Sweep coagulation: structures, mechanisms and practice

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ABSTRACT: The paper examines the links between floc structure and the operational problems which surround the use of alum and similar hydrolysing salts in the sweep floc domain. Structure is described on the basis of primary particle bonding, and arising from the rheological properties of the bulk precipitate within the floc water. Evidence suggests that primary particle bonding is controlled by electrostatic forces and that floc strength deteriorates when this basic mechanism is impaired. It is argued that effective rapid mixing is a vital feature of design when employing sweep coagulation. Difficulties in dewatering and the adsorption of a nonionic polymer added for strengthening and sludge conditioning are attributed to the behaviour of the bulk precipitate.

INTRODUCTION

Sweep coagulation, wherein raw water colloids become enmeshed in a voluminous precipitate of iron or aluminium hydroxide, is one of the most widely used methods of destabilising a turbid suspension. It has particular advantages in low turbidity waters, where the addition of large numbers of precipitate particles increases the probability of contact with raw water colloids and enhances floc growth. Studies by Packham [1] indicated that this form of coagulation was largely independent of the chemical nature of the colloids—an aspect which enhances its utility.

When compared with destabilisation by adsorption and charge neutralisation (ACN), sweep coagulation is more tolerant of departures from the optimum dosage conditions (particularly overdosing), which is clearly an advantage in process control. However, a key disadvantage of the sweep floc mechanism lies in its larger coagulant demand, which increases the cost of chemicals and produces voluminous sludges which are more difficult to dewater. For both alum and similar hydrolysing iron-based salts, operational experience has indicated that the flocs are weaker in conditions of low temperature [2]. In these circumstances, as in other situations of floc weakness, polymeric flocculant aids are often added to strengthen the floc. In spite of the wealth of experience which surrounds sweep coagulation, few studies have addressed the question of what happens to the precipitate. Where does it go? What does it do? Since many operational problems can stem from an unsatisfactory floc, asking such questions offers the prospect of developing more effective strategies for combating the problems. This paper describes a conceptual view of floc structure in the sweep floc domain and shows how it interacts with some of the operational aspects of treatment.

Chemical influences

As a preamble, it is necessary to outline what happens when a hydrolysing salt, such as alum, is dosed into water. Below pH 3, alum forms a coordinate structure with six water molecules and exists as the unhydrolysed species $[Al(H_2O)_6]^{3+}$. With increasing pH, $[Al(H_2O)_6]^{3+}$ can be hydrolysed extensively, forming species such as $Al(OH)^{2+}$ and $Al(OH)_2^+$, resulting in the formation of the solid phase $Al(OH)_3(s)$. Polynuclear species arise from linkages between the Al monomers through OH bridges, but their formation (timescale ~ 1 s) is much slower than the formation of the monomer. The actual polynuclear species present depend strongly on the concentration of the reactants, the pH of the solution, the temperature and time, by virtue of ageing effects. For solutions with a sufficiently high base concentration, there is evidence of the presence of one fairly large polynuclear species, the ion $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, known as Al_{13}^{7+}, which is known to contribute to coagulation structures [3,4]. Positively charged species are attracted to the negative charge sites on the raw water colloids and will adsorb or nucleate on the surface. Much of the remainder of the precipitate exists as a low charged sol or gel distributed across the floc volume.

FLOC STRUCTURE

Macroscopic view

To the casual observer, flocs are most easily described by their size and settling characteristics. Some flocs might be classed as 'small and compact' and settle quickly, while larger flocs (perhaps spectacular looking), settle slowly despite their size. Here, the controlling factor is the floc effective density ρ_e (the excess density over water), this measure providing a valuable insight into the floc structure. For flocs built by random collisions, size and density are linked, the interdependence usually being expressed in the form $\rho_e = Ad^{-n}$ in which d is a representative length and the terms A and n (>0) are empirical parameters. Parameter n is recognised as reflecting the fractal nature of the floc $n = 3 - d_F$, where d_F ($1 < d_F < 3$) is the fractal dimension. The fractal dimension describes the way in

which the floc solids are distributed throughout the floc volume [5]. The lower the d_F, the more 'open' or 'stringy' is the network of solids. Conversely the closer d_F is to 3, the more compact is the floc. If the density of the solid phase is ρ_s, it is relatively straightforward to show that the moisture content θ (under conditions of high moisture content) can be estimated from the formula

$$\theta \approx 1 - \frac{\rho_e}{\rho_w} \cdot \frac{\rho_s}{\rho_s - \rho_w} \qquad (1)$$

For example when $\rho_e/\rho_w = 0.001$ and $\rho_s/\rho_w = 2.5$, $\theta = 99.83\%$, the solid fraction represents 0.17% of the floc mass.

Although the fractal description of a floc provides a useful insight into its form, it gives little insight into its dynamics. For this, it is necessary to examine its microscopic properties.

Primary framework

From scanning electron micrographs (SEM) (see also Figs 8, 9) and supporting electrophoresis data [6,7], it was apparent that the precipitate exists in two principal states. Raw water colloids (termed as the primary particles) were found to be covered by an adherent positively charged deposit which was attributed to the deposition of the positively charged hydrolytic species described above. The remaining part of the precipitate (termed as the bulk precipitate) showed evidence of mobility, cohesiveness and had a low charge; this form of precipitate was attributed to amorphous $Al(OH)_3(s)$, but also contains forms of sulphate. From such data, it was argued that floc structure complied with the conceptual model illustrated in Fig. 1. The primary particles are envisaged as being held together through localised bridging promoted by electrostatic forces, the remaining space containing most of the bulk precipitate.

A schematic view of an electrostatic bridge is shown in Fig. 2. Bonding is promoted by attraction between the negative charges of the primary particles and positively charged deposit
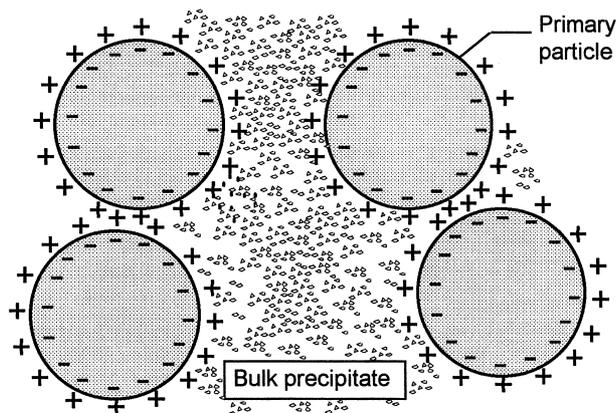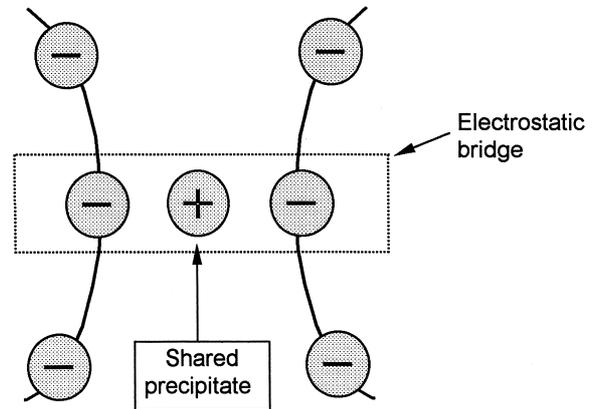

Fig. 2 Schematic view of electrostatic bridge based on point charges.

which lies between the particles. On the assumption that that the bonding behaves in the same way as two point charges q_1, q_2 separated by a distance r, then the bond strength, F, is defined by

$$F = \frac{1}{\epsilon_w} \frac{q_1 q_2}{r^2} \qquad (2)$$

where ϵ_w refers to the permittivity of the dielectric medium, e.g. water.

The implications of this type of bonding are shown in Figs 3 and 4. Figure 3 shows the zeta potential of four different materials which have been dosed with alum at pH 6.3 and controlled ionic strength. If the charge q_2 is associated with the
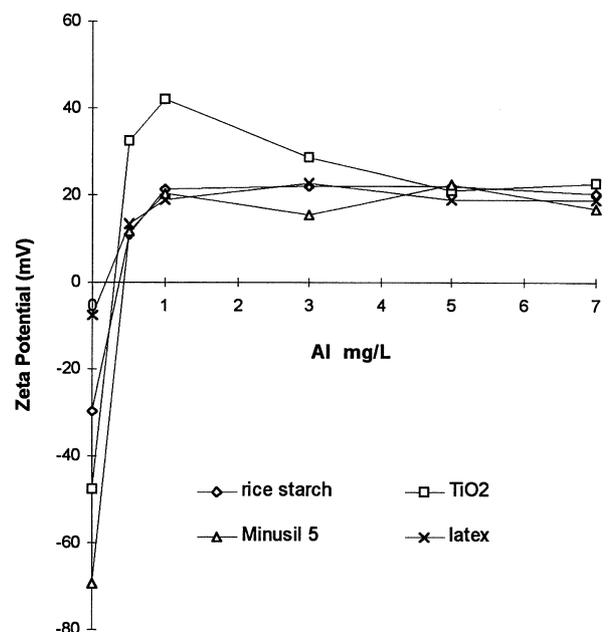

Fig. 3 Dependence of the zeta potential on the alum dose at pH 6.3 and SS $\approx$ 250 mg/L for four suspensions.
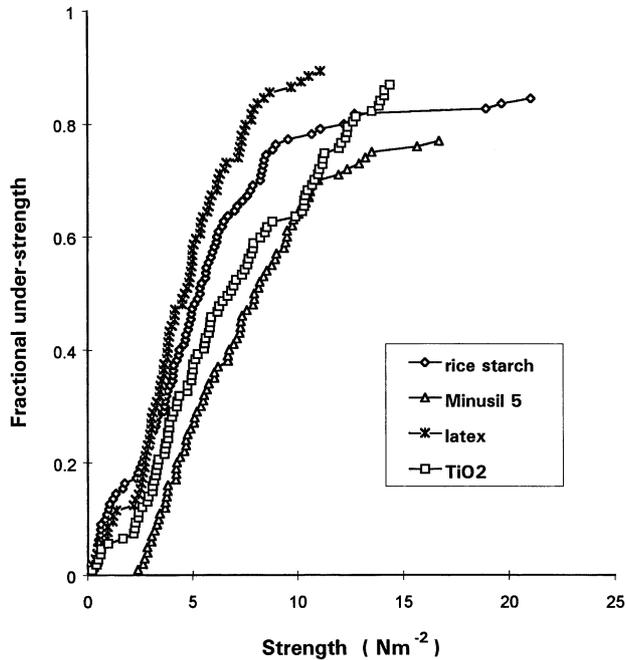

Fig. 1 Conceptual model of floc matrix.

Fig. 4 Floc strength distributions at 5 mg Al/L corresponding to the data shown in Fig. 3.

Water matrix

Although the floc void space is almost entirely water, the small fraction of solids which are present have a major bearing on its behavioural characteristics. The bulk precipitate is variously described as a sol or a gel, i.e. somewhere between the liquid and solid state. Hsu & Bates [9] report particle sizes in the range 5–25 nm, on the basis of electron microscopy, whereas polymeric crystalline forms are smaller [10]. Letterman *et al.* [11] quote the surface area of the precipitate as being roughly $300 \text{ m}^2/\text{g}$, which translates to $d \approx 8 \text{ nm}$ for an equivalent sphere of density 2500 kg/m^3 (approximately the dry density of the precipitate). Order of magnitude calculations (stemming from experimental data) indicate that the particle concentration within the floc is on the order of $10^{15}/\text{mL}$ [7]. Particles are bound by a combination of hydrogen bonds and van der Waals forces, existing in the form of coagulation structures characterised by a fractal dimension in the range 1.4–2.1 [3,4]. The presence of such structures alters the viscous behaviour of the water matrix, because any deformation of a coagulation structure (say by velocity shear) requires that additional work is done against the interparticle bonding forces (as well as between the water molecules) and arising from surface friction during deformation. The symptoms of this process are reflected in the rheological properties of the suspension as illustrated in Fig. 5.

The data shown in Fig. 5 refers to freshly precipitated aluminium hydroxide suspension at a particle concentration similar to that anticipated in the floc. It shows that the suspension behaves as a Bingham Plastic, i.e. behaves as a solid until the critical shear stress ($\approx 0.05 \text{ N/m}^2$) is exceeded. It is suggested that the water matrix behaves similarly, and is in keeping with the well-known rheological properties of sludges.

Another aspect which deserves comment is the ability of the solids to bind water. As with ions, each solid particle is surrounded by a shell of water. Close to the surface the water

zeta potential of the coating at 5 mg/L, then Fig. 3 shows that this is more or less identical for each of the suspensions. In contrast, the zeta potential of the primary particles varies according to the suspension, minusil being the most highly charged and latex the least. Charge q_1 is viewed as being associated with the zeta potential of the primary particles. Figure 4 shows the corresponding strength, the strength having been measured through an analysis of floc rupture behaviour above an oscillating grid, as described in [8]. For the individual trends, the vertical axis refers to the fraction of the flocs within a sample with strengths less than any selected reference strength. Where flocs *were not* broken i.e. strength exceeding the applied hydrodynamic forces, this is shown by the remaining fraction (1 – fractional under-strength) representing the 'gap' (≈ 0.2) at the top of the individual plots. Inspection of Fig. 4 shows that the strongest flocs are the minusil and the latex the least, the ranking exactly following magnitude of the product of the zeta potentials (before and after coating) and thereby the relative value of the product q_1q_2 shown in Eqn 2. The data provides strong evidence of an electrostatic component within the bonding mechanism. It also serves to illustrate that floc strength *is sensitive to the chemical nature of the suspension*. This appears to be a direct contradiction of Packham's findings noted above. However, Packham's conclusions were based on the character of the settled water (through turbidity measurements), whereas the data shown in Figs 3 and 4 refer to the character of the floc.
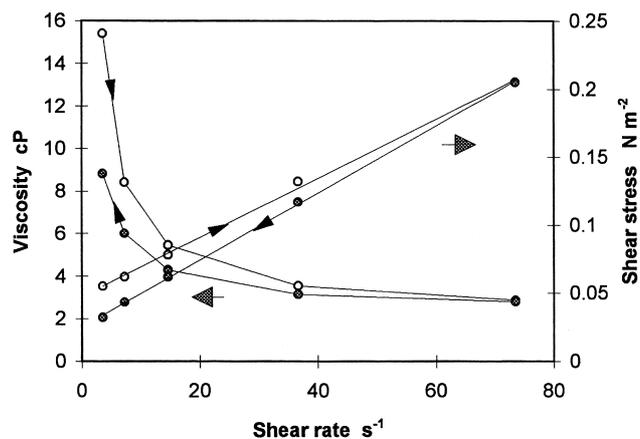

Fig. 5 Rheological character of the bulk precipitate at a concentration ≈ 1.5 mg/L at 20 °C.

is highly structured and is immobilised. From its influence on the physical properties of water, it appears that the structuring of water molecules continues well away from the surface, this being on the scale of 2.5–5 nm, which represents 10–20 molecular diameters [12]. In the case of aluminium hydroxide the bound water is about 1.4 g/g of dry solids [13]. Bound water, as described above, refers to the part of the aqueous phase which has properties which are thermodynamically dissimilar from free water. These properties include viscosity, freezing point and dielectric behaviour.

Although the bulk precipitate contributes to floc strength, it is emphasised that it is bridging amongst the primary particles which establishes the primary framework of structure. It can be viewed in much the same way as an internal steel framework of a building controls the strength of the total structure. From this, it follows that any factor which affects this underlying bonding mechanism will also influence floc strength; this aspect is illustrated in the following section.

STRENGTH FACTORS

Temperature

As noted in the Introduction, operational experiences with alum and hydrolysing iron-based salts have indicated that the flocs are weaker at low temperatures. This appears to contradict Camp's work in the 1940s [14] which led to the statement 'changes in temperature have no measurable effect on the time of floc formation, if coagulation takes place at the optimum pH'. This aspect was subjected to detailed investigation reported in [15] and generated the data shown in Fig. 6. This shows floc development at three reference temperatures, at optimised pH and controlled mixing. From this, it is apparent
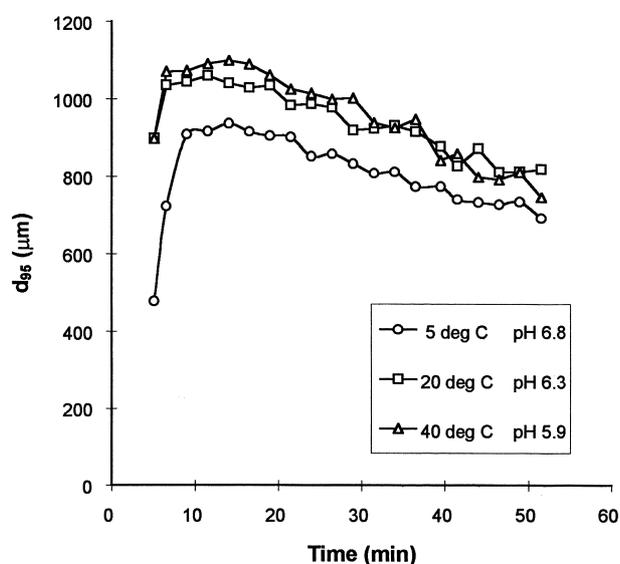
that temperature only has a minor effect on floc development provided the pH is at its optimum, thus supporting the views of Camp *et al.* [14]. Although flocs are slightly smaller at lower temperatures, this is a secondary effect. From knowledge of the mixing regimen accompanying the data shown in Fig. 6, the authors translated the effects of floc size into floc strength. This showed that floc strength diminished by 0.3% per °C as the temperature reduces. It is of interest to note that the permittivity of water *increases* by 0.45% per °C as the temperature is reduced; this increases the denominator in Eqn 1 and reduces magnitude of the electrostatic force (provided all other factors remain identical). Hence the temperature sensitivity of the size distribution shown in Fig. 6 *might* be attributed to changes in the permittivity of the dielectric (taken as water)—a feature which is consistent with our view of an electrostatic bonding mechanism. Additional discussion is included in the Appendix.

Lower temperatures necessitate a higher operating pH, the pH shift resulting from the shift of aluminium solubility with temperature [15,16]. If the pH is left unadjusted, then one enters the regime in which the pH is *below its optimum*. This can seriously inhibit floc development (leading to a smaller floc in a given time*) and is a likely explanation of the operational experiences noted above. Experimental observations and solubility theory described in [15] show that the pH shift is linearly related to the change in temperature (but of opposite sign), a feature which can be included in control algorithms.

Rapid mixing

Experiments reported in [17] showed that when sweep floc was dominant, the trends in the settled water turbidity as a function of the time after rapid mixing was insensitive to the rapid mixing conditions. From this it was concluded 'that extremely short dispersion times and high mixing intensities are not crucial as compared with adsorption destabilisation …' [18]. Generally, evidence of this nature will be welcomed by designers and operators alike, because it avoids the necessity of including sophisticated rapid mixers when dealing with sweep coagulation. Unfortunately, this is a misconception, stemming from a focus on the quality of the settled water, rather than on the nature of the floc. If the problems associated with a weak floc are to be avoided, then the aim should be to exploit electrostatic bonding as a means of producing stronger flocs. A necessary condition is that raw water solids receive a positively charged coating. When the coating arises from the nucleation of positively charged monomers, these only exist for a very short time (~ 1 s) before transforming to the amorphous precipitate [18]. During this time, they must be *dispersed throughout* the rapid mixer in order to avoid arriving as *neutrally charged* $Al(OH)_3$. So it is a race between the time to disperse the coagulant and the timescale of the chemistry. As

Fig. 6 Development of the upper floc sizes (d_{95}) as a function of temperature at pH optima (as shown) and 5 mg/L Al.

*Can be misinterpreted as a sign of weakness due to the smaller size.

such, this is identical to the thinking which surrounds the design of rapid mixers in conjunction with the ACN mechanism.

A second view, with quite different implications, stems from the potential contribution of polynuclear forms such as Al_{13} within the positively charged coating. In contrast to the aluminium monomers, Al_{13} is more stable (preserving its character for many days) [19] and exists within the range of pH which is associated with sweep floc. In such situations, the dispersion time is not so critical. However, whatever the source of the charge in the coated layer, the data shown in Fig. 7 illustrates the dangers of inadequate mixing.

Figure 7 shows the effect of adding a 250 mg/L Minusil 5 suspension 5 min after coagulant addition (simulating an extreme case of poor mixing). It is seen that the floc strength is significantly reduced compared with addition of the coagulant into the suspension with good rapid mixing. In the case of 'good practice' (implying good mixing), the zeta potential of the coated particle was $+22$ mV (in accordance with the data shown in Fig. 2) whereas in the case of the 'poor practice', the corresponding zeta potential was about -5 mV. It is therefore evident that the mixing practice has influenced the effective charge of the suspension. When the effective zeta potential after mixing is fairly low (as in the case of the 'poor practice'), the electrostatic bridging forces will also be low and are the likely cause of the reduced strength associated with the 'poor practice'.

Overdosing

Studies based on flocs from a suspension of rice starch granules coagulated with alum [8] showed that overdosing leads to reductions in both floc density and strength. An analysis of corresponding SEM data shows that the primary particles are less closely packed, these features being illustrated in Figs 8 and 9.
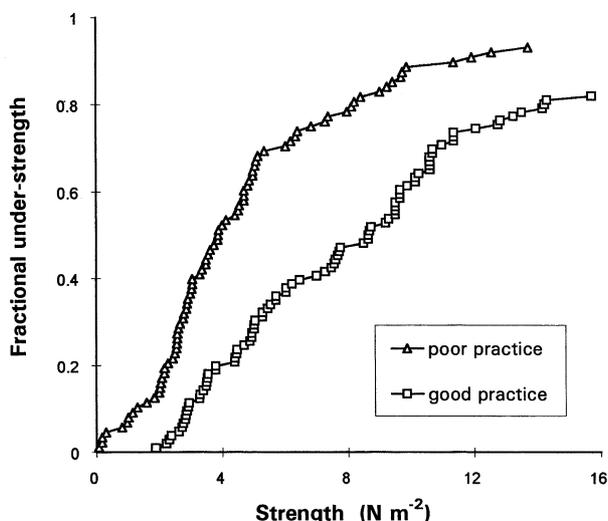

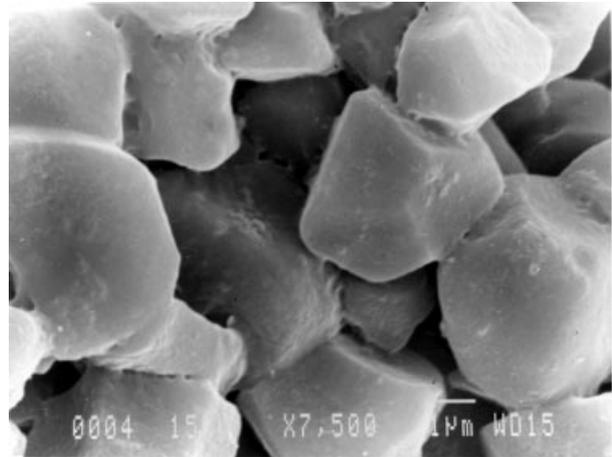Fig. 7 Sensitivity of strength to the rapid mixing status for a Minusil suspension.

Fig. 8 Coated rice starch granules at 3 mg/L and pH 6.3 using alum.

Figure 8 shows an under-dosed state (with little evidence of the bulk precipitate), the optimum dose being about 4–5 mg Al/L (depending on the criteria used). Figure 9 shows a lower packing density in an overdosed state, together with artefacts of the bulk precipitate caused by the dyeing process in sample preparation. A possible explanation is that the primary particles pick up more coating (as a mixture of both positively charged and neutral material) during the very early stages of flocculation, this reduces the effective surface charge. This factor, in combination with a thicker layer of precipitate between the primary particles at their closest point of contact, will reduce the bonding forces described by Eqn 2 by virtue of both the charge reduction and the distance factor.

In the extreme situation of a precipitate forming a large fraction of the floc mass (as in flocs from coloured waters), the strength will be dominated by the cohesion of the precipitate. Although the bulk precipitate is naturally cohesive, its bonding
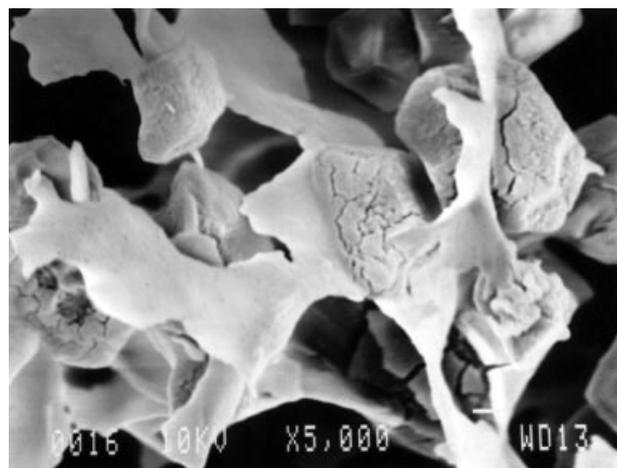

Fig. 9 Coated rice starch at 9 mg Al/L and pH 6.3 using alum.

is weak and vulnerable to erosion. It is probably the breakdown of this type of structure which leads to filter breakthrough and the associated problems of residual control. When associated with a strong structural framework formed by primary particles, the bulk precipitate is better protected from the external turbulent shear forces than when the framework is weak.

DEWATERING

Alum sludges are regarded as being difficult to dewater and necessitate conditioning. Here it is useful to recognise that just as a desert is built from grains of sand, so a sludge is formed from flocs. Thus it should anticipated that sludge dewaterability and floc structure are intertwined.

Dewaterability centres on two aspects of behaviour. First, there are the cohesive forces which must be overcome before water movement can take place—this refers to water binding in its broadest sense. Second, there are the frictional forces which accompany water movement during its release, these being reflected in the rheological properties of the suspension. For a sludge built from flocs of the type illustrated in Fig. 1, there are two distinctive structural components, the first stemming from the primary particles and second from the bulk precipitate. If we regard the size of the primary particles in a turbid water as being on the order of 1 μm (or greater) and the precipitate on the scale of, say $\sim$ 10 nm, it is apparent that these structural elements operate at very different scales. The pattern of behaviour will also be influenced by composition, alum sludges derived from lowland river waters having about 11% of their dry mass from the coagulant, whereas for sludges derived from reservoir waters this may be about 45% [20]. For reasons which will become apparent, it is the bulk precipitate that is of particular concern.

It has already been noted that aluminium hydroxide has a bound water content of about 1.4 g/g of dry solids. What is not clear is the significance of this figure in the context of dewatering. Most particles found in natural waters are hydrophilic and vary in their ability to bind water. Wastewater sludges, with a high organic content, have a larger bound water content than the hydroxide. The influence of the bound water content on the final moisture state of an alum sludge after mechanical dewatering is shown in Fig. 10. To appreciate the underlying significance of this plot, it is necessary to analyse its components. The floc mass M_f can be considered as arising from the dry solids mass (m_s), the mass of bound water (m_{bw}) and the mass of free water (m_{fw}). By definition $m_s = (1 - \theta)M_f$ (θ referring to the moisture content). From this, it follows that

$$1 - \theta = \left[1 + \frac{m_{fw}}{m_s} + \frac{m_{bw}}{m_w}\right]^{-1} \qquad (3)$$

Recognising that the ratio m_{bw}/m_s refers to the horizontal axis in Fig. 10 and that the vertical axis is $(1 - \theta)$, we can deduce the ratio m_{fw}/m_s. From this it is apparent that $m_{fw}/m_{bw} \approx 2.8$. This shows that much of the water remaining
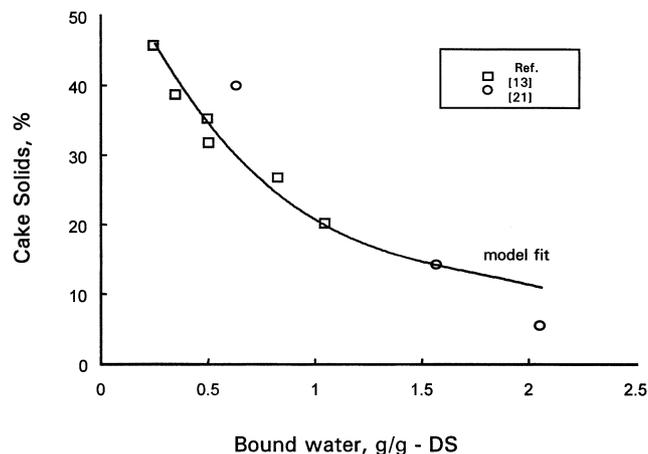

Fig. 10 Bound water content of an alum sludge in relation to cake solids following mechanical dewatering (adapted from [21]). The trend line is based on Eqn 3.

after mechanical dewatering is free or interstitial in nature, a conclusion reached by Robinson & Knocke [21]. Thus, in this instance, the bound water content is not a particularly useful guide to the dewaterability. This aspect may be demonstrated by centrifuging an unconditioned sample of freshly precipitated aluminium hydroxide. After the expenditure of much energy (during centrifugation), the resulting gel (with a consistency resembling toothpaste) has a final moisture content of about 98%, this being consistent with $m_{fw}/m_s \approx 50$. This ratio exceeds the boundwater ratio ($m_{bw}/m_s \approx 1.4$) by a factor of 36 and shows that the contribution of the boundwater is insignificant.

As water is withdrawn from a sludge, its volume reduces, implying that the solids are in closer proximity. In all suspensions, the viscosity increases with increasing solid volume concentration, rising rapidly as the suspension approaches its gel point [22]. Beyond the gel point, the system is networked and behaves as a compressible solid. Viscosity is also sensitive to particle size. The finer the material in the suspension, the greater the viscosity for a suspension for a given solids volume concentration [22]. Although the raw water primary particles may are likely to exist at a larger mass concentration than the precipitate under normal coagulation conditions, their effect on the viscosity is outweighed by the precipitate (forming say 5–40% of the dry mass) on grounds of particle size and number concentration, especially if it is recognised that the pore spaces (see Fig. 1) are filled with a jelly-like material. The increased viscosity makes it more difficult to release the water during dewatering. As is well known, the remedy of this type of problem rests with the control of the fines, either removing them (elutriation, as with wastewater sludges) or in the case of alum sludges, tying them together with polymers to form larger subunits. One effect of this process is that the suspension will behave as one of coarser texture, thus reducing the frictional forces and facilitating the rate of water release.

Polymer adsorption

Polymers are widely used in water treatment, serving as primary coagulants or servicing the needs of floc strengthening and sludge dewatering. While there is an abundance of information on the interaction of polymers with primary particles (generally the arena of cationic polymers), there appears to be a lack information focusing on their interaction with the bulk precipitate. As has already been discussed, the bulk precipitate is the weakest component of a floc and is clearly a candidate for strengthening. In the case of sludge dewatering, it is the structure of the bulk precipitate which needs to be addressed. The charge on the precipitate ranges from positive (as in the coated layer) to neutral or even slightly negative, depending on the pH and the particular chemicals in use. This appears to be the domain of nonionic and anionic polymers, our intention being to comment on the former.

Work in progress has focused on the interaction of Flocmiser 50 (Watermiser Ltd, UK) with freshly prepared aluminium hydroxide, with the view to gaining a better understanding of its role in the conditioning of a waterworks sludge derived from a low turbidity, coloured water. Flocmiser 50 is basically a nonionic polymer (2% anionic) which is used in potable water treatment. Studies on the polymer adsorption behaviour [23] have yielded the data shown in Figs 11 and 12.

Figure 11 shows a comparison of the adsorption characteristics of the bulk precipitate and a waterworks sludge of similar aluminium content. The similarity of the trends suggests that adsorption on the precipitate (within the sludge) is the dominant interaction. The stoichiometry shown in Fig. 12 is equivalent to 2.8 kg/tonne DS or 2.8 × 0.4 = 1.1 kg/tonne DS for a sludge with a 40% hydroxide content. The latter dose may be compared the value 1.5 kg/tonne DS, which was the estimate of the optimum dosage condition (for the same polymer and sludge) on the basis of capillary suction time (CST) and specific resistance to filtration (SRF) measurements [23]. Hence it
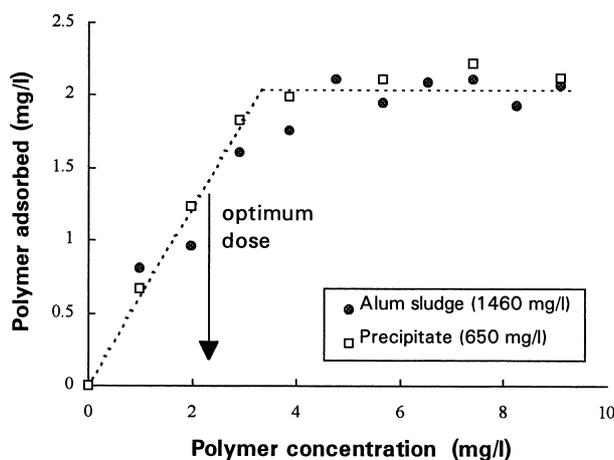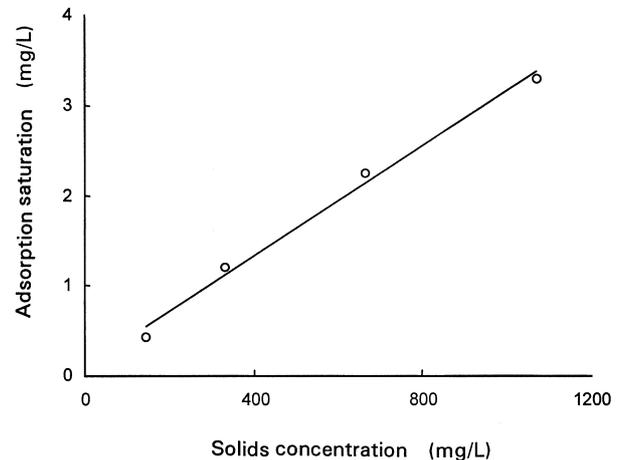
Fig. 12 Stoichiometry between saturation concentration for polymer adsorption and concentration of the bulk precipitate.

appears that adsorption of a nonionic polymer on the precipitate can represent the major determinant of the polymer demand for a sludge and polymer of the type described. Figure 11 indicates the position of the optimum dosage (based on CST and SRF measurements) on the adsorption trend and indicates that the optima for CST and SRF exist within a domain below the state of maximum polymer adsorption.

DISCUSSION

A number of issues have been raised where there appear to be contradictions between previously published investigations and data cited in this paper. Packham's view, that sweep coagulation is largely independent of the chemical nature of the suspension, is certainly not supported when the focus is on floc properties. The same is true of the status of rapid mixing in sweep coagulation [18], the data shown in Fig. 7 demonstrating that floc weakness can stem from poor rapid mixing. While we *agree* with the views of Camp *et al.* [14] concerning the role of pH and temperature on floc development, it must be emphasised that their conclusion was an inference which was not tested directly. In each of these cases, the authors have reached their conclusions on the basis of jar test analysis, this focusing on the quality of the settled water. The utility of the jar test is well established. However, it does not provide adequate insight into floc character. Indeed, there are considerable dangers in using jar test data to draw wider conclusions about the coagulation process in the absence of other information.

The data shown in Figs 3 and 4 provide strong evidence of the type of bonding advocated in the conceptual model. This is consistent with the data shown in Fig. 7, showing that a weak floc can emanate from both poor mixing and the electrical status of the surface coating. It has been pointed out that the data shown in Fig. 6 are consistent with the sensitivity of the permittivity of the dielectric medium (assumed to be commensurate with pure water) to changes in temperature as repre-

Fig. 11 Adsorption behaviour of Flocmiser 50 on bulk precipitate and a waterworks sludge at similar Al concentration.

sented through Eqn 2. Much of the thinking in the literature on particle bonding is dominated by DLVO theory [24]. While we accept the DLVO theory and the concepts it portrays (particularly when it comes to describing the bonding within the bulk precipitate) it is suggested that greater attention should be paid to electrostatic interactions of the type described in this paper. Although our analysis has been based on sweep coagulation, there are good reasons for anticipating that the same concepts apply to destabilisation by the ACN mechanism. Similar views (but from an entirely different perspective) have been expressed in Lartige *et al.* [25] The arguments of Lartige *et al.* stem from observations of the presence of Al_{13} in both forms of coagulation, perhaps indicating that it is the polymeric forms of the aluminium rather than the monomeric forms which dominate the electrostatic interactions. Such observations have a major impact on the significance of rapid mixing for both ACN and sweep coagulation and deserve further investigation.

The conceptual model, with its dual framework of primary particles and bulk precipitate, appears to provide an explanation for a wide variety of phenomena encountered in the pretreatment of water. Perhaps the most intriguing aspect lies in the role of the bulk precipitate. It is the phase which is most is most vulnerable to erosion at low concentrations and a source of dewatering problems at higher concentrations. Yet it is the phase which enhances flocculation and offers considerable adsorptive capabilities arising from its relatively large surface area. It is well known that humic materials adsorb onto flocs [26] and it is true of other substances, e.g. the removal of arsenic onto iron hydroxide flocs [27]. We have demonstrated that the bulk precipitate adsorbs nonionic polymers and consider that this mode of behaviour ranks as a major determinant of the optimum dosage of such polymers in alum sludge conditioning.

SUMMARY

The aim of this paper has been to describe a conceptual view of floc structure and to show how this can impinge on a number of operational problems related to floc properties. Evidence is provided of the sensitivity of floc strength to the primary charges on the suspension and on temperature. Such observations were consistent with an electrostatic bonding mechanism—possibly in the form of an electrostatic bridge. The conceptual model describes a dual framework of floc structure based on the raw water primary particles and the bulk precipitate. Information and arguments are presented which lead to the following observations and conclusions.

- The conceptual model provides a useful insight into an array of problems associated with the coagulation of particulate suspensions using a hydrolysing coagulant such as alum, and offers a framework through which to consider their solution.
- Floc strength is sensitive to both the primary charge on the colloid and to the effective charge in a coated layer.
- The interpretation of jar test data must be treated with caution when extrapolated to wider descriptions of coagulation and flocculation.
- Efficient rapid mixing should be regarded as a necessary component of process design when employing sweep coagulation.
- The bulk precipitate represents the weakest structural component of a floc and should be considered in problems of residual control.
- It is shown that a nonionic polymer bonds with the bulk precipitate, an interaction which appears to determine the optimum dosing of such polymers when used for conditioning a sludge prior to dewatering.

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APPENDIX

This appendix examines the interpretation of experimental data in the context of DLVO theory [24] and electrostatic bridging. DLVO theory describes the interaction of colloidal particles on the basis of electric double layers and electrokinetic phenomena. To simplify the discussion, consider the interaction of two spherical particles of radius a and Stern potential ($\sim$zeta potential ψ), separated (at the closest point of contact) by distance H. The interaction potential (V) can be regarded as a summation of a repulsive potential (V_R) (which results from the overlapping of the diffuse parts of the electric double layer round the particles) and an attractive potential (V_A) arising from van der Waals forces. Under this scheme, the interaction may be described by the summation

$$V = V_R + V_A \tag{4}$$

For the case of small double layer overlap (to simplify the discussion), V_R takes the form [28]

Table 1 Interpretation of experimental data/field experience re bonding mechanism

Behavioural feature	Electrostatic bridging	DLVO	Comment
Temperature effects associated with dielectric constant	Shows forces $\propto \varepsilon^{-1}$ i.e. strength decreases as the temperature is reduced.	Indicates forces $\propto \varepsilon$ i.e. strength increases as the temperature is reduced	Observations fit with electrostatic bridging.
Primary charges + coated layer re floc strength	Strength increases with product q_1q_2 implying that where one charge is fixed (as in coated layer) the strength should follow the primary charge	With coated particles of similar size and zeta potential, the strength should be similar on the basis that the particle interaction will be dominated by the coated layer	The character of the primary charge emerges in spite of the coating (Figs 3 and 4), the weakest flocs being associated with the smallest surface charge. It is difficult to reconcile these aspects with the DLVO model
Observations tend to show that when turbid and humic waters are stabilised by ACN, it leads to the production of flocs which are smaller than those produced by sweep floc	When the surface charge is deliberately neutralised (as in ACN), this effectively nullifies electrostatic bridging ($q_1q_2 = 0$) and removes it as a potential binding mechanism	Under the conditions described, DLVO theory will apply, with strength largely controlled by the van der Waals forces	This evidence illustrates that the force fields described by DLVO can only deliver 'weak' flocs, this being the reason why the flocs are small for a given level of mixing

$$V_R = 2\pi a \varepsilon \psi^2 \ \exp[-\kappa H] \tag{5}$$

in which ε is the permittivity of the liquid phase and κ, the inverse of the Debye length (which scales the width of the double layer). Parameter V_A is represented by

$$V_A = -Aa/12H \tag{6}$$

in which A is a Hamaker constant ($\sim 10^{-19}$ to 10^{-20} J). The negative sign denotes energy associated with attractive forces. The net forces in operation can be deduced from spatial gradient of the interaction energy, e.g. dV/dH. However, it should be recognised that the magnitude of such forces is moulded by the magnitude of the interaction energy. Here, the prime purpose is to identify the form of the controlling parameters rather than the intricacies of the interaction.

Inspection of Eqns 4 and 5 shows that when there is low surface charge ($\psi \approx 0$), $V \approx V_A$ i.e. the interaction energy is dominated by van der Waals attraction and the flocs should be at there strongest in this situation. When the magnitude of the effective surface charge increases (as measured by the zeta potential), there are indications that the floc sizes diminish, a symptom of weaker bonding [29].

Table 1 summarises the likely interpretation of experimental evidence and general experience vis-à-vis DLVO theory and electrostatic bonding as a bridging mechanism

The suspensions leading to the plots shown in Figs 3 and 4 were all of similar size (2–5 μm [30]). In these circumstances together with the comments shown Table 1, it is difficult to see how DLVO theory can explain the sensitivity of the strength to the zeta potential of the primary particles or how it delivers the 'extra' strength (by a factor of 10 or greater) which are associated with the sweep floc in non-neutral conditions. Such arguments point towards the existence of an additional binding mechanism which is Coulombic in character.