hydroxide precipitates. This is reflected by the reduced potential of kaolin particles (see Figure 5.10.b). However, the effect on the aggregation process may be somewhat different from that at the stage of collision efficiency limited aggregation (Figure 5.9.a, at 0 mg/L of silica). In this case, the improvement of the aggregation of suspension is mainly seen in terms of aggregate size, rather than the growth rate as in the case of previous section. Therefore, the promoted aggregation of the kaolin suspension may be attributed to enhanced precipitate formation in terms of size and strength in presence of dissolved silica. Also, in this case, the charge effect is not so critical to the aggregation process, whilst some other characteristics of precipitates, such as volume, size or even structures, may play important part. For this reason, even when presence of dissolved silica is 80 mg/L and the EM of particles is reduced to around -1.2 unit, no decreased aggregation is observed, whereas in the collision limited aggregation, the aggregation of kaolin suspension is greatly hindered at this EM of particles (Figure 5.9.a, at silica 80 mg/L). However, the aggregation of the suspension is completely stopped when the EM of particle is reduced around 1.5 unit. This means that, at this electrical charge, the aggregation of primary aluminium precipitate is prevented and the precipitates is colloidal stable in their primary size. No aggregation can occur either though charge effects through adsorption or through enmeshment of large volumes of precipitates.
6.2.2.3 Mechanisms of influence at pH 8

General

Characteristics of flocculation of kaolin suspension by alum at high alum concentration and at pH 8 is that aggregation can proceed quickly after addition of alum; and that the charge of aluminium hydroxide precipitates is around IEP. The influence of dissolved silica on coagulation show much stronger effect at this pH than at pH 7. At very low concentration of dissolved silica, the flocculation of kaolin suspension can be improved, while at a normal concentration of dissolved silica, the flocculation can be prevented (Figure 5.11.a and 5.11.b).

Interactions between aluminium and dissolved silica on the charge effects

The dissolved silica has strong effect on kaolin particles after addition of alum at this pH value. There are two reasons for it. First, the interaction between aluminium and dissolved silica reduces the electrical charge of aluminium hydroxide precipitate. It has been reported (Yokoyama 1987) that, at pH 8, interaction between the two chemicals may form more negative species than aluminate ion. Secondly, the interaction may make aluminium hydroxide colloidal stable or even more soluble.

Influence on aggregation between primary aluminium hydroxide precipitate

The influence of dissolved silica on aggregation of primary aluminium hydroxide precipitates is different from that at pH 7. At this pH, dissolved silica has stronger effects on aggregation of primary aluminium hydroxide precipitate: quite a low concentration of dissolved silica can affect the aggregation greatly compared with that at pH 7 and 6. At very low concentration of dissolved silica, the aggregation can be enhanced significantly, and this enhancement may due to the enhanced co-precipitation rather than from the charge effect. For, the electrical charge may drop to negative
value of EM that is not ideal for aggregation process, while the PI values indicate an improved precipitation (Figure 5.18, Figure 5.11.b at 5 mg/L SiO₂). Further increasing the concentration of dissolved silica, the aggregation process is hindered and even totally prevented. This may be because the primary aluminium hydroxide precipitates become colloidally stable with high negative charge, or more soluble, so that aggregation of primary aluminium hydroxide precipitates can be hindered or prevented.

Mechanisms

The influence of dissolved silica on flocculation of suspension shows itself through the influence on aluminium precipitation. A comparison between Figure 5.18 and Figure 5.11.a shows that when presence of dissolved silica can improve the aggregation of primary aluminium hydroxide precipitate, it improves the aggregation of kaolin suspension correspondingly. While when presence of dissolved silica decreases or prevents the aggregation of the primary aluminium hydroxide precipitate, the aggregation of kaolin suspension is decreased or prevented. One major difference here is that promotion of aggregation of the primary particles does not agree with the charge effect very well. For instance, at 5 mg/L of dissolved silica, the EM of aluminium hydroxide precipitate become around -1 unit from 0. According to the electrical charge effect described by the DLVO theory, the aggregation of the particle should decrease. Oppositely, the aggregation become better in such case. This may indicate that inclusion of silica ion in the precipitates may enhance the precipitation through chemical bonding. For example, presence of silica may provide some chemical bonds for the precipitate, which strengthen the structure of the precipitate. Therefore, when more precipitates are formed with greater strength and volume, the aggregation of the whole suspension can be promoted. However, this kind of improvement of precipitation can be only found at very low concentration of dissolved silica.
6.2.2.4 Implication to practical aggregation process

*Effective retention time*

In water treatment process, in order to obtain large aggregates or flocs, certain retention time has to be provided. In the past, it is commonly expected that in both zone 2 and zone 4 flocculation, primary aggregates or flocs should form very quickly after addition of coagulants. It is believed that in the zone 2, aggregation will begin immediately after charge neutralisation of clay particles; so will the zone 4 aggregation after addition of coagulant. From our experiment, in the zone 2 coagulation, aggregation can begin after addition of alum. However, in the zone 4 flocculation, it will depend on pH and concentration of alum. At pH 8, aggregation can begin quickly at both the two zones of flocculation. At pH 7 and below, the zone 4 flocculation can be a very slow aggregation process even in the optimum coagulant dosage region. For example, from Figure 5.4.b, at pH 7, alum 40 μM, one can see that at this dosage, the supernatant turbidity is very low, and no substantial decrease of the supernatant turbidity is achieved when further increasing the alum dose, indicating that the dosage is in the optimum region. However, from Figure 5.4.a, one can see that there is a lag time around 5 minutes. That is, if retention time for flocculation basin is 15 minutes, only 10 minutes is effective for the growth of aggregates in such case. In practice, this may mean that aggregates cannot grow large enough for an effective removal through gravity separation method. This is not ideal for the water treatment process.

In this case, the influence of dissolved silica on the aggregation can be very useful. Since even at very low concentration (below the average concentration of dissolved silica in waters), such as 10 mg/L, the coagulation can be promoted, and begin after addition of the coagulant.
**Shift of optimum pH for coagulation**

In the water treatment process, it is important to know the optimum pH region for one coagulant and the influence of some chemicals on it. From this study, the dissolved silica can prevent coagulation by alum at pH 8 and above at low levels; and at the same time, it shifts the effective region to acidic side. This can be seen from comparison between Figure 5.6.b and Figure 5.12.b, or Figure 5.13.b. It is seen that at 20 mg/L dissolved silica the region is shifted from around 6.8-8.4 to around 6.5-7.7; and at 50 mg/L of dissolved silica the flocculation zone is shifted and narrowed 6.4-7.3.

From Figure 5.14, one can see that when presence of dissolved silica reduces the EM of kaolin particles after addition of alum to around -1.5 unit, the aggregation of suspension is prevented.

**6.2.2.5 Conclusion**

Influence of dissolved silica on flocculation is related to the effects on the properties of co-precipitates, the electrical charge and strength and the colloidal stability. At pH 6 and 7, where the electrical charge of the aluminium hydroxide precipitate is high and the primary precipitate is colloidally stable. Reduction of the positive charge by dissolved silica may improve the aggregation of the primary precipitates, hence improving the aggregation of the whole kaolin suspension. This effect can be very favourable to the water treatment process, for it can improve effective retention time for aggregate growth.

At pH 8, the aluminium hydroxide precipitate may at the IEP and is colloidally unstable. So, aggregation of the primary precipitates can proceed quickly. In this case very low concentration of dissolved silica may promote the precipitate formation simply by the inclusion of silica ion in the precipitates, so that the aggregation of the whole kaolin suspension can be improved. When presence of dissolved silica makes the
electrical charge of the precipitate very negative, the primary aluminium hydroxide precipitate become colloidally stable or even soluble, the aggregation of primary precipitates is prevented. As a result, the aggregation of the whole suspension is prevented.

The dissolved silica has much stronger influence at pH 8 and above on the aggregation than at low pH values 6 or 7. This is because at around pH 8, the electrical charge of the aluminium hydroxide precipitates is around zero, interaction between aluminium and dissolved silica can make it negative at low concentration. So that, the aggregation can be prevented at the lower concentration of dissolved silica.

For these reasons, presence of dissolved silica can narrow and shift the coagulation pH region to the acidic side. That means normal concentration of dissolved silica in waters can prevent the alum coagulation.

6.3 Effects of calcium on coagulation influenced by dissolved silica

When dissolved silica prevents the flocculation of kaolin suspension by alum, addition of calcium in such system, can restore the flocculation (see Figure 5.20.a&b, 5.21.a&b). Below, the mechanism will be discussed.

6.3.1 Mechanism of calcium influence

From 6.2, the mechanism for the prevention of flocculation of kaolin suspension after addition of alum by the presence of dissolved silica is that interactions between aluminium and dissolved silica change the electrical charge of the aluminium hydroxide precipitate making it more negative. So that, there is no aggregation between the primary precipitates, nor between kaolin particle and the precipitate. As a result, no aggregation occurs in the system.
By addition of calcium in such suspensions, the negative charge of kaolin is reduced, when the EM of kaolin particle is around -1 unit, the aggregation begins. When the EM of particles is around -0.8, the aggregation is fully restored. As calcium alone can only generate a weak aggregation, this restoration of aggregation must involve the enhanced precipitation or primary precipitate aggregation. From Figure 5.21a&b, addition of calcium in such system, not only causes the aggregation to be restored at the pH values where aggregation occurs after addition of alum, but the region for the aggregation of kaolin suspension extend to the high pH region where alum alone cannot generate coagulation at the dosage employed. For instance, at pH 9 and 10, addition of alum 40 μM, only dissolved negative aluminium hydrolysis species can form due to the high solubility of aluminium hydroxide at these pH values. In this case, coagulation cannot occur neither by charge effects nor by precipitate. As a result, there is no aggregation at these pH values (see Figure 5.6.a&b). The fact that, addition of calcium can generate good flocculation, may indicate that there is co-precipitation between aluminium and dissolved silica as well as calcium. This co-precipitates can be adsorbed on to kaolin particle surfaces and even can aggregate with the kaolin particles. The electrical charge of the co-precipitate is nearly not affected by the pH between 8 and 10.

It is worth noting that the coprecipitation can occur between fulvic acid and calcium carbonate crystals, which lead to enhanced removal of fulvic acid in ground waters (Liao and Randtke 1985). In addition, it has been reported that in the system of Fe(OH)$_3$/SiO$_2$, uptake of H$_4$SiO$_4$ does reduce sulphate adsorption, but it had a negligible effect on cadmium adsorption (Meng and Letterman 1996). Therefore, it is possible for the calcium interact with the HAS precipitate.
6.3.2 Implication to practical process

The influence of calcium on the aggregation of kaolin suspension is favourable for water treatment process. For in water treatment, it is expected that the coagulant should possess wider optimum pH region, which would be convenient for process control.

6.3.3 Conclusion

Addition of calcium in the coagulation system of kaolin, dissolved silica and alum can restore the coagulation which is prevented by dissolved silica. The mechanism may be that co-precipitation between the HAS precipitate and the calcium, or some other form of coprecipitation, so that aggregation can occur through enmeshment mechanism.

6.4 Mechanisms of influence of dissolved silica on Iron (III) coagulation

6.4.1 Mechanism of the influence on coagulation

The mechanism of flocculation of kaolin suspensions by ferric chloride is basically the same as that by alum. The main difference is the electrical charge of the precipitate. As observed in the Figure 5.24, the IEP of ferric (chloride) precipitate is around pH 7, while aluminium (alum) precipitate is around pH 8.

As in the case of aluminium, one general effect of dissolved silica on the aggregation system is to reduce the positive charge. Therefore, at low dose of ferric chloride, aggregation of the kaolin suspensions will be affected by the charge effects: the aggregation becomes weaker as the electrical charge becomes more negative (Figure 5.26). At high dose of ferric chloride, when the electrical charge of the primary ferric hydroxide precipitate is very high (e.g, at pH 6), the precipitate may be colloidally
stable. So after single layer adsorption on kaolin particles, the suspension will stay
stable for the reasons discussed before (6.1.2). In this case, if presence of dissolved
silica reduces the positive charge to a low level, aggregation between the primary
precipitates may begin and as a result the whole suspension is flocculated (Figure
5.25). At IEP of the precipitate (pH 7), presence of dissolved silica makes the
precipitate negative, no improvement on aggregation is observed, indicating that no
enhancement of the precipitation at any level of dissolved silica. When the charge of
the precipitates reaches very negative, the aggregation is prevented Figure 5.27. This
indicate that presence of dissolved silica can make the primary iron hydroxide
precipitate colloidally stable with high negative electrical charge, so that aggregation of
clay suspension cannot generated either through charge effect or through sweep effect.

6.4.2 Implication to practical process

From this results, one important effect of dissolved silica is that when coagulation of
suspension is prevented due to charge reversal effect, at some low level it can promote
the coagulation (see Figure 5.25). This indicate that presence of dissolved silica can
broaden the coagulation region to acidic side.
CHAPTER SEVEN

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1 Conclusions

This work has examined the mechanisms of flocculation of kaolin suspensions by the hydrolysing metal salt coagulants: alum ($\text{Al}_2(\text{SO}_4)_3$) and ferric chloride ($\text{FeCl}_3$). The influence of dissolved silica on the flocculation has been examined systematically. The mechanisms of the influence have been discussed, based on the experimental results. From this study, some conclusions can be drawn as follows.

1. Mechanism of coagulation by alum, at low dosage (zone two coagulation), will follow the electrostatic patch model due to the uneven adsorption of highly charged positive polymeric hydrolysis species. Therefore, the flocculation will not necessarily depend on the overall charge effect over the particle surface; instead it will depend on the conditions for interactions between patches and uncoated areas on particles surfaces.

2. At high dosage levels, the mechanisms of coagulation in zone four will depend on solution pH. At low pH (e.g., 6 and 7), in case of alum, after the charge reversal and restabilisation of the kaolin suspensions, flocculation can begin with a slow kinetic process. In such case, there are similar kinetic characteristics of aggregation between the kaolin particles and the primary aluminium hydroxide precipitates. This indicates that the coagulation of kaolin suspension is controlled by the aggregation of primary aluminium hydroxide precipitates. With increasing alum dosage, both the coagulation of kaolin suspension and the primary aluminium precipitates can proceed almost
immediately after addition of alum. In this stage, the flocculation of the suspension is dominated by the sweep flocculation.

3. At a high constant dosage of alum, the kinetics of flocculation of the kaolin suspension depends on the solution pH. So does the aggregation of primary aluminium hydroxide precipitates. The similarity between the two kinetic processes indicates that the flocculation of the suspension is dominated by the aggregation of the primary aluminium hydroxide precipitate. The characteristics of aggregation of the primary aluminium hydroxide precipitate as a function of solution pH is caused by the electrical charge of the precipitates, which varies according to solution pH. The EM of kaolin particles after adsorption of aluminium hydrolysis species indicates that the precipitate is highly positively charged at pH 6 and 7, and the charge decreases as the pH increases. At around pH 8, it is at the IEP. The electrical charge of the primary precipitate will decide the collision efficiency between them, and hence control the kinetics of aggregation of the primary aluminium precipitates.

4. The influence of dissolved silica on flocculation of kaolin suspension by the hydrolysing metal salt will be different depending on alum dose. At low alum dose, where only dissolved aluminium hydrolysis species is dominant in solution, interactions between dissolved silica and aluminium may form HAS species that reduce the electrical charge of aluminium hydrolysis species or make them soluble and so less adsorbable. Since at low dosage of alum, the flocculation follows the electrostatic theory, the effect of dissolved silica on the electrical charge will affect the flocculation accordingly. That is, when the influence of dissolved silica on the charge is favourable to the electrostatic patch mechanism, flocculation of the kaolin suspension can be improved; and vice versa. Moreover, when interaction between dissolved silica and aluminium leads to HAS species so negative that no charge neutralising effect could take place, the flocculation of suspension will be prevented.

5. At high doses of alum, the interaction between dissolved silica and aluminium will form HAS co-precipitates, which modifies the electrical charge and colloidal properties
of the aluminium hydroxide. One general trend is that the interaction can reduce the electrical charge of aluminium hydroxide precipitates. Since the electrical charge of aluminium hydroxide precipitate is a function of solution pH, reduction of the electrical charge has different effect on aggregation of primary aluminium hydroxide precipitate, and hence the flocculation of the kaolin suspensions. At the high dose of alum, where aggregation of primary aluminium hydroxide precipitate shows a slow kinetic process at pH 6 and 7, reduction of the high positive electrical charge can reduce the energy barrier that tends to prevent aggregation of the primary aluminium precipitates, so this aggregation can be promoted. As a result, aggregation of the whole suspension can be enhanced. At a high dose of alum where the aggregation of the primary aluminium hydroxide precipitates proceeds rapidly, interactions between aluminium and silicic acid can also improve the flocculation of suspension in terms of higher FI values and residual turbidity. However, high concentration of dissolved silica could reduce the positive electrical charge of aluminium hydroxide precipitate greatly to a very negative value so that the primary aluminium precipitates may be colloidally stable with the high negative charge and no aggregation between them could occur. In this case, flocculation of kaolin suspension cannot occur either through charge effect or through enmeshment mechanism. As a result, flocculation is completely prevented.

6. The intensity of influence of dissolved silica on flocculation of kaolin suspensions depends greatly on solution pH. At around pH 8, where the aluminium precipitate is at the IEP, the effect on flocculation is more sensitive than at low pH (e.g., 6 or 7). At very low level of dissolved silica, the aggregation of the primary aluminium hydroxide precipitates is improved, as is the flocculation of the kaolin suspension. Here, the improved aggregation of primary aluminium hydroxide precipitates is accompanied by decreasing electrical charge to a negative value. This may indicate that this enhancement of co-precipitation is simply due to the inclusion of silica in the precipitate rather than charge effects. However, such an effect is only found at this very low concentration of silicic acid.
In contrast, at a normal concentration in waters (e.g., 15-20 mg/L), presence of dissolved silica can prevent the aggregation of the primary aluminium hydroxide precipitates and hence the flocculation of kaolin suspension. This may be because very negative species can be formed at this pH, or even the interaction between aluminium and silicic acid can increase the solubility of aluminium hydroxide, so that no aggregation of primary precipitate could occur. In such a case, flocculation of kaolin suspension is prevented, because no charge effect or enmeshment mechanism could take place.

7. Calcium can counteract the inhibition effects of dissolved silica on coagulation of the kaolin suspension and even improve the flocculation in such cases. The mechanism may be that calcium in solution may undergo co-precipitation with the HAS precipitate, or even it may interact with the dissolved HAS species to form co-precipitate at high pH. In addition, where negatively charged colloidal HAS precipitate can form (e.g., at pH 8 around), Ca$^{2+}$ might coagulate them through the simple DLVO theory, thus it promotes the aggregation of the primary precipitates and the flocculation of the suspension.

8. Dissolved silica has similar effects on coagulation of kaolin suspension by ferric chloride. It can reduce the electrical charge of iron hydrolysis species and iron hydroxide precipitate, so that the flocculation of kaolin suspension can be influenced accordingly. At some low concentration of dissolved silica, the flocculation of kaolin suspension can be improved, whereas at high concentration the flocculation of kaolin suspension can be prevented completely.

9. Due to the charge effects and corresponding effects on the primary aluminium hydroxide precipitate, presence of dissolved silica can shift and narrow the flocculation region of solution pH to acidic side. In such case, presence of calcium can counteract this effect, even improve flocculation especially at high solution pH (e.g., 8-10).
10. Influence of solution chemistry on flocculation by hydrolysing metal salts can conveniently be examined by using the particle monitor and PDA. Using this instrumentation, useful information on precipitation and flocculation of suspensions can be obtained.

7.2 Suggestion for Further Work

1. Influence of dissolved silica on aggregation of primary ferric hydroxide precipitates would be useful to examine the effects on ferric salts as coagulants. Therefore, a systematic examination would be interesting.

2. Since there are many anions in waters which also exert some influence on flocculation of clay suspensions, the effect of dissolved silica in these cases would be worth investigating.

3. Flocculation of some hydrophilic colloids, such as humic substances, etc., by hydrolysing metal salts is of great importance. Mechanisms of flocculation by the coagulants of these colloids is different. An examination of dissolved silica on flocculation of such kinds of colloid system would be interesting and important.
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