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# DEVELOPMENT OF COAGULATION THEORY AND PRE-POLYMERIZED COAGULANTS FOR WATER TREATMENT

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# DEVELOPMENT OF COAGULATION THEORY AND PRE-POLYMERIZED COAGULANTS FOR WATER TREATMENT

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## ABSTRACT

This paper reviews the history of chemical coagulation and its effects on the water quality control and management, considers how the most favourable coagulant species and pre-polymerized inorganic coagulants may be prepared by reference to the appropriate coagulant chemistry, and evaluates the overall performance of some pre-polymerised coagulants in comparison with that of conventional coagulants for water treatment.

*Key Words*: Coagulation; Coagulant chemistry; Pre-polymerised coagulants; Water treatment

## INTRODUCTION

Clean and safety drinking water is essential for human beings. Drinking water quality is defined in terms of physical, chemical and biological parameters, and limiting values are set either as national regulations within countries or as recom-

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mendations from international organisations. Of particular importance are those of the World Health Organisation (WHO), the US Environmental Protection Agency (USEPA) and the European Union (EU). In the UK the Department of the Environment in England and Wales, the Scottish Office and the Department of Environment in Northern Ireland are responsible for monitoring drinking water quality.

'Pure' water does not occur naturally other than in very small quantities and most water is usually polluted by the air and ground. The impurities may be organic or inorganic, either dissolved or in particulate form. They can arise from the biological degradation of natural organic substances, and may be highly coloured. Many impurities lie in the general colloidal size range, usually $< 1\ \mu m$, and most are negatively charged. Their colloidal dispersions are stabilised due to electrostatic repulsion, which usually overwhelms the attractive van der Waals' forces, and prevents particle aggregation.

Colloidal impurities in water include microorganisms such as bacteria and viruses, natural organic matter (NOM), and clay-metal complexes. NOM is the major source of colour in natural waters, and are the main precursors of disinfection by products. To comply with prescribed drinking water standards, water treatment plants remove these impurities using a sequence of treatment processes, usually coagulation-flocculation, sedimentation or filtration, and disinfection.

One of the main purposes of the initial treatment steps is to remove suspended solids and colloidal impurities, improving disinfection efficiency and minimizing the formation of disinfection byproduct. Coagulation-flocculation destabilizes and aggregates small, stable colloidal impurities into larger particle units called flocs, which are efficiently removed in the subsequent solid-liquid separation stages of sedimentation (or flotation) and filtration.

Coagulation involves three basic steps: coagulant addition and mixing, colloid particle destabilisation, and floc formation. Coagulation describes the initial colloid destabilisation, principally by charge neutralisation after adding the coagulant. Flocculation describes the subsequent aggregation of μm- and sub-μm-size particles into mm-size flocs. Because coagulation and the early phase of flocculation occur very rapidly, in practice there is little distinction. Hence, the term either 'coagulation' or 'flocculation' could be used to describe the overall treatment process.

## COAGULATION HISTORY IN PAST 100 YEARS

Although coagulation history goes back to three thousand years ago, the modern use of coagulants for water treatment started approximately 100 years ago, when ferric chloride and aluminium sulphate were used as coagulants in full-scale water treatment plants[1,2]. Scientific based study on coagulation also started since then, when the well known Schulze-Hardy rule[3,4] was proposed to explain the coagulation mechanism. In 1917, Smoluchowski[5] developed the theory of particle collision function, which forms the basis of understanding the changes in particle number in flocculation process. Mattson[6] firstly derived that the hydrolysis products of aluminium and iron were more important than the trivalent ions themselves, although this approach was widely accepted and accorded its proper position in coagulation chemistry 30 years later. Black and co-workers[7] conducted a series of studies on the effect of pH and various anions on the time of floc formation. For the next few years, the principal research emphasis on coagulation was study of mechanical methods to produce better flocs and search for better coagulant aids including bentonite, silicates, and limestone.

Colloid interaction was studied in detail starting from the 1940s, the best known of which are van der Waals attraction and electrical interaction (which can give either repulsion or attraction, depending on conditions). These contributions form the basis of the classical DLVO theory of colloid stability, which was independently proposed by Deryagin and Landau[8] and Verwey and Overbeek[9]. Later, a new coagulation theory was developed by Langelier and Ludwig[10], who distinguished two mechanisms for the removal of colloidal particles: (a) the double layer compression, a process to allow the particles to overcome the repulsive forces and thus agglomerate and precipitate; and (b), precipitate enmenshment, a process in which small particles are physically enmeshed by metal precipitates when they are forming and settling. These two mechanisms have been elaborated upon and substantiated on a theoretic basis by LaMar and Healey[11], who proposed the terms 'coagulation' based on (a) and 'flocculation' based on (b).

A significant step in the development of a comprehensive theory of coagulation during 1960s was the introduction of micro-electrophoresis [12] to the study of colloidal destabilzation, which allowed the quantification of zeta potential on colloidal particles. Study of the stoichiometric relationship between the coagulant dose required to neutralize the colloids and the concentration of colloidal particles in water also started since that decade. These studies[13-16] pointed out the effect of chemical factors such as pH, ionic strength and the properties of colloids to be removed on the surface potential of colloidal particle. These studies also re-emphasized the importance of hydrolysed products, as originally proposed by Mattson, and have resulted in more widespread recognition of the necessity for basing coagulation mechanisms on the formation of specific hydrolysed metal coagulants.

Study of coagulation mechanism and the approaches to improve the coagulation performance are always linked with the needs to match the water quality standards. This was highlighted since 1970s, when haloforms and other halogenerated organic compounds (e.g., trihalomethanes, THMs) were firstly found in the treated waters[17], which are resulted from the reactions of natural organic matter (NOM) with disinfectant – chlorine. Reduction of NOM became the most important objective of coagulation/flocculation, although itself sometimes may not be enough to reduce the NOM to the acceptable level. It is well know now that activated carbon is effective in removing organic compounds from water. Since the drinking water standards become more rigorous, many water treatment plants have accepted use of the granular activated carbon (GAC) filters. For best results, GAC filters should be installed downstream of the clarification and filtration unit processes. Thus, if the coagulation process can achieve the greatest removal of NOM, the load of GAC filters will be significantly reduced and its running life can be extended.

Since 1980s, optimization of coagulation performance for the removal of NOM has been systematically studied[18], using various real surface waters, by evaluation of a range of variables such as mechanical conditions for coagulation/flocculation, sequences of chemical addition, coagulant type and doses, coagulation pH, restabilization zones and water quality characteristics including water temperature. Another tool added to the coagulation technology was the streaming current detector (SCD)[19], which is a means of determining the magnitude of zeta potential on colloidal particles in a suspension. The actual current is caused by movement of counter-ions beyond the shear plane of surfaces within the sensor; the fluid motion carrying these ions results from piston reciprocation within a closed-ended cylinder in contact with a sample flow. The output from the instrument is indicative of the zeta potential or electrophoretic mobility of the colloidal particle. SCD has been used widely together with jar test in controlling the coagulant dose and hence, coagulation process.

In the 1990s, NOM and other precursors of the disinfection by-products are still the main impurities to be caused concern. The outbreak of cryptosporidiosis in the USA[20] led to the re-concern of microrganism impurities, including *Cryptosporidium*, *Giardia*, *Legionella*, and various viruses. Microbiological particulates can be controlled through a multiple barrier or integrated water treatment process design that uses coagulation, filtration and disinfection. To achieve the expected targets, coagulation is essential to ensure attachment of particulates to the filter media, therefore, the microbial particulates can be effectively removed.

Coagulation/flocculation are affected by upstream treatment, e.g., pre-oxidation process, and affect the downstream processes – settling/flotation, filtration, activated carbon adsorption, oxidation and disinfection. During this decade, the effect of pre-ozonation on the coagulation performance, the coagulation treatability of various raw waters and different fractions of NOM (i.e., NOM fractions with different molecular weight, charge density and hydrophilic/hydrophobic affinity), and the impact of coagulation performance on the effectiveness of activated carbon adsorption have been, and still are being studied. In addition, *enhanced coagulation*, either by addition of excess coagulant dose and lowering the coagulation pH [21, 22], or through developments in coagulant chemistry to prepare the more effective coagulants[23], have been evaluated for improving the removal of NOM and general coagulation performance. Moreover, computer models of coagulation/flocculation have been developed and studied, including the models to predicate the coagulant dose required and the removal efficiency of NOM, and to describe the physical aspects of coagulation/flocculation (e.g., particle collisions).

## COAGULANT CHEMISTRY

Conventional chemicals used for coagulation are mainly aluminium or iron-based salts. When added to water, Al/Fe(III) ions hydrolyse to form soluble monomeric and polymeric species and solid precipitates. The solubility equilibria of $Al^{3+}$ and $Fe^{3+}$ in water are listed in Table 1.

The aqueous equilibrium chemistry of Al in water has been explained[24] by considering five monomers ($Al^{3+}$, $Al(OH)^{2+}$, $Al(OH)_2^{\ +}$, $Al(OH)_3$ (molecule) and $Al(OH)_4^-$), three polymeric species ($Al_2(OH)_2^{\ 4+}$, $Al_3(OH)_4^{\ 5+}$ and $Al_{13}O_4(OH)_{24}^{\ 7+}$) and a solid precipitate ($Al(OH)_3$ (s)). Several other formulae for polymeric Al species can also be found in the literature, but it seems that $Al_{13}O_4(OH)_{24}^{\ 7+}$ (often denoted by $Al_{13}$) is the most effective and stable polymeric Al species in water treatment[26]. Similarly, the Fe(III) hydrolysis products are considered [25] to be five monomers ($Fe^{3+}$, $Fe(OH)^{2+}$, $Fe(OH)_2^{\ +}$, $Fe(OH)_3$ (molecule) and $Fe(OH)_4^-$), a dimer and trimer ($Fe_2(OH)_2^{\ 4+}$ and $Fe_3(OH)_4^{\ 5+}$) and a solid precipitate ($Fe(OH)_3$ (am)). In addition, there exists a range of dissolved

***Table 1.*** Aluminium[24] and Iron (III)[25] Equilibria

| Reaction | log K (25°C) |
|---|---|
| $Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$ | -4.97 |
| $AlOH^{2+} + H_2O \rightleftharpoons Al(OH)_2^{\ +} + H^+$ | -4.3 |
| $Al(OH)_2^{\ +} + H_2O \rightleftharpoons Al(OH)_3 + H^+$ | -5.7 |
| $Al(OH)_3 + H_2O \rightleftharpoons Al(OH)_4^- + H^+$ | -8.0 |
| $2Al^{3+} + 2H_2O \rightleftharpoons Al_2(OH)_2^{\ 4+} + 2H^+$ | -7.7 |
| $3Al^{3+} + 4H_2O \rightleftharpoons Al_3(OH)_4^{\ 5+} + 4H^+$ | -13.97 |
| $13Al^{3+} + 28H_2O \rightleftharpoons Al_{13}O_4(OH)_{24}^{\ 7+} + 32H^+$ | -98.73 |
| $Al(OH)_3(am) \rightleftharpoons Al^{3+} + 3OH^-$ | -31.5 (estimated) |
| $Al(OH)_3(c) \rightleftharpoons Al^{3+} + 3OH^-$ | -33.5 |
| $Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$ | -2.2 |
| $FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^{\ +} + H^+$ | -3.5 |
| $Fe(OH)_2^{\ +} + H_2O \rightleftharpoons Fe(OH)_3 + H^+$ | -6 |
| $Fe(OH)_3 + H_2O \rightleftharpoons Fe(OH)_4^- + H^+$ | -10 |
| $2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{\ 4+} + 2H^+$ | -2.9 |
| $3Fe^{3+} + 4H_2O \rightleftharpoons Fe_3(OH)_4^{\ 5+} + 4H^+$ | -6.3 |
| $Fe(OH)_3(am) \rightleftharpoons Fe^{3+} + 3OH^-$ | -38.7 (estimated) |
| $\alpha\text{-}FeOOH(c) + H_2O \rightleftharpoons Fe^{3+} + 3OH^-$ | -41.7 |

polymeric Fe(III) species with medium and high molecular mass during the hydrolysis process, prior to the formation of precipitates. These Fe(III) polymeric species may be represented by the following general formulations: $Fe_x(OH)_y{}^{(3x-y)+}$ or $[Fe_xO_y(OH)_{x+r}]^{(2x-2y-r)+}$, these are kinetically stable and their thermodynamic equilibrium state depends on the conditions of preparation[27-29].

The coagulation mechanisms that arisen when using inorganic Al/Fe(III) salts can broadly be classified as either charge neutralisation or sweep coagulation[30]. Under the charge neutralization mechanism, a series of Fe(III) or Al hydrolyzing species with cationic potentials can be strongly adsorbed on to negatively-charged particles and dissolved organic species, hence reducing their charge and consequently causing precipitation and particle aggregation. Furthermore, neutralization or reversal of the negative particle potential could give a significant reduction of hydration forces, allowing the particles to approach closer and giving a stronger van der Waals attraction. Adsorption can continue beyond neutralization to reverse the charge at colloidal surfaces. In this way the repulsive energy barrier to coagulation is established again and colloids are re-stabilized. As shown in Fig. 1, charge neutralization typically occurs in low pH ($<6$) and low ionic strength waters, and compared to sweep coagulation generally requires a lower coagulant dose and produces less sludge; in such conditions coagulant overdosing may cause colloid restabilization and thus worsen treatment performance.

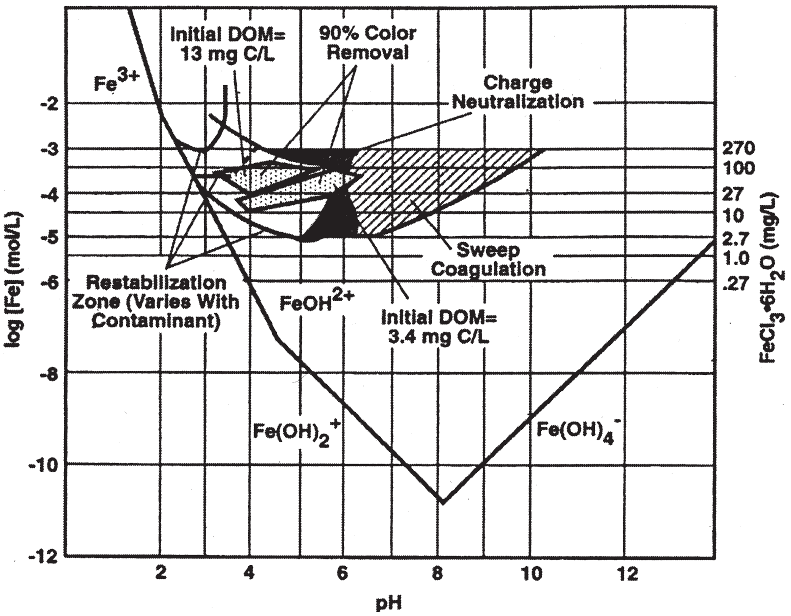

*Figure 1.* Diagram for ferric chloride coagulation.[31]

When the dosages of Fe(III) or Al coagulants used in water treatment are greater than those required for the precipitation of $Fe(OH)_3$ (s) or $Al(OH)_3$ (s), particles and dissolved organic species become enmeshed in these precipitates as they are forming and settling. This process is often referred to as sweep coagulation. Dissolved species, such as fulvic and humic acids and heavy metals, may adsorb onto the surface of the hydroxide precipitates. Coprecipitation of anions, such as phosphate or fluoride, may occur, although these substances may also adsorb onto metal hydroxide surfaces. In the treatment of low turbidity and low DOC waters by conventional design (coagulation, flocculation, sedimentation, and filtration), this mechanism is used extensively in order to enhance flocculation kinetics. Particle aggregation in low turbidity waters is limited by the number of collisions or contact opportunities that exist in the suspension and usually not by chemical destabilisation. High coagulant doses are used to increase the floc volume, enhance flocculation kinetics, and produce a settlable floc. Therefore, in sweep coagulation, the optimal dose and pH are less sensitive to variation in the water quality than for the case of charge neutralisation; also the removal performance of trace impurities are generally better. The main disadvantages of sweep coagulation are that a relatively greater dose is required and more sludge is produced. Typically, this type of coagulation is associated with alkaline, highly buffered surface waters.

As discussed previously, in the conventional coagulation process the appropriate dose of a Al/Fe(III) salt is added directly to the raw water. In the pH range of natural waters, approximately 6 to 8, this causes extremely rapid and uncontrolled hydrolysis, and frequently, very rapid precipitation. A major drawback in such use of Al/Fe(III) salts is the inability to control the nature of the coagulant species formed, and the performance of Al/Fe(III) coagulants may worsen with changes in the nature of the raw water (e.g., water temperature, pH, concentrations of suspended particles and colloidal impurities). It is possible that Al/Fe(III) hydrolysis products may adsorb to colloidal surfaces to neutralize the charge or may chemically interact with dissolved components in the raw water. For these phenomena the rate of coagulant - impurity interaction must be faster than the rate of the hydroxide precipitation. Typically this condition is only met for waters with a $pH < 6$, with a relatively low dose of Al or Fe(III) and with a colloidal concentration above a critical value (moderate to high concentrations). However, it may be difficult to operate a treatment process in an optimal dose range if it is too narrow or if the raw water quality frequently changes. In addition, if the coagulation is operated at low pH ($< 6$) and the coagulant dose exceeds the optimum, the treated water quality will worsen due to colloidal restabilization caused by charge reversal at the colloidal surface. To guarantee the treated water quality and to cope with changes in temperature and the nature of raw water, water treatment plants normally operate coagulation at high doses and elevated pH ($pH > 6$). As a result, greater operational costs are incurred due to the high coagulant dose used and a larger amount of sludge to be disposed of.

One successful and important method of improving the effectiveness of inorganic Al/Fe(III) coagulants is to partially hydrolyse the Al/Fe(III) salts prior to their addition to the raw water and thus preform optimal polymeric Al/Fe(III) species, the actual coagulants. In this way, the coagulant chemistry can be controlled and the preferred solution conditions for the formation of the desired coagulant species can be maintained. The resulting advantages of the preformed polymeric Al/Fe(III) coagulants are that they can work efficiently over a wide pH range and cope with changes in the water temperature and the nature of the raw water. Thus, by use of pre-polymerised inorganic coagulants, water treatment plants can be operated over a wider range of chemical and physical characteristics of the raw water with less change in the operational conditions.

## PRE-POLYMERISED Al/Fe(III) COAGULANTS

Pre-polymerised inorganic coagulants have been developed and used in water and wastewater treatment since 1980s. Originally, they were mainly polyaluminium chloride (PACl)[32] and polyferric chloride (PFCl)[33]. Both PACl and PFCl are made by partial hydrolysis of acid aluminium chloride or ferric chloride solution using a specific reactor. The nature of the polymeric species formed depends on various factors such as the concentration of Al or Fe(III); the basic ratio **r**, defined as the molar ratio of the metal ions to hydroxide ions; base concentration; base addition rate; and the hydrolysis duration of Al/Fe(III) solution (aging time) and aging temperature. The most important parameters that govern the nature of the species are the basic ratio and the ageing temperature and time [26-29].

A variety of techniques can be used to characterise the resulting polymeric solutions. Commonly used techniques are a timed ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid) colorimetric method[34], and a membrane ultrafiltration method[28,29]. The ferron timed colorimetric technique is based on the differences in the rates of reactions of various Al/Fe species with ferron to assess the properties of monomeric, polymeric and precipitated Al/Fe species. The size distribution of Al/Fe species in the polymeric solutions were evaluated using a membrane ultrafiltration technique, with decreasing molecular weight (MW) cutoff, apparent MW distributions can be obtained by measurement of the metal concentration in the solutes. Such distributions can only be taken as an indication of the actual species present in the polymeric Al/Fe solution. In addition to the above two common characterisation techniques, a nuclear magnetic resonance (NMR) spectroscopy method and a radiation scattering technique are used to specifically investigate the nature and the structure of the pre-formed polymeric Al/Fe species.

The structure of the polymer $Al_{13}$ has been detected by NMR spectroscopy method[26], with the central Al atom in tetrahedral coordination, and the 12 other aluminium atoms are in octahedral coordination (Fig. 2). Fig. 3 shows that $Al_{13}$

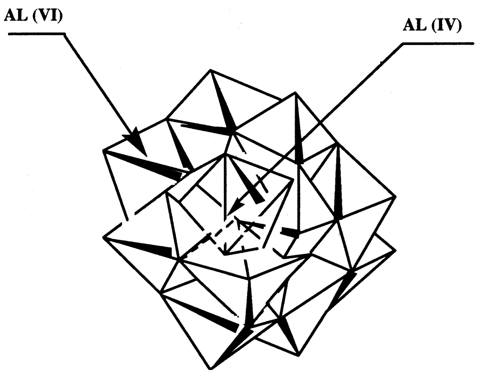

***Figure 2.*** Structure of the $Al_{12}{}^{VI}(OH)_{24}Al^{IV}O_4(H_2O)_{12}{}^{7+}(Al_{13})$ polymer.[26]

concentration corresponds approximately to 90% of total Al at a basic ratio of [OH]/[Al], **r** = 2.0.

Another new iron-based polymeric coagulant, polyferric sulphate (PFS), has been developed and systematically studied [28, 35, 36]. In general, PFS is made using a technique which involves oxidizing ferrous state iron solution at high temperature and/or high pressure, and subsequently ageing it with heating and/or base addition. Fig. 4 shows a MW distribution of the PFS. It can be seen that with increasing the basic ratios (**r** values), the 0.5 to 10K MW fractions increased and

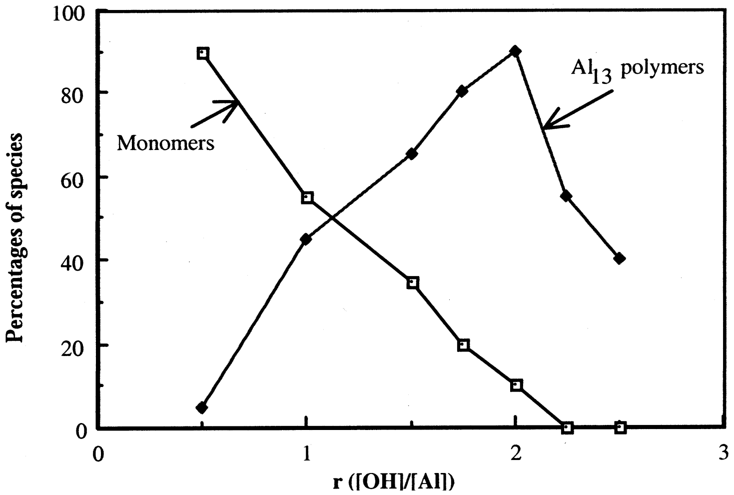

***Figure 3.*** Distribution of the Al species in PACl solutions versus **r** ([OH]/[Al]).[37]

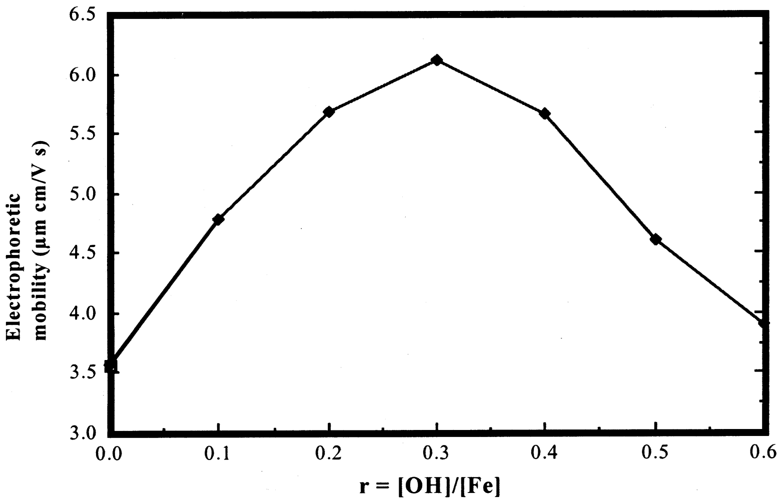

*Figure 4.* The effect of the basic ratio (**r** values) on the molecular size distribution of polyferric species.[28]

reached a maximum at **r** = 0.3. The fraction decreased from the maximum as the **r** value increased between 0.3 and 0.6. Moreover, the fraction of smaller MW species (<0.5K) decreased with increasing **r** values.

Fig. 5 presents the variation of the electrophoretic mobility (EM) of PFS solutions versus **r**-values. It can be seen that when **r** = 0.3, the PFS carried the great-

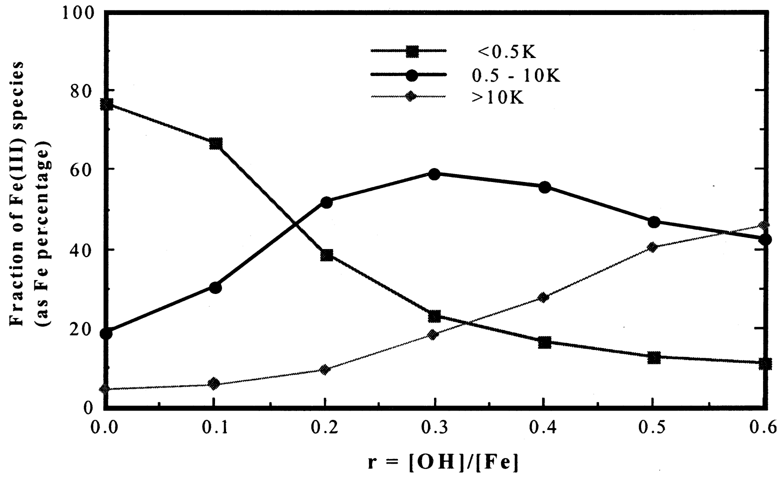

*Figure 5.* The effect of the **r** values on electrophoretic mobility of polyferric species.[28]

est cationic charge. By comparing the results of MW distributions (Fig. 4) with those of EM (Fig. 5), it can be concluded that the polymeric species with MW of 0.5 to 10 K carried the largest proportion of cationic charge. Thus, the greater the percentage of 0.5 to 10 K species, the greater the cationic charge in PFS products.

The evidence of the existence of pre-polymerised species has been confirmed by a study on the chemical nature of precipitates formed with PFS and ferric sulphate (FS) [38]. The test is based on the assumption that if identical precipitates were formed by each coagulant, PFS and FS, then upon dissolution they should show the same reactivity with ferron. If the nature of the precipitates of the two coagulants were different, then their reactivity with ferron would be different. The results indicated that the species in the re-dissolution solutions from FS precipitates were predominantly $Fe(OH)_3$, whilst those from PFS precipitates were predominantly higher MW polymers. This was also evident from the investigation of their zeta potential – pH behaviour. Re-suspended precipitates of PFS carry a significantly higher cationic charge compared to those of FS (Fig. 6). The preliminary characterisation of precipitates using the ferron technique, and particle size and electrophoretic mobility measurements, has confirmed that there are distinct differences in the nature of the precipitates formed by PFS and FS. However, a detailed examination of the chemical structure of the two types of precipitates to explain the different behaviour is the subject of further work.

Another new kind of polymeric aluminium coagulant - polyaluminium silicate sulphate (PASS) has been used in drinking water treatment and is commercially available worldwide [39-41]. It is claimed that the optimal and stable coagulant

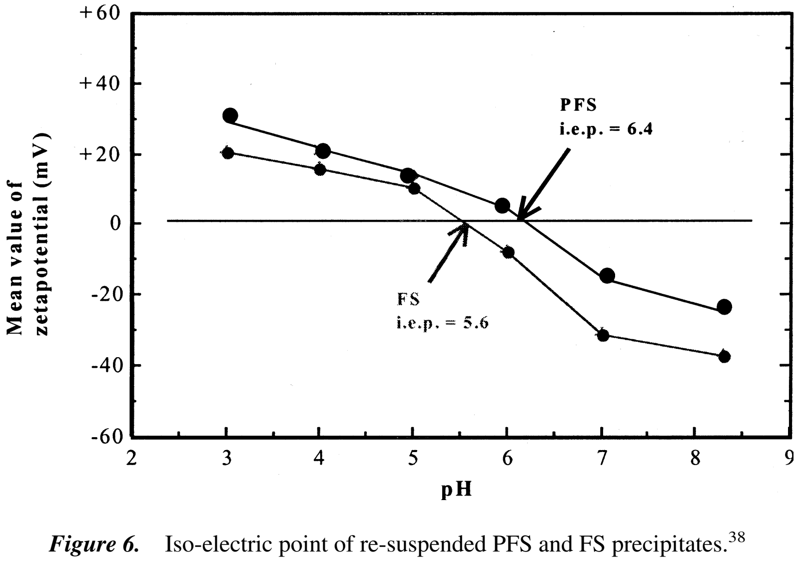

*Figure 6.* Iso-electric point of re-suspended PFS and FS precipitates.[38]

species of PASS can be prepared by controlling the molar ratio of Al to Si in the PASS solutions, and the temperature and agitation speed. Characterisation of PASS by membrane ultrafiltration shows that there are two sharply distinct groups of species with molecular weight greater than 100 kDa (40%) and less than 1 kDa (30-50%).

## COMPARATIVE COAGULATION PERFORMANCE OF PRE-POLYMERIZED AND TRADITIONAL COAGULANTS

Pre-polymerised inorganic coagulants have been shown their superior performance in water and waste water treatment, and these can be concluded as their wider working pH range, a lower sensitivity to low water temperature, lower doses required to achieve the equivalent treatment efficiency, and lower residual metal-ion concentrations [42]. For removing particulate materials and NOM from surface water, pre-polymerised coagulants have shown a superior performance to conventional coagulants. In comparison to AS and FS, the use of PFS in water treatment is expected to reduce treatment costs through a lower coagulant dose and subsequently lower sludge handling requirements[27]. PFS has also demonstrated high removal efficiency for algae and algal-derived organic matter[43]. However, in some cases, PFCl[33] has not shown a superior performance in comparison to ferric chloride (FCl) for removing colour and NOM from natural surface waters. Nevertheless, one advantage of the use of PFCl is its lower sensitivity to water temperature variation, which is of particular benefit to the water industry.

Poly-alumino-iron sulphate (PAFS) is relatively a new kind of pre-polymerised coagulants[44]. An example of the comparative performance of PAFS in comparison with the FS and AS at two water temperatures (18°C and 4°C) for treating a model coloured water can be seen in Table 2. Generally, PAFS behaved better than the other two coagulants, and the performance of PAFS was unaffected

***Table 2.*** Comparison of Coagulation Performance† Using Model Coloured Water at 18°C and 4°C (at pH 5)

| | Colour R%* | | UV-Abs (254 nm)R% | | DOC R% | | Residual Fe (mg/L) | | Residual Al (mg/L) | |
|---|---|---|---|---|---|---|---|---|---|---|
| Coagulant | 18°C | 4°C | 18°C | 4°C | 18°C | 4°C | 18°C | 4°C | 18°C | 4°C |
| PAFS | 92 | 91 | 86 | 83 | 75 | 72 | 0.07 | 0.08 | 0.12 | 0.14 |
| FS | 73 | 67 | 70 | 63 | 61 | 56 | 0.23 | 0.28 | 0.01 | 0.01 |
| AS | 75 | 64 | 72 | 60 | 63 | 55 | 0.01 | 0.01 | 0.39 | 0.49 |

† Coagulant dose = 0.15 mM as Al+Fe, or as Al, or Fe;
* R% = Percentage reduction.

*Table 3.* Residual Concentrations of Al and Fe

| Dose (mg Al/l) | AS |  | PAFS |  | Dose (mgPFS Fe/l) | FS |  | PFS |  |
|---|---|---|---|---|---|---|---|---|---|
|  | pH 5 | pH 6 | pH 5 | pH 6 |  | pH 5 | pH 6 | pH 5 | pH 6 |
| 2 | 0.21 | 0.06 | 0.07 | 0.04 | 4 | 0.31 | 0.42 | 0.22 | 0.21 |
| 4 | 0.16 | 0.03 | 0.03 | 0.02 | 8 | 0.18 | 0.33 | 0.12 | 0.11 |
| 6 | 0.09 | 0.04 | 0.03 | 0.02 | 12 | 0.16 | 0.31 | 0.1 | 0.08 |
| 8 | 0.08 | 0.03 | 0.03 | 0.01 | 16 | 0.15 | 0.22 | 0.08 | 0.05 |

by the water temperature, but FS and AS were significantly affected, with evidence of a reduction in the removal percentages of colour, UV-abs and DOC, and an increase in residual concentrations of the metal in the treated waters at 4°C.

The appeared advantage in using pre-polymerized coagulants in water treatment is of lower residual metal concentrations in the treated waters. Table 3 shows the comparative residual concentrations in the treated water when treating a model coloured water. It is evident that the residual concentrations with PAFS and PFS are consistently lower than those treated with AS and FS, respectively. A significant advantage using PAFS for water treatment is that it can achieve the lower residual concentrations of Al and Fe.

## CONCLUSIONS

Fundamental studies of coagulation chemistry indicate that a range of hydrolysed Al/Fe species but not Al or Fe salt itself are responsible for the removal of suspended particles and dissolved impurities in the water. By development and uses of polymeric inorganic coagulants, the coagulation performance with Al and Fe coagulants could be improved for removing both particles and dissolved organic matter.

Coagulation/flocculation has played, and will still play an important role, directly or indirectly, in the control of particulates, microrganisms, NOM, synthetic organic carbon, precursors of disinfection by-products (DBPs), and some inorganic ions and metals, and ultimately, in the control of drinking water quality. The water and environmental industry world-wide continues to regard the performance of coagulation/flocculation processes as a major factor in improving overall water treatment efficiency, and is paying particular attention to aspects such as: the development and use of more effective coagulants/flocculants; the optimization of treatment configuration, dosing control, sludge handling and process design; and to more fundamental studies of the properties and behaviour of coagulating chemicals.

## REFERENCES

1. I.S. Hyatt, US Patent 293,740, issued Feb. 19, 1884.
2. P.T. Austen and F.A. Wilber. Annual Report of the State Geologist of New Jersey, p. 141, (1884).
3. H. Schulze. Jour. Prakt. Chem., 27, 320 (1883).
4. W. B. Hardy. Proc. Royal Soc. London, 66, 110 (1900).
5. M. Smoluchowski, Phys. Chem., 92, 129 (1917).
6. S. Mattson, J. Phys. Chem., 32, 1532 (1928).
7. A.P. Black, J. AWWA, 26, 1713 (1934).
8. B.V. Deryagin and L.D. Landau, Acta Physicochim, URSS, 14, 733 (1941)
9. E.J.W. Verwey and J.Th.G. Overbeek. Theory of the Stability of Lyophobic Colloids. Amsterdam: Elsevier (1948).
10. W. F. Langelier and H. F. Ludwig, J. AWWA, 41, 163 (1949).
11. V. K. LaeMar and T. W. Healy, J. Phys. Chem., 67, 2417 (1963).
12. A. P. Black and D. G. Willems, J. AWWA, 53, 589 (1961).
13. J.B. Pilipovich, A.P.Black, E.A.Eidsness and T.W. Stearns, J. AWWA, 50, 1467 (1958).
14. A.P.Black, J. AWWA, 52, 492 (1960).
15. A.P.Black and D.G. Willems, J. AWWA, 53, 589 (1960).
16. A.P.Black and C.L. Chen, J. AWWA, 57, 354 (1965).
17. J.J. Rook, Wat. Treatment Exam, 23, 234 (1974).
18. AWWA Research Committee Report, J. AWWA, 81, 72 (1989).
19. S. K. Dentel and K. M. Kingery, J. AWWA, 81, 85 (1989).
20. w.r. Mackenzie, n.j. hoxie, m.e. proctor, m.s. gradus, et al, New England J. of Medicine, 331, 161 (1994).
21. R. C. Cheng, S. W. Krasner, J. F. Green, and K. L. Wattier, J. AWWA, 87, 91 (1995).
22. G. Crozes, P. White, and M. Marshall, J. AWWA, 87, 78 (1995).
23. J. Q. Jiang and N. J. D. Graham, Environmental Technol, 17, 937 (1996).
24. C. F. Baes Jr. and R. E. Mesmer, “The Hydrolysis of Cations”, John Wiley and Sons, New York. (1976).
25. C. M. Flynn, Chem. Reviews, 84, pp. 31 (1984).
26. J.Y. Bottero, J.M. Cases, F. Fiessinger, and J.E. Poivier. J. Phys. Chem., 84, 2933 (1980).
27. A.M. Tenny and J. Derka, Water Supply, 10, 167 (1992).
28. J. Q. Jiang, “Development and Uses of Polyferric Sulphate as a Coagulant for Water Treatment”, PhD Thesis, Imperial College of Science, Technology and Medicine, London (1995).
29. K.A. Gray, C. Yao, and C.R. O’Melia, J. AWWA, 87, 136 (1995).
30. W. Stumm and C. R. O’Melia, J. AWWA, 60, 514 (1968).
31. A. Amirtharajah, K.E. Dennett, and A. Studstill, Wat. Sci. Technol., 27, 113 (1993).

32. B.A. Dempsey, R.M. Ganho, and C.R. O'Melia, ibid, 76, 141 (1984).
33. A. Leprince, F. Fiessinger, and J. Y. Bottero, J. AWWA, 76, 93 (1984)
34. P.J. Murphy, A.M. Posner, and J.P. Quirk, Aust. J. Soil Sci., 13, 189 (1975).
35. BPM Industries, US Patent No. 5332565 (1994).
36. Tsurumi Soda, Japanese Patent No. 47205 (1994).
37. J.Y. Bottero and J.L. Bersillon, in 'Advances in Chemistry Series 219', Washington, DC, American Chem. Soc. P.115 (1989)
38. J. Q. Jiang and N. J. D. Graham, Wat. Res., 32, 930 (1998).
39. Alcan International Ltd., PCT Int. Publ. No. WO 92/00803 (1992).
40. T. Hasegawa, X.C. Wang, K. Hashimoto, and N. Tambo, Conference paper at the '6th World Filtration Congress', Nagoya (1993).
41. Kewmira Kemi Aktiebolag, European Patent No. 551061A1, (1993).
42. H. Odegaard, J. Fettig, and H.C. Ratnaweera, In "Chemical Water and Waste Water Treatment", (Eds. H. H. Hahn and R. Klute), Springer-Verlag, Berlin Heidelberg, p. 189 (1990).
43. J. Q. Jiang, N. J. D. Graham, and C. Harward, Wat. Sci. Technol. 27, 221 (1993).
44. J. Q. Jiang and N. J. D. Graham, In "Chemical Water and Waste Water Treatment", (V), (Eds. H. H. Hahn, E. Hoffmann, and H. Odegaard), Springer-Verlag, Berlin, p. 15 (1998).

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