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## High floc strength with aged polyelectrolytes.

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### Abstract

The ageing of powdered polyelectrolyte solutions has shown that while the viscosity of these solutions decreases rapidly with time, the flocculation performance and the strength of the flocs produced does not alter over periods >200 days. This was shown for polyacrylamides of cationic, anionic and non-ionic charge. The use of tap or deionized water did not adversely affect the results unless a biocide capable of associating with the polyelectrolyte was added. These results contradict the common belief that solutions made with powdered polyelectrolytes should not be stored for long periods of time as their performance decreases after being stored for several days. The results indicate that powdered polyelectrolyte solutions are suitable for intermittent process operations, such as sewer overflow treatment and that dosing and handling of the solutions can be made easier by ageing of the solutions.

*Keywords:* polyelectrolyte, ageing, floc strength, sewage

### Introduction

Traditionally inorganic coagulants have been used to increase the rate of solid/liquid separation by aggregating small particles into large agglomerates. Such processes produce faster settling entities and flocs that are more readily captured in filtration. However, these flocs are fragile and break readily when exposed to moderate shear rates, which limits the separation rates that can be achieved. Stronger, faster forming flocs are required in order to achieve faster solid/liquid separation. Polyelectrolytes are often used in addition to inorganic coagulants in these circumstances, as polyelectrolytes are known to produce stronger flocs than inorganic coagulants. Tambo and Hozumi [1] estimated that clay flocs produced by non-ionic polymers were 48 times stronger than alum flocs.

Elevated concentrations of polyelectrolyte have been used to increase the strength of alum flocculated sewage, enabling Gray et al. [2] to filter sewage through a coarse depth filter at rates of up to 50 m<sup>3</sup>/m<sup>2</sup>.h. Davey et al [3] used a similar approach to continuously screen sewage at rates of >100 m<sup>3</sup>/m<sup>2</sup>.h.

The shear rate at which separation occurs has also been shown to affect the optimum polyelectrolyte dose for separation [2], with low shear rates (50 s<sup>-1</sup>) providing the optimum dose for settling. At high shear rates (230s<sup>-1</sup>), the optimum polyelectrolyte dose increased to about 10 times that of the dose required at low shear rates, as stronger flocs were required. The higher shear rates also allowed any electrostatic barriers that might be present to be overcome by the higher kinetic energy of the

particles, similar to the shear flocculation process previously described by Warren [4]. The size of the flocs produced at high shear rates and high polyelectrolyte doses was also greater than those produced at low shear rates and the lower optimum polyelectrolyte dose, making separation processes such as screening easier to operate.

These results also indicate that conventional jar tests performed at low shear rates do not provide information on optimum polyelectrolyte concentrations for producing strong flocs, and that floc strength continuously increased with increasing polyelectrolyte doses. This conclusion was also supported by jar tests performed at higher shear rates ( $230 \text{ s}^{-1}$ ), where the turbidity of the supernatant following settling was significantly lower than the turbidity obtained at low shear rates, for polyelectrolyte doses far in excess of the low shear rate optimum. High rate filtration results [2] also recorded better removal rates at polyelectrolyte doses higher than the low shear rate optimum.

The effect of different cationic polyelectrolytes on floc strength has also been studied by Becker et al [5] and Gray and Ritchie [6]. Floc strength was expressed as a critical mixing speed (CMS), where flocs formed at low speed were subjected to increasingly higher shear rates. The shear rate at which an abrupt rise in turbidity following settling occurred was termed the CMS, and therefore a high CMS was indicative of stronger floc strength. It was shown [5, 6] that polyelectrolytes of a medium charge density (CD) and very high molecular weight (MW) were the optimum for the production of strong flocs. The residual polyelectrolyte left in solution [5] was an order of magnitude lower for the very high MW polyelectrolyte compared to the high MW polyelectrolyte for the CMS of interest in their high rate screening process. This outcome is significant, as the residual polyelectrolyte dose is important when the treated water is to be discharged to natural environments or is to be recycled to processes that are polyelectrolyte sensitive. Careful selection of the polyelectrolyte type can therefore lower the dose required and limit potential side effects from their use. Davey et al. [3] demonstrated this by being able to lower the polyelectrolyte dose required to achieve high levels of TSS removal when using a rapid fine screening technology on sewage ( $110 \text{ m}^3/\text{m}^2\cdot\text{h}$ ) from  $9 \text{ mg/L}$  to  $2 \text{ mg/L}$  by selection of a very high MW polyelectrolyte.

In many industrially important processes, such as sewer overflow treatment, the process is run intermittently but may be continuously on stand-by to commence operation with only a few minutes notice. This suggests that emulsion polymers would be more suited to these applications, as they can be mixed into aqueous solutions in only a minute or two while powdered polyelectrolytes may take several hours to dissolve. Furthermore, manufacturers claim that solutions made from powdered polyelectrolytes only last for a few days, so make up of fresh solutions would be required several times a week. Emulsion polymers are considerably more expensive than powder polyelectrolytes (2 - 3x based on active component), and there is a financial benefit to be obtained if powder polyelectrolytes could be used for processes that operate intermittently. Therefore, experimental work was undertaken to examine the effect of ageing of powder polyelectrolyte solutions over time periods of several months on polyelectrolyte solution viscosity, jar test performance and floc strength.

## Experimental

The effect of ageing on powder polyelectrolyte solutions was determined by measuring the viscosity of the stock solutions and determining the effectiveness of the polyelectrolytes in jar tests as a function of time. Three polyelectrolytes from CIBA (Allied Colloids) were tested in this manner: Zetag 32 (low charge density, high molecular weight, cationic), E10 (low charge density, high molecular weight, anionic) and LT20 (high molecular weight, non-ionic).

Three solutions of each polymer were made, with the grade of water varying between solutions. The grades of water used were de-ionised, tap and tap water with 2.5 w/v% of a household disinfectant named Pine-o-Clean (solution of benzalkonium chloride). Each of these grades of water should differ in respect to the amount of biological activity present, and it was considered that this might affect the rate of polymer degradation in solution.

The concentration of polyelectrolyte in the stock solutions was 5 g/l, which is typical of the concentrations of stock solutions used in the water industry. The solutions were aged for at least 24 hours before use and the solutions were kept at room temperature (20°C) in the dark (cupboard) throughout the course of the experiments. All samples were contained in clear glass jars.

The viscosity was measured with a Brookfield DV-II viscometer. All measurements were performed with the samples equilibrated to 25°C.

Jar tests were performed to test whether the ageing of polyelectrolyte solutions resulted in a change in flocculation performance. The jar tests were performed on a buffered clay suspension and the turbidity of the supernatant used as a measure of performance. The dose of each polyelectrolyte used in the jar tests was chosen so as to give less than optimal results. This was considered to be more sensitive to changes in polyelectrolyte quality than was use of the optimum dose as typical turbidity versus polyelectrolyte concentrations are flat near the optimum dose. Therefore, operation at less than optimal polyelectrolyte concentrations should provide more sensitivity to changes in polyelectrolyte condition, but will also increase the experimental error associated with reproducibility of the tests. A fresh solution of each polyelectrolyte was made in de-ionised water the day before jar testing, and was used as a control to account for variations between clay suspensions.

The jar test suspension consisted of 1 litre of deionised water plus 5 ml of pH 7.0 phosphate/citrate buffer (1M) and 1g of kaolin clay (Merck #1906.2500). With a stirrer speed of 200 rpm, the required polyelectrolyte dose was added to the jar (0.5% solution in respective medium) and stirred at 200 rpm for 30 s. The stirrer speed was then lowered to 60 rpm for 60 s. After this time, the stirrer was switched off and the contents settled for 2 minutes. The upper portion of liquid phase was sampled for turbidity measurement. The error for the turbidity measurements was  $\pm 10\%$ .

An indication of floc strength was determined by measuring the CMS using the method reported by Gray and Ritchie [6]. This technique involved running a series of jar tests using the same suspension. The initial jar test was conducted at low mixing speeds, and the mixing speed was gradually increased until an abrupt increase in the

supernatant turbidity was detected. The speed at which the increase in turbidity was detected was termed the critical mixing speed (CMS). This technique was reproducible to within  $\pm 50$  rpm.

## Results and Discussion

The results of the viscosity measurements are shown in Figures 1, 2 and 3. The viscosities of de-ionised and tap water solutions all decreased noticeably during the first sampling period of 40-50 days, whereafter the viscosity decreased more slowly. A drop in viscosity may indicate a shortening of the polyelectrolyte chains, possibly due to bacterial action or hydrolysis. However, Narkis and Rebhum [7] suggest that the decrease in viscosity is because the polyelectrolyte chains became untangled from each other and thus acted as independent molecules rather than as a gel. This was confirmed by their results in which the polyelectrolyte from aged solutions with lowered viscosities was precipitated from solution with acetone and then re-solubilised. The reconstituted solutions had viscosities similar to those of fresh polyelectrolyte solutions indicating that the drop in viscosity was reversible and therefore not a result of degradation of the polymer chains.

The viscosities of the polyelectrolyte solutions in pine-o-clean were considerably different to the solutions made in de-ionised and tap waters. This effect was thought to be the result of complexation between the polyelectrolyte and an active ingredient in pine-o-clean, benzalkonium chloride. Benzalkonium chloride is a quaternary ammonium compound, and may act as a cationic surfactant. The viscosity of Zetag 32 solution in the Pine-O-Clean solution was significantly lower than the viscosities of the same Zetag 32 solutions made in de-ionised and tap water from day 1. This indicates that the association between the Zetag 32 and Pine-O-Clean solution was rapid, and the plateau in viscosity between day 1 and 50 indicates that it reached an equilibrium state during this time.

Similarly, the change in viscosity of the anionic E10 polyelectrolyte was rapid, with an increase in viscosity occurring between 0 and 46 days ageing. The viscosity increase indicates greater association between the polyelectrolyte chains. The benzalkonium chloride is a positively charged surfactant that will readily associate with the negatively charged E10, and greater association between the polymer chains may arise via bridging between the benzalkonium chloride and E10 molecules or via hydrophobic associations between polymer chains.

Similarly, the viscosity of the neutral LT20 polyelectrolyte also increased with ageing when Pine-O-Clean was added to the solution. For neutral polymer, the viscosity increased steadily over the 204 days of the experiment, again indicating that associations between polymer molecules increased with time.

The jar test results are shown in Table 2. There is variability in the results arising from errors in reading the turbidity, variations in the clay suspensions used for the jar tests and from the repeatability of the experiments. The error in reading the turbidity was  $\pm 10\%$  and variations between clay suspensions was accounted for by use of the control experiment, in which fresh polyelectrolyte was used in a jar test to recalibrate the performance of non-aged polyelectrolyte with the suspension. The variability

arising from the repeatability of experiments occurs because the sub-optimal polyelectrolyte dose was used, and therefore minor variations in the polyelectrolyte concentration can have a significant effect on the final settled turbidity value.

Polyelectrolyte solutions made in de-ionised and tap waters did not show any significant change in performance with time, while the performance of all polyelectrolyte solutions made with Pine-O-Clean were poorer than the control results. Associations between benzalkonium chloride and the polyelectrolytes appear to decrease the effectiveness of the polyelectrolyte solutions, probably by neutralising the active sites on the polymers and these results shall not be further discussed.

The jar test turbidity results of the negatively charged E10 polyelectrolyte solutions made with tap water and deionised water were predominately within  $\pm 10\%$  of the control experiment. Therefore, these results were mostly within the turbidity reading error. The one exception was for the E10 made with tap water after 89 days ageing, where this polymer out performed the control test and so indicated that there was no decrease in performance of the E10 with time.

The variation of the turbidity results was larger for the Zetag 32 and LT20 polyelectrolytes, and this was ascribed to the performance of these polyelectrolytes being more sensitive to variations in polyelectrolyte dose than the negatively charged E10. The sensitivity of the polyelectrolyte performance is generally larger the greater the percentage distance away from the optimal dose the applied dose is [8]. That is, the rate of change in polyelectrolyte performance decreases as it approaches the optimal dose, and therefore variations in the sensitivity of the turbidity results will exist between polyelectrolyte types.

The jar test turbidity results for the LT20 polyelectrolyte made in tap water and deionised water have lower values than the control experiments at the end of the experiment i.e. after 95 and 213 days. Therefore, the performance had not decreased relative to the control experiment over the time frame of the experiments and the variation in the final turbidity values with time were the result of experimental variation.

The performance of Zetag 32 showed a similar variability to the E10 results, and although the turbidity values after ageing the polyelectrolyte for 220 days was greater than the control turbidity value, it is still suggested that the performance of the polyelectrolyte did not decrease with time. Indeed the results Zetag 32 aged for 96 days were either within the turbidity reading error of the control value or were lower than the control value. While the turbidity values after ageing the polyelectrolyte for 220 days were greater than the control experiment by more than the error in reading the turbidity, and it might be argued that this indicates a drop in polyelectrolyte performance, the results obtained for flocculation of raw sewage with polyelectrolyte aged for longer than 200 days and the floc strength measurements support the assertion that there was no decrease in polyelectrolyte performance with ageing of the polyelectrolytes.

Table 3 shows the results for the performance of the aged polyelectrolytes with coagulated sewage. The differences between the aged polyelectrolyte solutions and fresh control solutions were very small, indicating that any degradation of the

polymer solutions over the 200+ days of ageing did not affect flocculation performance. The greatest variations in performance occurred for short settling times, where the variability between experiments is greatest because the rate of change in turbidity is at its fastest. However, after 2 minutes settling, the polyelectrolytes made with deionised and tap water, the settled turbidity values were either the same or lower than the control values.

Similarly the floc strength measurement also indicate that there was no decrease in the strength of flocs produced by aged polyelectrolyte solutions compared to fresh polyelectrolyte solutions (see Table 4). Indeed, there was no difference in the floc strength after ageing the polyelectrolyte solutions for over 200 days for each of the three polyelectrolyte types tested.

These results demonstrate that ageing of polyelectrolyte solutions over time frames in excess of 200 days does not significantly decrease the flocculation performance of the solutions or the subsequent strength of flocs produced by the solutions. The viscosity of the solutions decreases dramatically over this time frame, but the results are in keeping with the results of N. Narkis and M. Rebhun [7] who suggested that the drop in polyelectrolyte solution viscosity was because of disentanglement of polyelectrolyte molecules with time rather than degradation of the polymer. This indicates that powdered polyelectrolytes are suitable for use in sewer overflow situations, as their effectiveness does not diminish with time. Furthermore, the decrease in solution viscosity with time will make handling and dosing of powdered polyelectrolyte solutions easier.

## **Conclusions**

During the ageing of powder polyelectrolyte solutions a dramatic decrease in the solution viscosity was observed over a period of >200 days. However, the flocculation performance and floc strength of the polyelectrolytes were not affected by ageing indicating that no significant degradation of the polyelectrolyte chains occurred over the time. The use of tap or deionized water did not adversely affect the performance of the polyelectrolytes over time except when biocidal additives that associated with the polyelectrolytes were added. This was true for polyacrylamides of cationic, anionic and non-ionic charge.

These results indicate that powdered polyelectrolyte solutions can be stored for significant periods of time without loss of performance, and that they would be suitable for intermittent process operations such as those experienced for sewer overflow treatment. It also suggests that handling and dosing of powdered polyelectrolytes can be made easier by ageing the polyelectrolyte solutions without loss of performance.

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