

## Properties of flocs formed using different coagulants

M.A. Yukselen\* and J. Gregory\*\*†

\* Marmara University, Department of Environmental Engineering, Kadikoy 81040, Istanbul, Turkey

\*\* Department of Civil and Environmental Engineering, University College London, Gower Street, London WC1E 6BT UK

† Corresponding author

**Abstract** The effects of shear on the formation and break-up of flocs generated using aluminium sulphate ("alum"), polyaluminium chloride and a cationic polyelectrolyte have been investigated using conventional jar test procedure and by continuous optical monitoring. Using the experimentally determined optimum dosage, the breakage of flocs was followed at a high stirring speed, corresponding to average shear rate ( $G$ ) of about 330–520  $s^{-1}$ . Most of the breakage occurred within a few seconds of increasing the shear rate. After each breakage the stirring rate was reduced to the original value to allow the flocs to re-grow. For alum and polyaluminium chloride, it was found that only limited re-growth of flocs occurred indicating a significant irreversibility of the floc break-up process. Residual turbidity increased after floc breakage and re-growth, indicating a reduction in sedimentation rate of the re-grown flocs, consistent with the continuous monitoring results. For the cationic polyelectrolyte, the re-growth of flocs occurred to a much greater extent and floc breakage was almost fully reversible.

**Keywords** Coagulants; floc breakage; flocculation; floc strength

### Introduction

Coagulation/flocculation are important processes in water and wastewater treatment and have great fundamental and practical interest. Formation of flocs is a dynamic process, which depends on various factors including shear conditions and floc strength. It is important to have information on floc structure since this greatly influences the removal efficiency of solids in particle separation processes.

In water treatment, coagulants based on hydrolysing metal salts are frequently used, because of their effectiveness, availability and relatively low costs (Bratby, 1980). The efficiency of these coagulants arises partly from their ability to form cationic hydrolysis products that are strongly adsorbed on negative particles and can neutralise their charge. Formation of an amorphous hydroxide precipitate can also play a very important practical role in coagulation/flocculation processes.

There is a growing interest in the use of polymeric hydrolysis products of aluminium. Polyaluminium chloride (PACl), which has several claimed benefits over aluminium sulphate (alum) can be prepared by controlled neutralisation of aluminium chloride solution and is available in many commercial forms. However, it is not clear how the mechanisms of coagulation differ between different products. By examining floc breakage and re-formation behaviour under controlled shear conditions, it is possible to gain information on floc structure and on the mode of action of different coagulants.

Dewaterability of sludge generated in water treatment plants is frequently used to assess the effect of coagulants. Understanding the ways in which floc formation influences the dewatering properties can provide valuable information regarding the optimal use of coagulants. Despite numerous studies, the relationship between sludge properties and dewatering characteristics remains unclear.

In stirred tanks, flocs grow initially at a rate which is determined mainly by the applied

shear, the particle concentration and the collision efficiency (and hence on the degree of particle destabilisation caused by the added coagulant). As flocs become larger, further growth is restricted by the applied shear for essentially two reasons. Existing flocs may be broken as a result of disruptive forces (Blaser, 2000) and the collision efficiency of particles in a shear field becomes lower as particle size increases (Brakalov, 1987). A dynamic balance between floc growth and breakage can lead to a steady-state floc size distribution, where the limiting size is dependent on the applied shear rate (Mühle, 1993).

Studies of floc formation and breakage with hydrolysing metal salts (Francois, 1987; Spicer *et al.*, 1998; Gregory and Yukselen, 2002) have shown that stirring conditions have a very significant influence on floc growth. When flocs are subjected to a higher shear rate, they undergo breakage. On restoring the previous low shear conditions, flocs can grow back to the previous size, or breakage may be irreversible to some extent. (Francois and Van Haute, 1984; Clark and Flora, 1991). In the latter case, only limited re-growth occurs.

Synthetic organic polymers are also widely used to destabilise particles and promote flocculation. Their mode of action is reasonably well understood (Gregory, 1996) and can involve polymer bridging in the case of high molecular weight materials and charge neutralisation and electrostatic patch effects with polyelectrolytes. It is generally found that polymeric flocculants give rather stronger flocs than those obtained with hydrolysing metal coagulants.

In this study, formation, breakage, re-formation and dewaterability of flocs produced by polyaluminium chloride (PACl), alum and a cationic polyelectrolyte were investigated and compared using optical monitoring and other techniques under different cycled-shear conditions.

## Materials and methods

### Suspension

Kaolin clay (Imerys, St Austell, Cornwall, UK) was used as a model suspension. 200 g of kaolin was dispersed in 500 mL of deionised water in a high-speed blender. To obtain full dispersion it was necessary to raise the pH of the suspension to about 7.5, which was achieved by adding 5 mL of N/10 NaOH. After blending at 4,000 rpm for 10 minutes the clay suspension was diluted to 1 L with deionised water and allowed to stand overnight in a measuring cylinder. The top 800 mL was decanted and its solids content was determined gravimetrically and found to be 135 g/L. This was diluted to give a final solids content of 50 g/L. The particles were mostly below about 5  $\mu\text{m}$  in size, with a mean size of about 2  $\mu\text{m}$ , determined by an Elzone 280 PC particle counter.

For the flocculation tests, the stock suspension was diluted in London tap water to give a clay concentration of 50 mg/L. London tap water has high total hardness (ca. 280 mg/L as  $\text{CaCO}_3$ ) and alkalinity (ca. 240 mg/L as  $\text{CaCO}_3$ ) and a pH of around 7.4. The high calcium content (around 2 mM  $\text{Ca}^{2+}$ ) causes destabilisation of the kaolin particles, which slowly coagulate. This would give problems in interpreting the results with hydrolysing coagulants. To avoid this difficulty, a small amount of commercial humic acid (Aldrich) was added to the stock kaolin suspension. Humic acid adsorbs on the clay particles and gives enhanced stability against divalent metal ions such as  $\text{Ca}^{2+}$ . Humic acid solution was included in the stock 50 g/L kaolin to give a concentration of 0.5 g/L. The diluted samples for all of the coagulation experiments had a turbidity of about 100 NTU, determined by a Hach Model 18900 turbidimeter.

### Coagulants

Aluminium sulphate hydrate [ $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$ ; Fisons, >96%] alum was used. Stock alum solutions were prepared at a concentration of M/10. These were stored in a refrigerator at 5°C and renewed every two weeks.

Two commercial polyaluminium chloride (PACl) products (XL-9 and XL-1) from Kemira (Kemi AB, Helsingborg, Sweden) were used. XL-9 had a degree of neutralisation,  $r$  ( $=\text{OH}/\text{Al}$ ), of 2.1, supplied as a 4.6 wt.% Al solution whereas XL-1 had a degree of neutralisation of 1.9, supplied as a 5.1 wt.% Al solution. These solutions were used directly, without prior dilution.

A commercial cationic polyelectrolyte Magnafloc 1697 [poly(diallyldimethylammonium) chloride, polyDADMAC], with an intrinsic viscosity of about 0.2, corresponding to a molecular weight of around 50,000, and a high charge density (about 6 meq/g) from Allied Colloids Ltd (now Ciba Specialty Chemicals) was used. This was supplied as a 40% aqueous solution and was diluted to give a stock solution of 0.1% or 1 g/L.

### Apparatus

A continuous optical flocculation monitor (PDA 2000, Rank Brothers Ltd, Cambridge, UK) was used in a modified jar test procedure. The test suspension was contained in 1 L beakers with stirrer units from a Flocculator 90, semi-automatic jar test device (Kemira Kemwater, Helsingborg, Sweden). This enables the rapid mixing and slow stirring speeds and times to be pre-set. For dynamic monitoring, sample from one beaker was circulated through transparent plastic tubing (3 mm id) by means of a peristaltic pump. The pump was located after the PDA instrument to avoid effects of possible floc breakage in the pinch portion of pump. The tubing was clamped in the PDA instrument so that the flowing sample was illuminated by a narrow light beam (850 nm wavelength). The PDA 2000 measures the average transmitted light intensity (dc value) and the rms value of the fluctuating component. The ratio (rms/dc) provides a sensitive measure of particle aggregation (Gregory and Nelson, 1986). In this work, the ratio value is called the Flocculation Index (FI). More details of the experimental method have been given by Yukselen and Gregory (2002a).

### Procedure

Using standard jar tests with 800 mL of test suspension (50 mg/L kaolin and 0.5 mg/L humic acid in London tap water) the optimum amounts of coagulants were determined, after rapid mix at 300 rpm ( $G = 336 \text{ sec}^{-1}$ ) for 15 seconds, slow stirring at 30 rpm ( $G = 11 \text{ sec}^{-1}$ ) for 10 minutes and settling for 30 minutes, supernatant samples were withdrawn for turbidity measurements. The  $G$  values were calculated following Mejia and Cisneros (2000), who used a similar jar test device.

For dynamic tests, the sample was pumped from a stirred beaker at about 25 mL/min through the tubing and the average (dc) and fluctuating (rms) components of the transmitted light intensity were monitored by the PDA instrument. Readings were taken every two seconds and the results were stored in a computer for subsequent spreadsheet analysis. The standard test procedure was modified as follows. After allowing 1 minute for steady-state readings to be established, the coagulant was dosed and the suspension was stirred at 300 rpm for 15 seconds. Then the stirring speed was reduced to 30 rpm and held at this value for the required time (10 minutes). In order to investigate the floc breakage and re-formation, the stirring speed was increased to 300 rpm for times ranging from 5 to 60 seconds and then reduced back to 30 rpm. All experiments were carried out 2–3 times and very little variation was observed.

For the second phase experiments (comparison of the hydrolysing coagulants with a cationic polyelectrolyte) conditions were slightly modified. After rapid mix at 400 rpm ( $G = 518 \text{ sec}^{-1}$ ) for 10 seconds, and slow stirring at 50 rpm ( $G = 23 \text{ sec}^{-1}$ ) for 10–30 minutes, flocs were broken at 400 rpm for 30 seconds.

## Results and discussion

Dynamic monitoring results for alum and two of the PACl coagulants show the change in Flocculation Index (FI) with time (Figure 1). In this set of experiments, stirring conditions were the same for all cases. Using alum (3.4 mg/L as Al) and two PACl products to give the equivalent dosage as Al, floc formation and breakage under repeated high stirring rates was evaluated. Since no significant changes were observed in the FI values after 10 minutes of slow stirring at this concentration, this duration was used throughout the experiments. The initial parts of the flocculation curves show the reproducibility of the process.

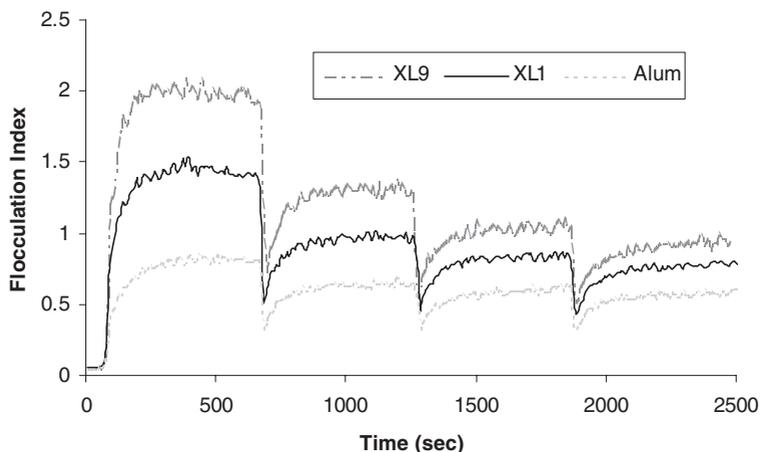
It is apparent that breakage is very rapid, as shown by the sharp fall in the FI value as soon as the stirring speed is increased. On returning to the slow stirring speed (30 rpm), some floc growth occurred, but the FI reached only a fraction of the previous value. The new plateau was lower than the first value and was reached rather more slowly. This floc formation and breakage cycle was repeated several times and the results show a progressive decrease in the FI value achieved on re-flocculation after each breakage period. However, as the number of cycles is increased, the FI tends to return more closely to its previous value.

The higher FI values obtained with the PACl products indicate larger flocs and correlate well with the residual turbidity data (Figure 2). Furthermore, it was observed that flocs grew to a limiting (plateau) size that decreased progressively with each cycle for all coagulants but again the PACl products have higher FI values.

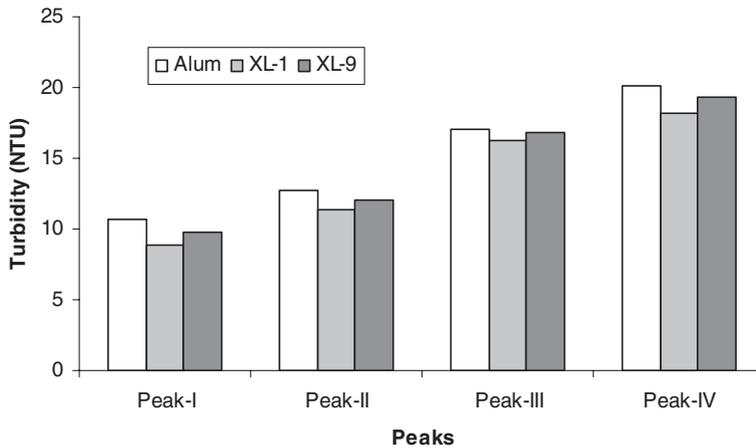
The residual turbidity data in Figure 2 are for samples taken at times corresponding to plateau values in the FI curves. Peak I is before floc breakage and peaks II–IV are for the successive re-grown flocs.

The effect of shear rate and duration of mixing was investigated using one of the PACl products (XL-1). Figure 3 shows the results of experiments with the same stirring conditions (rapid stirring at 300 rpm for 15 seconds, followed by a slow stirring at 30 rpm for 10 minutes) but with different breakage periods (5, 30 and 60 seconds) at 300 rpm. With shorter breakage periods, FI rises to higher values. It is clear from Figure 3 that this coagulant also shows irreversible floc breakage since the FI value recovers to only a fraction of its value before breakage. It is again clear that initial floc breakage is rather rapid, and with greater breakage periods there is evidence of a more gradual and limited recovery. Comparing with alum (Yukselen and Gregory, 2002a), under these conditions, PACl products performed better, indicating stronger flocs.

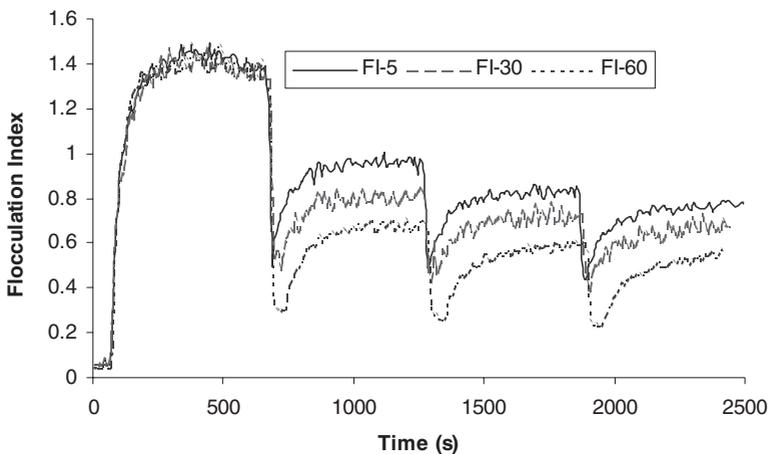
A comparison of floc breakage and reformation of various coagulants under the same conditions apart from the longer slow stirring times for the polyelectrolyte (rapid mix at



**Figure 1** Floc formation, breakage and re-formation for coagulants shown. Breakage at 300 rpm for 10 seconds in repeated cycles



**Figure 2** Residual turbidities at different stages of the cycled shear

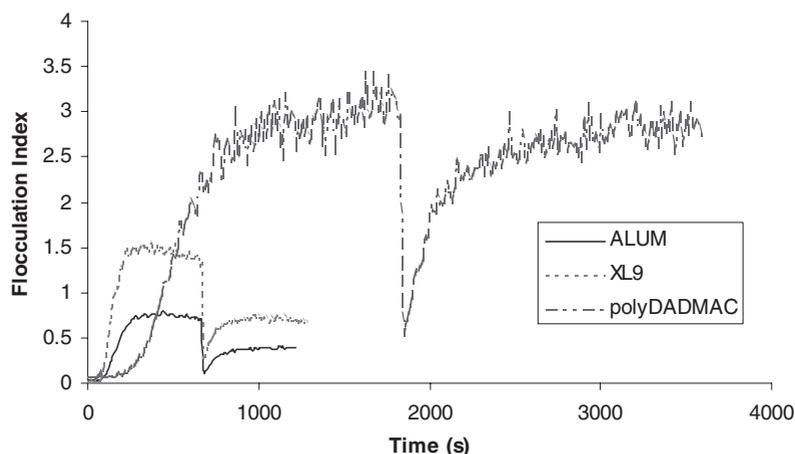


**Figure 3** Effect of different floc breakage times at 300 rpm (XL-1 coagulant)

400 rpm for 10 seconds, slow stir at 50 rpm and breakage at 400 rpm for 10 seconds) are illustrated in Figure 4. Tests were carried out with a high-charge cationic polyelectrolyte (PolyDADMAC), which showed almost complete reversibility of floc breakage, in sharp contrast to the hydrolysing coagulants. PolyDADMAC promoted the growth of very large flocs, with FI values about four times higher than those with alum and more than twice than XL-9, under the stated conditions, but significant aggregation did not occur until about 10 minutes after dosing the flocculant. The maximum FI value was reached after about 15 minutes. Breakage at 400 rpm was very rapid and gave about six-fold reduction in FI. Re-growth of flocs at 50 rpm was substantial but the final FI values were rather less than those before breakage, especially for the longer breakage periods.

These and other results give useful insight into the mode of action of coagulants, especially the roles of charge neutralisation and precipitate formation. The differences in FI value after each floc formation period reflect real differences in floc properties, as shown recently by Yukselen and Gregory (2002b).

In the case where hydrolysing coagulants are used under sweep conditions, floc formation begins very soon after coagulant addition, but flocs grow only to relatively small size. It is likely that hydroxide precipitation occurs shortly after dosing and that floc strength is limited by the relatively weak nature of the amorphous precipitate. The low molecular



**Figure 4** Comparison of different coagulants for the 30 second breakage at 400 rpm

**Table 1** Capillary suction times (CST) of flocs before and after the breakage for different coagulants

|                    | Alum | PACI (XL-1) | PolyDADMAC |
|--------------------|------|-------------|------------|
| CST Peak I (sec.)  | 73   | 48          | 20         |
| CST Peak II (sec.) | 95   | 62          | 21         |

weight of polyDADMAC gives larger and stronger flocs and this may be due to “electrostatic patch” attraction.

It is found that dewatering properties of the flocs formed using different coagulants follow the same trend as Flocculation Index i.e. higher FI values corresponding with better dewaterability (lower CST). Among the coagulants used polyDADMAC gave the best dewaterability, while alum gave the least. It is worth noting that CST did not change significantly before and after the breakage of polymer flocs supporting the reversibility of the floc formation for the polymer whereas with hydrolysing coagulants longer CST values were observed after floc breakage.

For flocs of given mass, it might be expected that higher density structures give faster dewaterability, because of smaller floc size and reduced drag. However, this ignores the possibility that lower density, porous flocs may be permeable to water and that significant flow could occur through as well as around. In some cases it appears that flocs with more open structure are more readily dewatered (Waite, 1999).

## Conclusions

The results presented here show floc formation, break-up and re-formation with alum, PACI products and a cationic polymer. The flocs formed with the commercial PACI products are larger and stronger than those with alum. The irreversible nature of floc break-up is common to all hydrolysing coagulants.

Significant differences between the typical hydrolysing coagulants under sweep floc conditions and the cationic polyelectrolyte, acting predominantly by charge neutralisation were found. Probably the most striking difference is the almost full reversibility of floc formation after break-up.

Although there have been previous reports on the irreversible nature of floc breakage in the case of hydrolysing coagulants, the underlying mechanisms remain unclear. The effect seems to be specific to the “sweep floc” regime. Irreversibility in this regime suggests that

chemical bonds are broken during floc disruption. In the case of polymeric flocculants slight irreversibility is associated with the bridging interactions.

### Acknowledgements

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