Pre-polymerised inorganic coagulants and phosphorus removal by coagulation - A review

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Abstract

This paper reviews the use of pre-polymerised inorganic coagulants in water and waste-water treatment, and discusses the removal of phosphorus by chemical precipitation and coagulation. Commonly used inorganic coagulants are aluminium or iron (III) based salts, but a range of hydrolysed Al/Fe species, and not the Al/Fe salt itself, are responsible for the removal of impurities from water. By the development and use of polymeric inorganic coagulants, the coagulation performance can be improved significantly in some cases. Chemical precipitation and coagulation in phosphorus removal are two different processes, with the former related to the compound solubility and the latter depending on the destabilisation-adsorption mechanism. Presently, there is uncertainty concerning the mechanisms and overall performance of phosphorus removal by pre-polymerised metal coagulants.

Introduction

Coagulants used for water and waste-water treatment are predominantly inorganic salts of iron and aluminium. When dosed into water the iron or aluminium ions hydrolyse rapidly and in an uncontrolled manner, to form a range of metal hydrolysis species. A range of factors such as the nature of the water, the coagulation pH and the dose of coagulant together influence the range of species formed and subsequently, the treatment performance. Considerable interest and attention have been paid in recent years to preparing pre-hydrolysed metal-ion coagulants, based on either aluminium (e.g. poly-aluminium chloride) or ferric iron (e.g. polyferric sulphate). These have been shown to perform better in some cases, in comparison with conventional coagulants such as aluminium sulphate (AS) or ferric sulphate (FS). The superior performance of pre-polymerised coagulants is attributed to 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.

Eutrophication has been recognised as one of the main environmental concerns in recent years. The consequences of eutrophication in water bodies (lakes, rivers, etc.) often include the following phenomena: a decrease in depth of water bodies by progressive silting; a colouring of the water (green to brown); a reduced transparency; an oxygen depletion in the deeper levels; a greater biomass, with the appearance of species indicative of eutrophication (especially of Cyanophyceae, or blue-green algae). The process of eutrophication, when it happens naturally, may take a very long time, and this may be measured in thousands of years. However, the rapid pace of development in recent times has led to an acceleration in this natural process as a result of human waterside activities which carry organic matter and nutrients (nitrogen and phosphorus, in particular) in to the natural water bodies through the disposal of agricultural, municipal and industrial waste waters. In some cases, this has led to severe degradation in the quality of such water bodies within the period of a generation.

The objectives of this review are: to summarise the process of chemical coagulation and the use of pre-polymerised inorganic coagulants in water and waste-water treatment; to assess the present use of chemical precipitation and coagulation as a means for phosphorus removal; to evaluate the overall performance of pre-polymerised coagulants in comparison with that of conventional coagulants; and to discuss the relevant coagulation mechanisms for treating water and waste water.

Coagulation/flocculation processes

Coagulation is an established process for transforming small particles into larger aggregates (flocs) and for adsorbing dissolved organic matter onto particulate aggregates so that these impurities can be removed in subsequent sedimentation/flotation and filtration stages. The coagulation process consists of three sequential steps: coagulant formation, colloid/particle destabilisation, and particle aggregation. Coagulant formation and colloid/particle destabilisation are promoted in a rapid-mixing stage where treatment chemicals are added and dispersed throughout the water to be treated. Particle aggregation (floc formation) is then promoted in a flocculation stage where interparticle collisions create large floc particles amenable to separation from the treated water. In water and waste-water treatment practice, the terms ‘coagulation’ and ‘flocculation’ are not synonymous. ‘Coagulation’ is used to describe the initial process whereby the original colloid dispersion is destabilised, principally by charge neutralisation. ‘Flocculation’ describes the subsequent process whereby the destabilised colloids in the micron and sub-micron size range undergo aggregation and particle growth into millimetre-sized flocs. Since the coagulation stage, and the early phase of the flocculation, occur very rapidly, their distinction in a practical treatment sense has very little meaning. Thus, in this review, the simple term of ‘coagulation/flocculation’ is used to describe the overall treatment process.

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 chemistry of Al in water can be explained by considering five monomers (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$

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TABLE 1
ALUMINIUM* AND IRON (III)# EQUILIBRIA

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

* From Base and Mesmer (1976)
\# From Flynn (1984).

(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 (Bottero et al., 1980). Similarly, the aqueous equilibrium chemistry of Fe(III) in water has been explained by considering 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 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:

$$Fe_x(OH)_y^{(3x-y)+} \text{ and/or } [Fe_xO_y(OH)_{x+r}]^{(2x-2y-r)+}$$

These are kinetically stable and their thermodynamic equilibrium state depends on the conditions of preparation (Tenny and Derka, 1992; Jiang and Graham, 1995; Gray et al., 1995).

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 water temperature and in the nature of the raw water. It is possible that Al/Fe(III) hydrolysis products may adsorb to colloidal surfaces to neutralise 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 restabilisation 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 operate over a wider range of conditions of chemical and physical characteristics of the raw water without changing the coagulant dose and coagulation pH.

Conventional and pre-polymerised inorganic coagulants

By far the most commonly used inorganic coagulants are aluminium sulphate ($Al_2(SO_4)_3$), ferric sulphate ($Fe_2(SO_4)_3$) and ferric chloride ($FeCl_3$). Although it was originally thought that their effectiveness could be explained in terms of the highly charged Al^{3+} and Fe^{3+} ions and the Schulze-Hardy rule, this is now known to be greatly oversimplified. Because of hydrolysis, the simple Al^{3+}, Fe^{3+} ions do not exist in solutions around neutral pH and a range of hydrolysis products are responsible for the destabilising effects on colloid impurities.

Different hydrolysis products can cause different treatment performances. 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. Thus, the nature of the formed coagulating species can not be controlled, and the performance of Al/Fe(III) coagulants may worsen with changes in the physical and chemical characteristics of the raw water.

In order to improve the effectiveness of Al/Fe(III) coagulant chemicals in water and waste-water treatment, pre-polymerised inorganic coagulants have been developed. Originally, such kinds of coagulants developed were principally those of polyaluminium chloride (PAC) (e.g. Dempsey et al., 1984) and polyferric chloride (PFC) (e.g. Leprince et al., 1984). Both PAC and PFC are prepared by undertaking a 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^{3+} or Fe^{3+}, the basic ratio, **r**, defined as the ratio of the moles of base added and/or bound to the moles of Al^{3+} or Fe^{3+} ions ($[OH^-]/[Al^{3+}]$ or $[Fe^{3+}]$), the hydrolysis duration of the Al/Fe(III) solution (aging time), the anions in solution, the mixing mode of base with the Al/Fe(III)

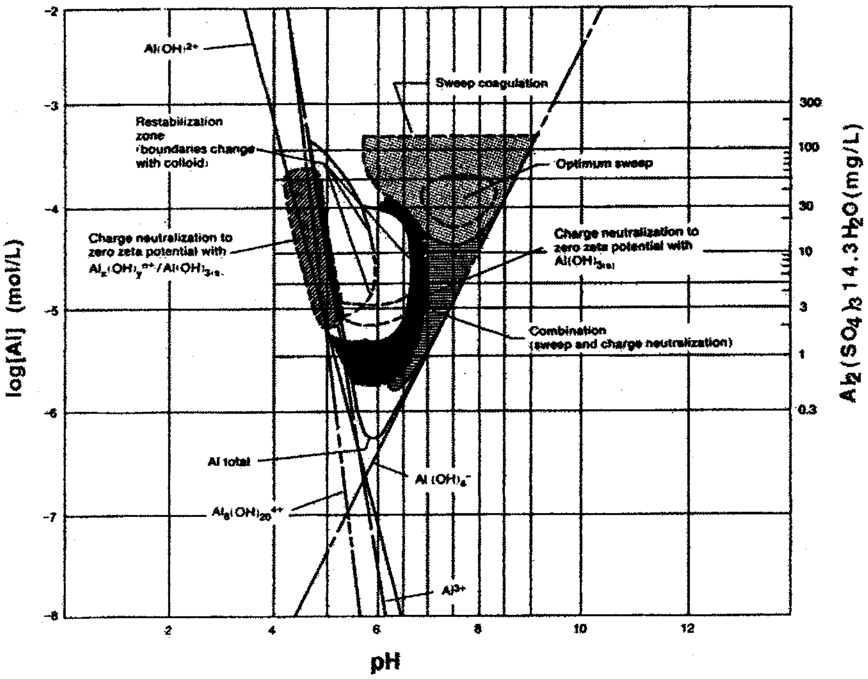

Figure 1

Operational diagram for aluminium sulphate coagulation (From Vik et al., 1985)

solution, and the nature and strength of the base. The most important parameters that govern the nature of the species are the basic ratio **r** and the aging temperature and time.

The recent development of inorganic polymeric coagulants for water and waste-water treatment has been comprehensively reviewed (Jiang and Graham, 1997a). Some relatively new kinds of such coagulants are of particular interest. Polyaluminium silicate sulphate (PASS) (Arnold-Smith et al., 1997) is commercially available and has been used in drinking-water treatment at full scale. It is claimed that optimal and stable coagulant species of PASS can be prepared by controlling the temperature and agitation speed, as well as the molar ratio of Al to Si.

Another new iron-based polymeric coagulant, polyferric sulphate (PFS) (Jiang et al., 1993), has been developed and systematically studied. In general, PFS is prepared by a technique involving the oxidation of ferrous state iron solution under conditions of high temperature and/or high pressure, and subsequently aging with heating and/or base addition.

More recently, a new kind of polymeric inorganic coagulants, poly-alumino-ferric sulphate (PAFS) (Jiang and Graham, 1997b), has been developed and evaluated for water treatment. PAFS is a pre-polymerised mixed solution of aluminium and iron, and its properties and performance generally vary with the total metal-ion concentration, the molar ratios of Al-to-Fe, and OH-to-metals.

Coagulation/flocculation by inorganic metal coagulants

The use of inorganic metal salts (normally Al/Fe(III) salts) for coagulation/flocculation is very well-established in the field of water treatment, although real progress in the understanding of the fundamental scientific mechanisms involved has been made only relatively recently. In simple terms, the mechanisms can be summarised as: charge neutralisation and sweep coagulation (See Figs. 1 and 2). Charge neutralisation, as a principal mechanism, typically occurs in low pH (<6.5), low ionic strength waters (e.g. upland waters) and compared to sweep coagulation generally requires a lower coagulant dose and produces less sludge; in such conditions coagulant overdosing may cause colloid restabilisation and thus worsen treatment performance. Sweep coagulation, in contrast, occurs principally at near neutral pH and at coagulant doses greater than 0.03 mM as Fe or 0.05 mM as Al and 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 mixing process can have a major effect on coagulation/flocculation with Al/Fe(III) salts. The conventional method of application is to have a fairly brief 'rapid-mix' period (< 5 min) at quite a high rate of shear, followed by a much longer period (< 30 min) of slow stirring, during which orthokinetic flocculation takes place. During the rapid-mix period, the hydrolysis, adsorption, and precipitation processes are probably completed, together with some initial flocculation.

As well as being extensively used for the coagulation/flocculation of suspended particles, Al/Fe(III) salts are also able to remove dissolved natural organic matter (NOM), especially high molecular mass materials such as humic substances, which cause colour in natural waters. This is achieved by a combination of precipitation, in the form of a colloidal metal-humate complex, followed by flocculation of the precipitates. Adsorption of organic matter on metal hydroxide particles may also be involved. In this application, optimal pH values are somewhat lower than neutral. Because of the strong interaction with humic substances, the presence of these materials can lead to significantly higher dosages of Al/Fe(III) salts required to give coagulation/flocculation of suspended particles, and a linear relationship between the dosage of metal coagulants and the concentration of humic substances has been established.

Figs. 1 and 2 present the solubility of a range of hydrolysis species and the mechanisms of coagulation of coloured waters using alum and ferric chloride. Equilibria of Al and Fe (III) have been listed in Table 1. The coagulant dose and coagulation pH are the two of the most important factors to influence the hydrolysis species formed, the coagulation mechanism and coagulation performance. Solubility and equilibria of Al/Fe(III) hydrolysis species are pH and metal concentration dependent. Taking Fe(III) coagulant as an example (see Fig. 2), when the pH and Fe(III) concentration of the solution are below 2 and above 10 mM, respectively, the predominant species are Fe^{3+} ions, but when the pH of the solution is in the range of 2 to 8, the main species are $Fe(OH)_2^+$ and $Fe(OH)^{2+}$. Destabilisation does not occur when the dose of Al/Fe(III) coagulant is below a critical value (e.g. < 0.01 mM as Fe), but overdosing will cause restabilisation at low pH values (e.g. pH < 5). For both high pH (> 6.5) and coagulant dose (>0.03mM), amorphous ferric hydroxide precipitates are formed which enmesh and coprecipitate the colloidal impurities and settle together.

Other research studies have also shown the effect of Ca on the improved destabilisation of colloidal particles and NOM when

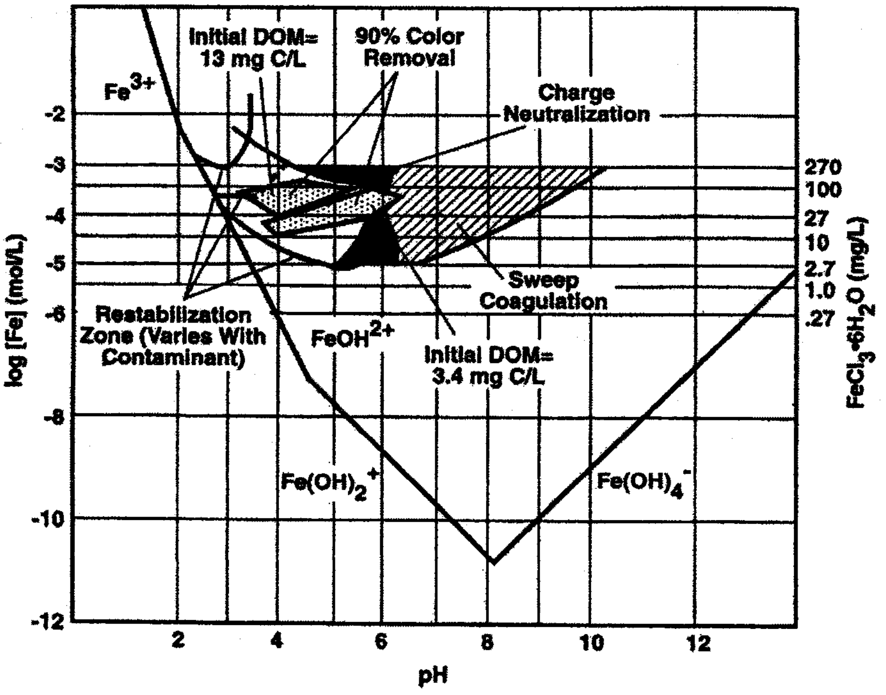

Figure 2
Operational diagram for ferric chloride coagulation
(From Amirtharrajah et al., 1993)

moderate to high concentrations (> 4 mM) of Ca have been employed or are present in water (e.g. Chang and Singer, 1991). Ca complexes and neutralises some of the charges associated with particles and aqueous NOM, thereby reducing the net surface charge of them. Since the valency of Ca is two, relatively high concentrations of Ca are required, compared to the trivalent Al/Fe cations, to compress the double layer and to reduce the surface charge of colloids according to the Schulz and Hardy rule and DLVO theory. A number of studies (Dowbiggin and Singer, 1989, Edwards and Benjamin, 1991, Chandrakanth and Amy, 1996a, Chandrakanth et al., 1996b) have indicated that coagulation can benefit from the use of pre-ozonation, but only if the pre-ozonated NOM can bind more Ca after ozonation. An increase in Ca association with the ozonated NOM results in the inhibition of adsorption of anionic species (such as oxalate) onto the colloidal particle surface. Also, an increase in ligand sites on the surface-sorbed NOM by ozone leads to increased NOM complexation with Ca. These effects lead to a reduction in particle stability through surface charge reduction.

Overall performance of pre-polymerised coagulants in comparison with conventional coagulants for water and waste water treatment

Pre-polymerised inorganic coagulants have been used in the full-scale treatment of waste water and industrial effluent, and some of them been used in drinking-water treatment. The results of a range of studies have shown that polyaluminium chloride (PAC) (Dempsey et al., 1984) and polyferric chloride (PFC) (Leprince et al., 1984) have a high treatment efficiency for turbidity, heavy metals, and chemical oxygen demand (COD), and a superior performance at low water temperature in water and waste-water treatment. However, PFC (Leprince et al., 1984; Tang and Stumm, 1987, Gray et al., 1995) has not shown a superior performance in comparison to ferric chloride (FC) for removing colour and NOM from natural surface waters. Notwithstanding this, one advantage of the use of PFC is its lower sensitivity to water temperature variation, which is of particular benefit to the water industry.

PASS (Arnold-Smith et al., 1992) is commercially available now and has been used in drinking-water treatment in Europe, North America and Asia. Laboratory- and full-scale tests have shown that compared to conventional AS and FC or FS, PASS needs less pH adjustment and a lower dose to achieve the equivalent treatment performance. PASS has also demonstrated better performance at low temperature, improved removal of NOM and filtration properties, and lower coagulant residual concentrations in the treated water.

For removing particulate materials and NOM from surface water, PFS has shown a superior performance to conventional coagulants (e.g. Jiang et al., 1994; 1996a; 1996b). The reduction of turbidity and NOM was found to be greater with PFS than FS (or FC) for the same coagulant dose used, and 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. PFS has also demonstrated a high removal efficiency for algae and algal-derived organic matter (Jiang et al., 1993).

Tenny and Derka (1992) compared the treatment efficiency of hydroxylated ferric sulphate (HFS) with AS at two water treatment plants in the city of Highland Park, Illinois, USA. HFS was found to produce either an equal or superior treated water quality to AS. The main advantage in the use of HFS, however, was the reduction of the treatment cost, comprising a 38% saving in the costs of the coagulant and a lower cost in sludge disposal due to a denser sludge and subsequently faster dewatering.

Other applications of polymeric coagulants include the pre-treatment of waste waters from various industries, such as dyes, tannery, paper and pulp, and the treatment of waste sludges. The general results from these studies (Mikami et al., 1984; He et al., 1987; Wu and Liu, 1989; Du, 1990) have shown that polymeric coagulants have:

- a higher treatment efficiency for turbidity, colour, heavy metals and COD, based on the same equivalent coagulant dose;
- a superior working performance at lower water temperatures (e.g. 4°C);
- lower Fe residuals;
- lower coagulant cost to achieve the same removal efficiency; and
- faster sludge settling rates and lower costs for sludge dewatering.

In general, the superior performance of the polymeric inorganic coagulants is believed to be due to the presence of a range of preformed polymeric species having both high cationic charge and medium to high molecular weight. Recent studies (Jiang and Graham, 1998) have investigated the fundamental behaviour of the coagulant hydrolysis and precipitation after dosing into the bulk water and the nature of the resulting solid phase that is formed. The results have suggested that the preformed polymeric species with high cationic charge are able to persist long enough to substantially enhance the rate of colloid charge neutralisation and chemical complexation. Such studies have provided valuable information of how and why polymeric coagulants behave in a different way to conventional coagulants.

Phosphorus removal by chemical precipitation and coagulation

Phosphorus occurs in natural water and waste waters mainly as inorganic phosphates such as orthophosphates and polyphosphates. Both domestic and industrial waste flows are the major sources of phosphorus arising in municipal waste water. About 30 to 50% of the phosphorus in domestic waste water comes from human wastes and the remaining 50 to 70% comes from synthetic detergents, as these contain phosphate components that are used for clothe-washing. The industrial sources of phosphorus generally originate from fertiliser manufacturing, commercial laundry and so on.

The presence of excess phosphorus in the effluent discharged to natural water bodies has long been known to be the cause of algal blooms and eutrophication. The average molar ratio of nitrogen, phosphorus and carbon in algal protoplasm is approximately 15:1:105 and if any of these components is less than this ratio, it will limit the algal growth. It can be seen therefore, that very small amounts of phosphorus can cause substantial algal growth and its removal is more effective compared to nitrogen for preventing eutrophication.

One of the main problems in drinking-water management is the presence of varieties of algae in raw waters, especially for eutrophic water bodies during conditions favourable to rapid algal growth. These problems include the presence of taste and odours, clogging of filters (Ives, 1955), and the formation of disinfection by-products such as trihalomethanes and haloacetic acids (Hoehn et al., 1980; Oliver and Shindler, 1984; Wachter and Andelman, 1984). The algae are a heterogeneous group of cryptogamic plants which have little in common with each other except their characteristic oxygen evolving type of photosynthesis. They exhibit great diversity in size and appearance, with unicellularity and multicellularity.

Because of the problems associated with algal blooms and eutrophication of fresh waters, attempts have been made to reduce the concentration of phosphate entering water bodies. Phosphate may enter water bodies either from point sources (e.g. sewage outfalls) or diffuse sources (e.g. runoff from farmland). In Europe, legislation has been promulgated by the European Community (EU) (the ‘Urban Waste Water Directive’) which will, amongst other restrictions, limit the phosphorus concentration discharged into sensitive water courses from treatment works to 2 mg/ℓ, for works serving population equivalents of 10 000 to 100 000, and 1 mg/ℓ for works serving population equivalents greater than 100 000 (Horan, 1992). At present, typical UK domestic waste waters contain phosphorus concentrations in the range of 10 mg/ℓ (Horan, 1992).

Phosphate removal using chemical precipitation and coagulation has been carried out for a number of years (e.g. Kirk et al., 1984; Diamadopoulos and Vlachos, 1984). Precipitation and coagulation are two distinct processes for removing impurities from water, although coagulation also involves precipitation. Coagulation is based on the destabilisation of stable particulate suspensions in water, while chemical precipitation is based on the formation of an insoluble product compound. The mechanism of chemical phosphate removal may involve the two processes together and is influenced by the aqueous characteristics such as pH. The following sections will firstly detail the removal of phosphorus by chemical precipitation and then review the performance and mechanism of phosphate removal by coagulation using either conventional or pre-polymerised inorganic coagulants.

Phosphate removal by chemical precipitation

Chemical precipitation is a commonly used process in water treatment. The removal of impurities from water by precipitation depends on the solubility of the various complexes formed in water. Experience with this process has produced a wide range of treatment efficiencies.

The metal ions involved in the precipitation of phosphate in water treatment are aluminium, ferric iron (Fe(III)), ferrous iron (Fe(II)), calcium and magnesium. Equilibria of the solubility of phosphates can be seen in Table 2 and the related solubility of the metal phosphates can be seen in Fig. 3, which shows that $FePO_4$(s) (strengite) and $AlPO_4$ (s) (variscite) are the stable solid phases if phosphate is precipitated in the pH range of 5 to 7. The pH of minimum solubility of $AlPO_4$ occurs at pH 6 which is one unit higher than that of $FePO_4$ (s) (pH 5). At higher pH values (pH > 7), the predominant phosphate precipitate is $Ca_{10}(PO_4)_6(OH)_2$ which has the lowest solubility among all the phosphate solids. If the pH of the water to be treated is above 6 and the water consists of Ca, the $Ca_{10}(PO_4)_6(OH)_2$ should be precipitated naturally. Moreover, according to Fig. 3, if the pH value is greater than 8 and the Ca concentration is high enough to precipitate the PO_4, the concentration of residual soluble phosphate will be less than 0.1 µg/ℓ, which can be considered as complete PO_4 precipitation. Adding Ca ions into water and raising the pH value, therefore, will be greatly beneficial to the removal of PO_4.

Phosphorus removal with lime is a non-stoichiometric process, as the lime dosage is not dependent on the concentration of phosphate removed but on the solubility product of $Ca(OH)_2$ which is frequently exceeded as the pH of the water increases and virtually all of the PO_4 will precipitate at pH values above 10. Lime is therefore ideal for removing high concentrations of PO_4 from small quantities of effluent (Farrimond and Upton, 1993).

The use of lime in the pretreatment of municipal waste water before the biological process has been studied. An equilibrium model (Marani et al., 1997) for predicting optimal treatment conditions to assure satisfactory phosphate removal efficiency has been developed which assumes phosphate and carbonate solubility is controlled by metastable $Ca_4H(PO_4)_3$ and $CaCO_3$, respectively. The model predicts that lime addition up to pH 9 may assure efficient removal of phosphorus and prevent carbonate precipitation which causes high lime dose and excessive sludge production.

Al and Fe salts are conventionally considered as precipitants for P removal. However, the understanding that the use of these salts leads to the direct formation of insoluble $AlPO_4$ and $FePO_4$ is now considered to be too simple to explain the P removal. Since the pH in natural surface water bodies is in the range of 5 to 9, dosing Al or Fe(III) salts into such kinds of water leads to Al^{3+} or Fe^{3+} ions hydrolysing rapidly, forming a range of hydrolysis species, and ultimately, metal hydroxide. Simple Al^{3+} or Fe^{3+} ions are unlikely to exist in such water bodies and therefore, the $AlPO_4$ (s) and $FePO_4$ (s) might not form or only form to a limited extent due to competition reactions between the Al^{3+} or Fe^{3+} ion hydrolysis and PO_4 precipitation. Alternatively, Ca and Mg ions may well be the principal ions for the PO_4 precipitation in natural surface water sources. In view of this, the use of Al or Fe(III) salts for PO_4

TABLE 2
EQUILIBRIA RELATED TO THE SOLUBILITY OF PHOSPHATES OF FE^{3+}, AL^{3+}, FE^{2+}, CA^{2+} AND MG^{2+}

Reaction	log K (25°C, I=0)
$FePO_4 \cdot 2H_2O$ (s) (strengite) $\rightarrow Fe^{3+} + PO_4^{3-} + 2H_2O$	-26
$AlPO_4 \cdot 2H_2O$ (s) (varsitite) $\rightarrow Al^{3+} + PO_4^{3-} + 2H_2O$	-21
$CaHPO_4$ (s) $\rightarrow Ca^{2+} + HPO_4^{2-}$	-6.6
$Ca_4H(PO_4)_3$ (s) $\rightarrow 4Ca^{2+} + 3PO_4^{3-} + H^+$	-46.9
$Ca_{10}(PO_4)_6(OH)_2$ (s) $\rightarrow 10Ca^{2+} + 6PO_4^{3-} + 2OH^-$	-114
$Ca_{10}(PO_4)_6(F)_2$ (s) $\rightarrow 10Ca^{2+} + 6PO_4^{3-} + 2F^-$	-118
$Ca_{10}(PO_4)_6(OH)_2$ (s) $+ 6H_2O \rightarrow 4[Ca_2(HPO_4)(OH)_2] + 2Ca^{2+} + 2HPO_4^{2-}$	-17
$CaHAl(PO_4)_2$ (s) $\rightarrow Ca^{2+} + Al^{3+} + H^+ + 2HPO_4^{2-}$	-39
CaF_2 (s) $\rightarrow Ca^{2+} + 2F^-$	-10.4
$MgNH_4PO_4$ (s) $\rightarrow Mg^{2+} + NH_4^+ + PO_4^{3-}$	-12.6
$FeNH_4PO_4$ (s) $\rightarrow Fe^{2+} + NH_4^+ + PO_4^{3-}$	-13
$Fe_3(PO_4)_2$ (s) $\rightarrow 3Fe^{2+} + 2PO_4^{3-}$	-32

From Stumm and Morgan (1996)

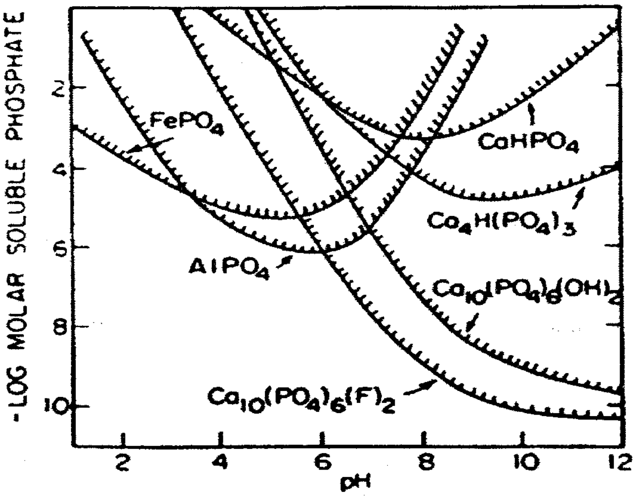

Figure 3
Solubility of metal phosphates
(From Stumm and Morgan (1996))

removal may be related more to the coagulation mechanism rather than chemical precipitation; this will be detailed in the following section.

Process and mechanism of PO_4 removal by coagulation/flocculation

In general, two major mechanisms have been considered to be linked to the coagulation of PO_4 with Al/Fe(III) salts:

- Formation of Al/Fe-hydroxo-phosphate complexes: $Me(OH)_{3-x}(PO_4)_x$. These complexes either adsorb onto positively charged Al/Fe(III) hydrolysis species or act as centres of precipitation for Al/Fe(III) hydrolysis products.
- Adsorption of PO_4 ions on to the Al/Fe(III) hydrolysis species. In the case of using conventional coagulants such as $Al_2(SO_4)_3$ or $FeCl_3$, amorphous $Al(OH)_3$ or $Fe(OH)_3$ are the predominant hydrolysis species in water treatment practice.

If pre-polymerised inorganic coagulants are used, polymeric species are predominant, and PO_4 ions may also complex with the positive sites of such species.

Phosphorus stoichiometry has been established based on synthetic or model waste waters and without considering the hydrolysis reactions of Al or Fe(III) salts. For Al salts, an empirical formula $Al_{1.4}PO_4(OH)_{1.2}$ has been suggested (Fettig et al., 1990) instead of $AlPO_4$. Thus, for the efficient removal of P, the molar ratio of Al to P appears to have increased from 1:1 to 1.4:1. For Fe (III) salts, a similar formula has been established and the molar ratio of Fe to P has also been increased. However, in the treatment of real waste waters the situation is more complicated than indicated by model waters. When an Al or Fe(III) salt is added into waste water, a range of competing reactions can occur, involving:

- Al or Fe(III) salt hydrolysis to form a range of hydrolysis species including some polymeric species and metal hydroxide;
- the formed hydrolysis species complex or adsorb the phosphate ions; and
- the formed coagulating species destabilise the other contaminants present in the waste water. In this way, these competing reactions increase the amount of Al/Fe(III) coagulants required to remove P.

An example of using real waste effluent to evaluate the coagulation performance for the removal of P is shown in Table 3. The coagulation pH for $Al_2(SO_4)_3$ was 6.5 and for $FeCl_3$ was 6, respectively, which were considered as the optimal pH under the study conditions. It can be seen that for greater removal percentages of total phosphate, the required dose of Al or Fe increases, and that all of the doses significantly exceed the theoretical demand. Under such conditions, however, phosphate removals are also combined with the removal of other impurities, such as colloidal particulate materials and organic substances (e.g. Storhang and Rusten, 1990).

The efficiency of phosphate removal has been found to depend on the pH, phosphate concentrations and suspended solids in the waste waters. A general model (Fettig et al., 1990) has been proposed to describe the phosphate removal process in terms of such factors, and is as follows:

$$[PO_4^{3-}]_{res} = 32.89 - 5.7\,(Al/P_o) - 9.77pH + 1.65\,(Al/P_o)^2 + 0.989\,pH^2 - 0.463\,(Al/P_o)\,pH$$

where, $[PO_4^{3-}]_{res}$ is the concentration (mg/ℓ as P) of the residual orthophosphates in the treated water, (Al/P_o) is the molar ratio of aluminium dose to the initial concentrations of orthophosphates.

The treatment strategy for phosphorus removal has been studied in order to increase the removal efficiency. Coagulation combined with filtration is a simple and effective method and a recent study (Xie et al., 1994) showed that when using polyaluminium chloride as a coagulant (with a Al/P molar ratio of 3 for the first period and then reducing to 2) and a dual media filter bed (with sand of 0.6 mm in diameter and anthracite of 1.2 mm), over 80% phosphorus could be removed and the filter bed could be operated continuously over 20 h. The combination of chemical and biological treatment steps have been reported to be capable of reducing the orthophosphate concentrations to as low as 0.01 mg/ℓ, with average total phosphorus levels of around 0.5 mg/ℓ (Thomas et al., 1996).

TABLE 3
COMPARISON OF ALUMINIUM SULPHATE AND FERRIC CHLORIDE AS COAGULANTS IN THE REMOVAL OF TOTAL PHOSPHATES[#]

Phosphate removal percentages	Ratio of metal to phosphorus by weight (Al or Fe(III) /P) $Al_2(SO_4)_3$ Primary treatment	$Al_2(SO_4)_3$ Secondary treatment	$FeCl_3$ Primary treatment	$FeCl_3$ Secondary treatment
90	2.05 (2.36)*	2.80 (3.22)	2.35 (1.3)	5.0 (2.77)
95	2.55 (2.93)	6.25 (7.18)	3.70 (2.05)	6.50 (3.60)
99	3.75 (4.31)	-	4.20 (2.33)	-

[#] From Narasiah, 1991
* Molar ratio in parenthesis

Use of pre-polymerised coagulants for phosphate removal has been studied previously. A range of published studies have shown that the higher the OH/Al ratio of polyaluminium chloride coagulant, the greater the dose that was required for the removal of phosphate (Fettig et al., 1990; Ødegaard et al., 1990; Ratnaweera et al., 1992; Diamadopoulos and Vlachos, 1996; Boisvert et al., 1997). Other researchers (e.g. Fettig et al., 1990; Ødegaard et al., 1990; Ratnaweera et al., 1992) have excluded this finding and suggested that the efficiency of P removal by coagulation depended on the charge density of the metal-hydrolysed species. They considered that partially hydrolysed metal species such as in polyaluminium chloride have a reduced total cationic charge and therefore should be less efficient in the charge neutralisation of P species. Based on this explanation, a single metal ion such as Al^{3+} should have the maximum, and a metal hydroxide (e.g., $Al(OH)_3$) have the minimum, ability to react and remove the PO_4. However, it has been discussed earlier that a range of hydrolysed Al/Fe(III) species are formed when an Al/Fe(III) salt is dosed into water, and hence the species that can react with the PO_4 will be a range of hydrolysed products, including the metal hydroxide, rather than the simple Al^{3+} and/or Fe^{3+} ions. A recent study (Galarneau and Gehr, 1997) has concluded that $Al(OH)_3$ has a significant removal efficiency for PO_4. The adsorption mechanism has strongly been suggested, which involves the PO_4 sorption on to $Al(OH)_3$, no matter how the $Al(OH)_3$ are provided, either from directly dosing alum to the water or from aluminium hydroxide precipitates (preformed aluminium flocs or sludges from water treatment plant). Thus, the PO_4 removal performance using Al salts can not be explained by the charge effect only.

Other research studies have indicated that PO_4 sorption on to coagulant floc is the principal mechanism of PO_4 removal for both Al/Fe(III) salts and/or their pre-hydrolysed forms. Work conducted by Hatton and Simpson (1985), using four raw sewage samples from different locations in England and containing moderate and high phosphate levels, showed that polyaluminium chloride was superior to $Al_2(SO_4)_3$ with respect to total P removal, although the removal efficiency of orthophosphates with polyaluminium chloride and $Al_2(SO_4)_3$ were similar for equivalent coagulant dosages. They attributed the superior performance of polyaluminium chloride (for total P removal) to the specific properties of PAC which could allow extra PO_4 to be removed by superior adsorption into the floc blanket.

The comparative performance of PO_4 removal with polyiron sulphate (PFX, OH/Fe(III) molar ratio of 0.37) and with $FeSO_4Cl$ showed that for 80% PO_4 removal from a soft water, the dosage of PFX was approximately 20% less than that of $FeSO_4Cl$ (Ødegaard et al., 1990). For achieving 80% PO_4 removal from hard water, the dose of PFX required was also lower and $FeSO_4Cl$ failed to achieve this removal percentage. It is clear from the results detailed above that there remains considerable uncertainty about the precise mechanism and performance of P removal by pre-polymerised metal coagulants and this needs to be investigated further.

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 colloidal impurities from water. By development and use of polymeric inorganic coagulants, the coagulation performance with Al or Fe coagulants can be improved for removing both particles and dissolved organic matter.

Eutrophication is widely recognised as an important water quality problem and control strategies have focused on P which is a limiting nutrient for algal development. Chemical precipitation and coagulation are commonly used methods for removing P from water. However, they are distinctly different processes whereby the former is related to the compound solubility and the latter depends on the destabilisation–adsorption mechanism. Currently, there is considerable uncertainty about the precise mechanisms and overall performance of P removal by pre-polymerised metal coagulants and this needs to be investigated further.

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