Hydrolyzing metal salts as coagulants*

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Abstract: Aluminium and ferric salts are widely used as coagulants in water and wastewater treatment. They are effective in removing a broad range of impurities from water, including colloidal particles and dissolved organic substances. Their mode of action is broadly understood in terms of essentially two mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous precipitate of metal hydroxide. The relative importance of these two mechanisms depends on many factors, especially pH and coagulant dosage.

Alternative coagulants based on prehydrolyzed forms of aluminium or iron can be more effective than the traditional materials in many cases, but their mode of action is not completely understood, especially with regard to the role of charge neutralization and hydroxide precipitation.

Basic principles of colloid stability and metal ion hydrolysis are briefly reviewed, and the action of hydrolyzing metal coagulants is then discussed, with some examples from recent experimental studies. Although it is possible to interpret results reasonably well in terms of established ideas, there are still some uncertainties that need to be resolved

INTRODUCTION

Hydrolyzing metal salts, based on aluminium or iron, are very widely used as coagulants in water treatment. These materials have been applied routinely since early in the 20th century and play a vital role in the removal of many impurities from polluted waters. These impurities include inorganic particles, such as clays, pathogenic microbes, and dissolved natural organic matter. As well as traditional additives, such as aluminium sulphate ("alum") and ferric chloride, other products containing prehydrolyzed metal ions are now commonly used. These include a range of materials known as polyaluminium chlorides.

Although the mode of action of metal coagulants is broadly understood, there are still some uncertainties, especially with regard to the nature of the active species, the role of dissolved salts in water, and the strength and break-up of aggregates formed. The mechanisms of action of prehydrolyzed forms are also by no means fully understood.

A brief review of the current position will be given, together with some examples of recent experimental results on model systems. Most attention will be paid to aluminium-based coagulants, although the broad principles also apply to ferric salts.

COLLOID STABILITY AND INSTABILITY

Particles in aqueous dispersions may interact in several ways, and their interactions determine whether the dispersion is *stable* or not. In this context, stability implies that the particles remain in a dispersed state for long periods, rather than forming aggregates (*coagulation* or *flocculation*). For long-term stability, some form of repulsion must operate between particles; otherwise, collisions of particles would result in attachment as result of the universal *van der Waals* forces of attraction. In water, particles are nearly always charged, and electrical repulsion between them may be responsible for their stability. A quantitative theory of colloid stability was developed by Deryagin and Landau [1] and Verwey and Overbeek [2] and now widely known as *DLVO theory*. There are other forms of interaction between particles, such as hydration and hydrophobic forces and effects associated with adsorbed polymers [3], but these will not be considered here.

DLVO theory treats colloid stability in terms of a balance between van der Waals attraction and electrical repulsion between particles. In practice, only the latter can be modified to a significant extent, and repulsion can be greatly affected by changing the ionic strength of the suspending medium or by modifying the surface charge of the particles. Increasing ionic strength effectively screens electrical repulsion and allows particles to approach each other more closely, so that van der Waals attraction may predominate. By adding salts that have *specifically adsorbing counterions* (i.e., opposite in charge to the particles) the particle surface charge may be decreased or neutralized so that repulsion between particles is reduced or eliminated altogether. This can be an effective way of promoting coagulation and is often used in practice. In such cases, addition of excess coagulant can cause charge reversal and *restabilization* of particles.

Another very important means of destabilizing particles is through the action of adsorbing polymers. Polymers of high molecular weight can adsorb simultaneously on two or more particles and bind them together by a process known as *polymer bridging.*

The action of hydrolyzing metal coagulants may be through charge neutralization effects or involve the binding of particles together by precipitated hydroxide.

HYDROLYSIS OF METAL IONS

Basic concepts

All ions in water are hydrated to some extent. In the case of Al^{3+} and Fe^{3+}, there is a primary hydration shell with six octahedrally coordinated water molecules, e.g., $Al(H_2O)_6^{3+}$. Hydrolysis of such ions is often represented as a sequential replacement of the water molecules by hydroxyl ions, and can also be thought of as a progressive deprotonation of water molecules in the primary hydration shell [4]. The simplest representation, for Al^{3+}, omitting the hydration shell for convenience, is:

$$Al^{3+} \rightarrow Al(OH)^{2+} \rightarrow Al(OH)_2^{+} \rightarrow Al(OH)_3 \rightarrow Al(OH)_4^{-}$$
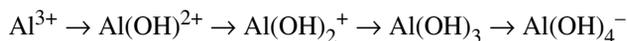
Since each step involves the loss of a proton, increasing pH causes the equilibria to be shifted to the right. Aluminium hydroxide has low solubility in water, and precipitation occurs at intermediate pH values. Further increase of pH causes the soluble aluminate ion to be formed. A similar sequence can be written in the case of Fe^{3+}. In this case, the hydroxide is much less soluble than aluminium hydroxide.

Because of the formation of insoluble hydroxides (and also polynuclear species—see below), the determination of hydrolysis constants is difficult, and there are significant discrepancies between published values (see e.g., Wesolowski and Palmer [5]). Hydrolysis constants may be defined for the successive deprotonations in terms of the following equations:

$$M^{3+} + H_2O \leftrightarrow M(OH)^{2+} + H^+ \qquad K_1$$
$$M(OH)^{2+} + H_2O \leftrightarrow M(OH)_2^{+} + H^+ \quad K_2$$

$$M(OH)_2^+ + H_2O \leftrightarrow M(OH)_3 + H^+ \qquad K_3$$

$$M(OH)_3 + H_2O \leftrightarrow M(OH)_4^- + H^+ \qquad K_4$$
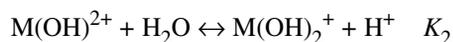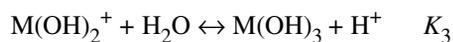
It is also necessary to define a solubility constant for the solid hydroxide:

$$M(OH)_3 \leftrightarrow M^{3+} + 3OH^- \qquad K_S$$
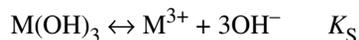
Although the most stable solid forms are gibbsite and goethite for aluminium and iron, respectively, these reach equilibrium very slowly (up to several months or more). It is usual to take solubility constants for amorphous precipitates, K_{Sam}, since these form quite rapidly and are much more relevant in practical applications of coagulants. However, solubilities of amorphous hydroxides are not known precisely and only estimated values can be given. Table 1 gives values for hydrolysis and solubility constants (in pK form), taken from Wesoloski and Palmer [5] for Al and from Flynn [6] for Fe. The values are for conditions of zero ionic strength and 25 °C. Reference [5] gives extensive data for Al at other temperatures and ionic strengths.

Table 1 Hydrolysis and solubility constants for Al^{3+} and Fe^{3+} for zero ionic strength and 25 °C. (Values taken from references [5] and [6].)

	pK_1	pK_2	pK_3	pK_4	pK_{Sam}
Al^{3+}	4.95	5.6	6.7	5.6	31.5
Fe^{3+}	2.2	3.5	6	10	38

As Martin [7] has pointed out, the hydrolysis constants for Al cover a much narrower range than those for Fe, which was ascribed to a decrease in coordination number for Al from 6 to 4, in passing from the hexahydrate to tetrahedral aluminate. For Fe, the coordination number remains 6 for all hydrolyzed species. The effect on species distribution is quite marked, as shown in Fig. 1, which shows
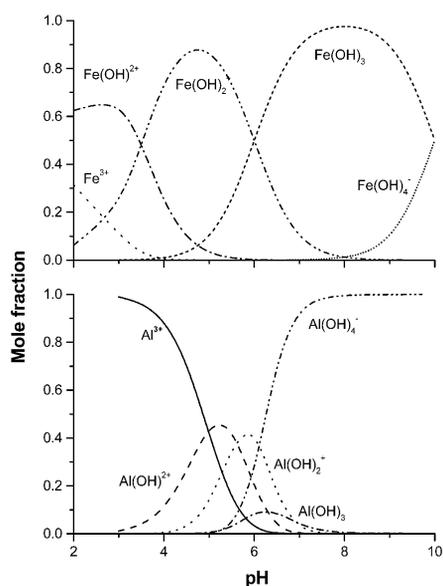
Fig. 1 Distribution of monomeric Fe and Al hydrolysis products as a function of pH.

the proportion of Al and Fe species in soluble form, in equilibrium with the amorphous hydroxide. In the case of Al, the dominant species in solution changes from Al^{3+} to $Al(OH)_4^-$ over little more than 1 pH unit. In contrast, the corresponding change for Fe occurs over a range of more than 8 pH units and intermediate species, such as $Fe(OH)_2^+$ and $Fe(OH)_3$, can represent more than 90% of soluble forms at intermediate pH values.

From the standpoint of coagulation, the total amount of soluble metal species is important. Figure 2 shows the concentration of monomeric hydrolysis products, in equilibrium with the amorphous hydroxide, over a range of pH values. For Al, there is a minimum solubility (about 2 μM) in the region of pH 6. Ferric species show a much lower solubility (around 20 nM) over a rather broad pH range.

These calculations can be significantly affected by the presence of certain anions, which form complexes with Al and Fe. These include fluoride, phosphate, and sulphate, which can give increased solubility of the metals, especially at lower pH values [8].

As well as effects on equilibrium species distribution, some anions can modify the rate of hydroxide precipitation. An important example is sulphate, which can enhance precipitation of aluminium hydroxide [9], essentially by association with highly charged polynuclear species (see below), thereby reducing the free energy barrier to the formation of solid particles. This is essentially a catalytic effect, since basic sulphates were not detected in the precipitates. Hayden and Rubin [10] found that the formation of settleable precipitates from aluminium sulphate solutions occurred over a much broader pH range than from solutions of aluminium nitrate.

Another very important aspect is the complexation of metals with dissolved organic matter in natural waters, but this will be discussed later in relation to the removal of organic matter by coagulation.
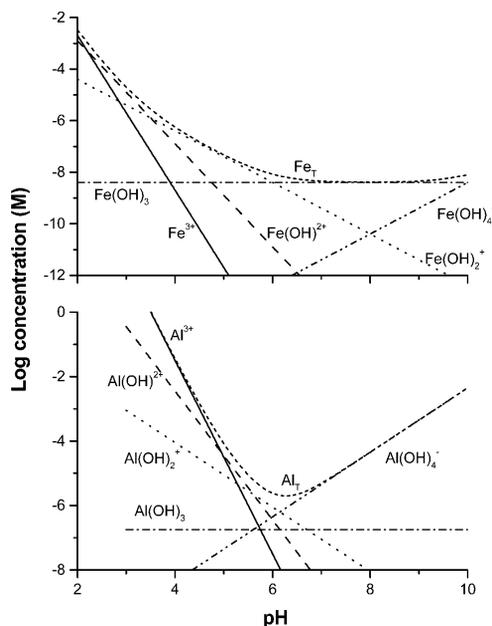
Fig. 2 Concentration of soluble Fe and Al species in equilibrium with amorphous hydroxides. (Fe_T and Al_T represent total soluble species.)

Polynuclear species

As well as the simple monomeric hydrolysis products considered above, it is well known that highly charged metal ions can form a range of polynuclear species [4]. For Al, these include $Al_2(OH)_2^{4+}$ and

$Al_3(OH)_4^{5+}$, and there are equivalent species for Fe. Appropriate formation constants are known for the dimers and trimers, but at low total metal concentration they do not greatly affect solution compositions, such as those shown in Figs. 1 and 2. Various polymeric species, such as $Al_6(OH)_{12}^{6+}$, have been proposed, but their existence has not been convincingly demonstrated. They might be regarded as intermediate forms in the conversion of soluble metal salts to solid precipitates. It is known that hydrolysis-precipitation processes at ordinary temperatures are very slow and that true equilibrium can take months or years to achieve.

One polynuclear hydrolysis product of aluminium is now well established and of some practical importance. This is the so-called "Al_{13}" polymer, $Al_{13}O_4(OH)_{24}^{7+}$, which can be formed by controlled neutralization of aluminium salt solutions. This has the Keggin structure, with one tetrahedral Al surrounded by 12 Al octahedra with shared edges. The structure has been confirmed by ^{27}Al NMR studies [11], small angle X-ray methods [12], and potentiometric titration.

Another Al hydrolysis-polymerization model involves the formation and condensation of hexameric rings, leading eventually to precipitation [13], but this "core-link" model is now less popular, as a result of studies on the formation of the tridecamer species Al_{13}. However, the mechanism whereby Al_{13} is transformed into a precipitate is not fully understood [14].

The speciation of Al solutions can be conveniently studied by a timed colorimetric reaction with ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid). This method was introduced by Smith [15] and is based on the observation that different forms of Al react at varying rates with ferron. Mononuclear Al species (Al_a) react almost instantaneously and polynuclear species (Al_b) much more slowly. Colloidal or precipitated Al (Al_c) shows practically no reaction with ferron. The proportion of polynuclear species (Al_b) determined by the ferron technique corresponds quite well with results from membrane filtration tests [16] and with the proportion of Al_{13} from NMR studies [17]. Typically, the proportion of the various species is determined as a function of the degree of neutralization of the aluminium salt solution, B (=OH/Al). For 0.1 M $AlCl_3$ solution, titrated with 0.5 M NaOH, the proportion of Al_b increased from around 33 to 83% as B was raised from 1.0 to 2.5. For values of B above 2.5, the amount of precipitate (Al_c) increases significantly [17]. In the same study, it was shown that the Al_b fraction was quite stable to dilution and to changes in pH, and only slowly converted to other forms. This is in marked contrast to monomeric hydrolysis products, which respond very rapidly to changes in chemical conditions. It is doubtful whether Al_{13} forms under conditions where aluminium salts are added to water at around neutral pH, to give low Al concentrations (typical of water treatment conditions). In this case, it is thought that monomeric hydrolyzed species predominate in solution and that amorphous precipitates form without the involvement of Al_{13} species.

Products based on prehydrolyzed aluminium are commercially used in water treatment applications and are generally known as *polyaluminium chloride* (see below). Many of these products contain large proportions of Al_{13}.

ACTION OF HYDROLYZING COAGULANTS

Charge neutralization

A simple mechanism for destabilization of negatively charged particles is the specific adsorption of cationic species from solution. Since aluminium and iron salts give cationic hydrolysis products, charge neutralization is a possible reason for the action of these materials as coagulants. Adsorption of cations on negative surfaces may occur for simple electrostatic reasons or by some form of surface complex formation. Since hydrolyzing coagulants are effective for a wide range of particle types, including bacteria, clays, and many others, it is unlikely that a single adsorption interaction is responsible.

It is commonly observed that particles can be destabilized by small amounts of hydrolyzing coagulant and that optimum destabilization corresponds with the neutralization of particle charge (determined, for instance, by electrophoretic mobility). Larger amounts of coagulant cause charge reversal,

so that the particles become positively charged and are thus *restabilized*. For relatively low particle concentrations, destabilization and restabilization typically occur with just micromolar concentrations of coagulant.

Although the species responsible for charge neutralization could be dissolved cationic hydrolysis products, it is clear from Fig. 2 that, for both Al and Fe, such species are only minor components at around neutral pH and above. It is not easy to determine how the presence of particles affects the distribution of hydrolyzed Al and Fe species, and kinetic factors might also be important. Although destabilization can occur at very low coagulant concentrations, these may still be well above the solubility limit for the amorphous hydroxide, especially for Fe (see Fig. 2). In such cases, it may be reasonable to think in terms of neutralization by charged precipitate. This could either be by a form of surface precipitation [18] or by the adsorption of colloidal hydroxide precipitated in bulk solution and transported to the particles. The latter mechanism is the basis of the *precipitation charge neutralization* (PCN) model [19]. In the case of aluminium hydroxide, the isoelectric point is around pH 8 [10], so that at lower pH values the precipitate would be positively charged and thus able to neutralize the negative charge of particles in water.

If charge neutralization is the predominant destabilization mechanism, then there should be a stoichiometric relationship between the particle concentration and the optimum coagulant dosage [20]. At low particle concentrations, low coagulant dosages should be required. Under these conditions, coagulation rates can be very low, and it is found that higher coagulant dosages are much more effective. This is due to extensive hydroxide precipitation and a process known as *sweep flocculation.*

Sweep flocculation

Although particles may be effectively destabilized by charge neutralization, there are two disadvantages in water treatment:

- Quite precise control of coagulant dosage is needed to give optimum destabilization.
- The particle collision rate and hence the coagulation rate depend on the square of the particle concentration and can be very low for dilute suspensions.

Both of these problems can be overcome if higher coagulant dosages are used, since considerable quantities of amorphous hydroxide precipitate are then formed. It has long been recognized [21] that, in many cases, optimal removal of particles from water is achieved under conditions of rapid hydroxide precipitation. In the case of aluminium coagulants, optimum pH conditions are close to the point of minimum solubility (see Fig. 2). Although precise mechanisms are still not fully understood, it is clear that impurity particles are enmeshed in the growing precipitate and hence can be removed from water by sedimentation. This process has become known as sweep flocculation, since particles are "swept out" of water by an amorphous hydroxide precipitate.

Sweep flocculation generally gives considerably improved particle removal than when particles are destabilized just by charge neutralization. At least part of the reason is the greatly improved rate of aggregation, owing to the increased solids concentration. Hydroxide precipitates tend to have a rather open structure, so that even a small mass can give a large effective volume concentration and hence a high probability of capturing other particles. It is also possible that binding of particles by precipitated hydroxide may give stronger aggregates.

The different mechanisms outlined above have led to the definition of four *zones* of coagulant dosage, with the following consequences for negatively charged particles:

Zone 1   Very low coagulant dosage; particles still negative and hence stable
Zone 2   Dosage sufficient to give charge neutralization and hence coagulation
Zone 3   Higher dosage giving charge neutralization and restabilization
Zone 4   Still higher dosage giving hydroxide precipitate and sweep flocculation

Example

An example of particle aggregation by charge neutralization and sweep flocculation is shown in Fig. 3. This shows the results of typical "jar test" experiments for a suspension of kaolin particles with aluminium sulphate as coagulant [22]. The particles were suspended in carbonate buffer, and the pH (after coagulant addition) was adjusted to 7.0. The coagulant was added to give different concentrations, and the suspension was stirred rapidly for a short period to ensure adequate mixing. The rapid mixing was followed by 15 min of slow stirring (50 rpm) to give opportunity for particle collisions and aggregate formation. The suspension was then allowed to settle for 20 min, and the residual turbidity was measured to give an indication of the degree of particle removal achieved. Immediately after the rapid mixing period, before appreciable coagulation had occurred, a sample was taken for determination of electrophoretic mobility (EM), which gives information on the surface charge of the particles.

Figure 3 shows the turbidity and EM data over a range of coagulant dosages up to 100 μM $Al_2(SO_4)_3$. There is a narrow range of concentrations (below 10 μM) where the EM values change from negative to positive, indicating reversal of particle charge by adsorbed cationic species. In this region, the residual turbidity goes through a minimum and then rises quite sharply to about the value for the original suspension. The minimum turbidity occurs at a coagulant dosage quite close to that giving zero EM, which strongly suggests coagulation as a result of charge neutralization. Restabilization at slightly higher dosages must then be due to charge reversal.

For coagulant dosages above about 20 μM, there is another region of reduced turbidity, but no significant change in the particle charge, since the EM value remains at about the same positive value. The turbidity in this region is significantly lower than in the charge neutralization region, and it is highly likely that hydroxide precipitation and sweep flocculation are responsible. Note that there is no restabilization at dosages up to 100 μM, since precipitation continues with increasing dosage. Since the isoelectric point of amorphous aluminium hydroxide is around pH 8, the precipitate is positively charged at pH 7, and the EM observed at the higher coagulant dosages is characteristic of the hydroxide rather than the clay particles.
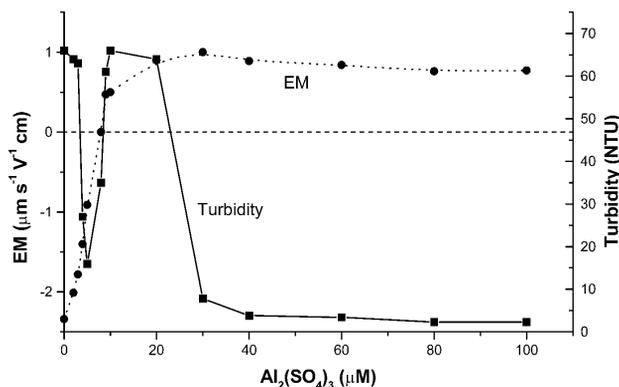
Fig. 3 Electrophoretic mobility (EM) and residual turbidity results for the coagulation of kaolin suspensions with varying dosage of aluminium sulphate at pH 7.

Removal of dissolved organic matter

As well as suspended particles, most natural waters contain dissolved natural organic matter (NOM), which needs to be removed. Hydrolyzing metal coagulants are often used for this purpose. Where dissolved organic matter is present in significant amounts (for instance, in highly colored waters), it can

be the main factor influencing the coagulant dosage. In fact, there is often a stoichiometric relation between the organic content of a water (usually measured as *dissolved organic carbon*, DOC) and the required coagulant dosage [23]. Optimum pH for removal of dissolved organics is usually rather less (typically, pH 5–6) than that for removal of suspended particles. When the coagulation process in water treatment is specially modified to ensure good removal of organic matter, it is often known as *enhanced coagulation*.

Organic matter in water consists mainly of humic substances, which have a rather complex and not fully characterized molecular structure. Nevertheless, they have a number of weak acid (mainly carboxylic) groups that ionize to give anionic sites at normal pH values in natural waters. There are two likely mechanisms for the removal of humic substances by hydrolyzing metal coagulants:

- Binding of metal species to anionic sites, thus neutralizing their charge and giving a reduced solubility. For fairly large molecules, this can lead to precipitation of the metal-humic complex, to form particles that can be removed by sedimentation or filtration.
- Adsorption of humic substances on amorphous metal hydroxide precipitate. At pH values around 5–6, the humic substances are negatively charged and Al and Fe hydroxides are positively charged, which would give strong adsorption and some charge neutralization.

In many practical cases, it is not easy to distinguish between these possible mechanisms, but in a recent study [24] both were shown to operate, depending on pH and coagulant dosage. Humic substances isolated from lake sediments in Xi'an, China were coagulated with aluminium sulphate at different pH values and over a range of dosages. The removal was monitored by the reduction in UV absorbance (at 254 nm) after a standard coagulation and sedimentation procedure. The electrophoretic mobility of the destabilized particles was determined immediately after rapid mixing of the coagulant. In this case, the EM values were converted to zeta potentials.

The results in Fig. 4 show the residual UV absorbance and zeta potentials as functions of alum dosage at pH 5.0. The alum dosage is expressed on the basis of humic substance concentration as mg Al per mg of total organic carbon (TOC). There is a region of significant reduction in UV absorbance between about 0.1 and 0.2 mg Al/mg TOC, which corresponds very well with the point at which the zeta potential reverses sign. This is strong evidence for a simple charge neutralization mechanism under these conditions. At higher alum dosages, there is another region where the absorbance is reduced, but this is not correlated with any significant change in zeta potential. The implication is that adsorption on a hydroxide precipitate is responsible for the removal.
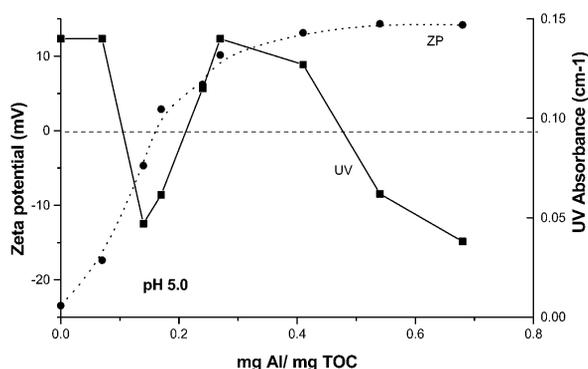
Fig. 4 Zeta potential (ZP) and UV absorbance (at 254 nm) after coagulation of humic substances with aluminium sulphate at pH 5 (see text).

At pH 7, the results are quite different. Figure 5 shows that there is an appreciable reduction in UV absorbance at around 0.2 mg Al/mg TOC, which gradually improves at higher dosages. The zeta potential remains negative over the whole dosage range, but approaches zero at the highest dosages. It is very likely that the removal of humic substances under these conditions is entirely by adsorption on precipitated aluminium hydroxide. The reduction in absorbance is slightly greater at the higher pH, especially at the higher alum dosages.
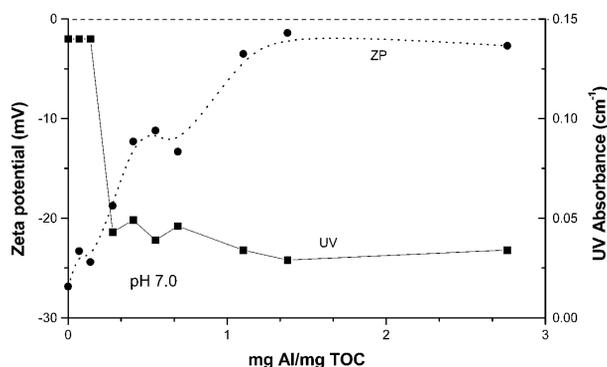
Fig. 5 As Fig. 4, but at pH 7.

Prehydrolyzed products

As well as traditional coagulants, based on Al and Fe salts, there are now many commercial products that contain prehydrolyzed forms of the metals, mostly in the form of polynuclear species (see above). In the case of Al, most materials are formed by the controlled neutralization of aluminium chloride solutions and are generally known as polyaluminium chloride (PACl). It is believed that many of these products contain substantial proportions of the tridecamer Al_{13}. Some information on the preparation of such materials and those based on iron is available [17] and no details will be given here.

The prehydrolyzed materials are often found to be considerably more effective than the traditional coagulants [25]. PACl products seem to give better coagulation than alum at low temperatures and are also claimed to produce lower volumes of residual solids (sludge). Because they are already partially neutralized, they have a smaller effect on the pH of water and so reduce the need for pH correction. However, the mechanisms of action of PACl and similar products are still not well understood.

Most explanations are in terms of the high charge associated with species such as Al_{13} and the consequent effectiveness in neutralizing the negative charge of colloids in water. The relatively high stability of Al_{13} means that it should be more readily available for adsorption and charge neutralization at around neutral pH. However, charge neutralization is not the only mechanism of coagulation and it is still not clear what role hydroxide precipitation plays in the action of prehydrolyzed coagulants.

It has been shown recently [26] that the volume of sediment produced in coagulation of clay suspensions by commercial PACl products is linearly proportional to the coagulant dosage. This implies that some form of sweep flocculation is operating, since the volume of hydroxide precipitate would be expected to depend on the amount of coagulant added. From dynamic studies with a range of hydrolyzing coagulants [27] it has been shown that PACl products give more rapid flocculation and stronger flocs than for alum at equivalent dosages.

Prehydrolyzed products are also effective for the removal of dissolved organic matter from water, but in this case they often appear to show no significant benefit over traditional coagulants.

CONCLUSIONS

The action of hydrolyzing metal coagulants is broadly understood, in terms of charge neutralization and effects associated with precipitated metal hydroxide. There are still some uncertainties, especially with regard to the role of various hydrolyzed species. The reasons for the effectiveness of prehydrolyzed products have not been adequately explored. A more detailed understanding of the behavior of these materials should lead to further improvements in the treatment of water and wastewater.

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