

SOME FACTORS AFFECTING THE PERFORMANCE OF POLYACRYLAMIDE FLOCCULANTS IN JUICE CLARIFICATION

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Abstract

The importance of various factors relating to the preparation of polyacrylamide flocculant solutions was investigated. For optimum results, these solutions should be agitated for at least 2 hours before use while water of high ionic content should be avoided. The quantity of calcium phosphate precipitated during the clarification reaction and the calcium concentration in clear juice are shown to influence differently the behaviour of polyacrylamide flocculants of varying degrees of hydrolysis.

Introduction

The lime-defecation process for the clarification of raw sugar cane juice relies on the in situ precipitation of calcium phosphate. This is achieved by the addition of lime ($\text{Ca}(\text{OH})_2$) to raise the pH and thus precipitate the natural calcium and phosphate content of the juice. This process flocculates the particles in the raw juice by binding them into the precipitate via the Ca^{2+} ions adsorbed at the particle-liquid interface¹.

The quality of the clear juice obtained by this method is thus dependent on the extent to which this flocculation process can scavenge the particles of the raw suspension. It has long been known^{3,5,7} that the extent of defecation is dependent on the amount of phosphate present in the original juice. Inorganic phosphate is frequently added to juices deficient in this requirement in order to obtain clearer juice, faster mud settling and better mud filtration⁹. Since the adjustment of juice pH with lime results in considerable addition of Ca^{2+} ions, the precipitation of the phosphate content of mixed juice is generally nearly complete. It has, however, been shown that addition of Ca^{2+} can improve the clarity of clear juice^{3,13}.

In order to improve the clarification system, polyacrylamide flocculants are added prior to the settling stage. These flocculants are copolymers of acrylamide and sodium acrylate (generally known as partially hydrolysed polyacrylamides) and possess molecular weights in excess of one million. The percentage of sodium acrylate groups is referred to as the degree of hydrolysis (DH). For their optimum use, care must be exercised in the preparation of the solution. The generally recognized principles of polymer solution preparation are a careful addition of the solid powder to the water so as to independently disperse the individual granules; gentle agitation of the solution for a sufficient period of time to ensure complete dissolution and equilibration; temperatures below 50°C ; a two stage preparation in which a stock solution is prepared and diluted prior to use; and the avoidance of centrifugal pumps which can damage flocculant molecules⁴.

The purpose of this investigation was to determine what magnitude of influence polymer solution preparation parameters have on clarification efficiency. The parameters considered were time of agitation of the stock solution, solvent ionic strength, flocculant solution concentration and solution pH. The second stage of this study concerned the influence of the amount of P_2O_5 precipitate and the concentration of calcium in clear juice on the behaviour of polyacrylamide flocculants.

Experimental

The laboratory clarification unit and its operation have already been described¹⁰. Turbidities of clear juice were determined as the absorbance at 800nm in a 1cm cell using a Zeiss PM4 spectrophotometer. Initial settling rates of the limed suspension were found graphically from the initial linear section of the measured settling curves. Final mud volumes were deter-

mined by the extrapolation of a plot of mud volume against reciprocal time⁸.

The minimum time required for flocculant solution preparation was determined on Superfloc A130, dissolved in distilled water at 0,05% and 0,5% concentration and agitated for periods between 15 min. and 6 hours before application. The flocculant dosage was 0,8 ppm on juice. All flocculant solutions were prepared by sprinkling the granular solid into the vortex of a stirrer. The effect of flocculant solution concentration on its efficiency in clarification was determined with Superfloc A130 (0,8 ppm on juice). Solutions were prepared in distilled water at various concentrations between 0,01% and 0,5%. The influence of dilution was investigated by diluting the higher concentrations immediately prior to application.

The influence of the nature of the water used as solvent was studied with regard to pH and ionic concentration. The effect of the former was determined by adjusting the pH of flocculant solutions with either 0,1M HCl or 0,1M KOH. The flocculants investigated were Superfloc A110 (approx. 30% DH), Superfloc A150 (Approx. 60% DH) and Talosep A3 (approx. 40% DH). Flocculants were prepared in distilled water as 0,05% solutions and applied at 3,3 ppm on juice. The effect of solvent ionic strength was studied by dissolving Talosep A3 (0,05% concentration applied at 1,7 ppm on juice) in water whose ionic strength had been adjusted with NaCl. Specific conductance determinations were used as a measure of ionic concentration. Samples of distilled water, factory condensate and factory tap water were also investigated. Juice for the above tests was obtained from IL.

The effect of the amount of phosphate precipitated was studied at constant calcium concentration in clear juice (320 ppm). The P_2O_5 content of a JB mixed juice sample was adjusted with H_3PO_4 and then the juice was clarified with $\text{Ca}(\text{OH})_2$ using a liming pH of 7,5 (at 70°C). The clarification behaviour of the limed suspension was analysed without flocculant, with Superfloc A110, with Superfloc A130 (approx. 45% DH) and with Superfloc A150. These flocculants were prepared as 0,05% solutions in distilled water and dosed at 2 ppm on juice. The role played by the calcium concentration in clear juice was investigated at a P_2O_5 concentration of 320 ppm in mixed juice. The calcium concentration in mixed juice was adjusted with calcium chloride and the pH raised to 7,5 with 2M KOH. Mixed juice samples were obtained from IL and TS.

Results

The relationship between initial settling rate and the time for which the solution is agitated prior to use is shown in Figure 1 for Superfloc A130. It is clear that for this polymer an equilibrium in solution is attained after 2 hours and that further agitation does not bring any improvement in the settling rate. This equilibration time is unaffected by polymer concentration. Although settling rates are affected by the period of agitation, a steady turbidity value and final mud volume had been attained even after only 15 minutes. Due to their high viscosity, flocculant solutions are generally prepared at concentrations of 0,5% or below. Low concentrations facilitate dosing and produce more efficient mixing with the limed juice. Figure 2 illustrates the effect that varying concentrations have on settling rates and shows that below a concentration of 0,05% a rapid decrease in flocculant efficiency occurs, whereas above this concentration a constant settling rate was observed. The variations in flocculant solution concentration appear to have no effect on

turbidity or final mud volume.

The conformation of the flocculant polymer in solution and thus its efficiency in promoting clarification is dependent on the pH and ionic strength of the solution. Once again, these parameters affect only the settling rates and do not produce a noticeable influence on turbidity or final mud volume. The magnitude of the effect of pH of the flocculant solution on the settling rate depends on the DH of the flocculant. It can be seen from Figure 3 that the optimum flocculant (Talosep A3) shows the greatest effect, increasing its activity as the pH of the solution is raised. The other two flocculants with DH above and

below the optimum show very little change in activity with pH. Figure 4 shows the influence that dissolved ionic species in the

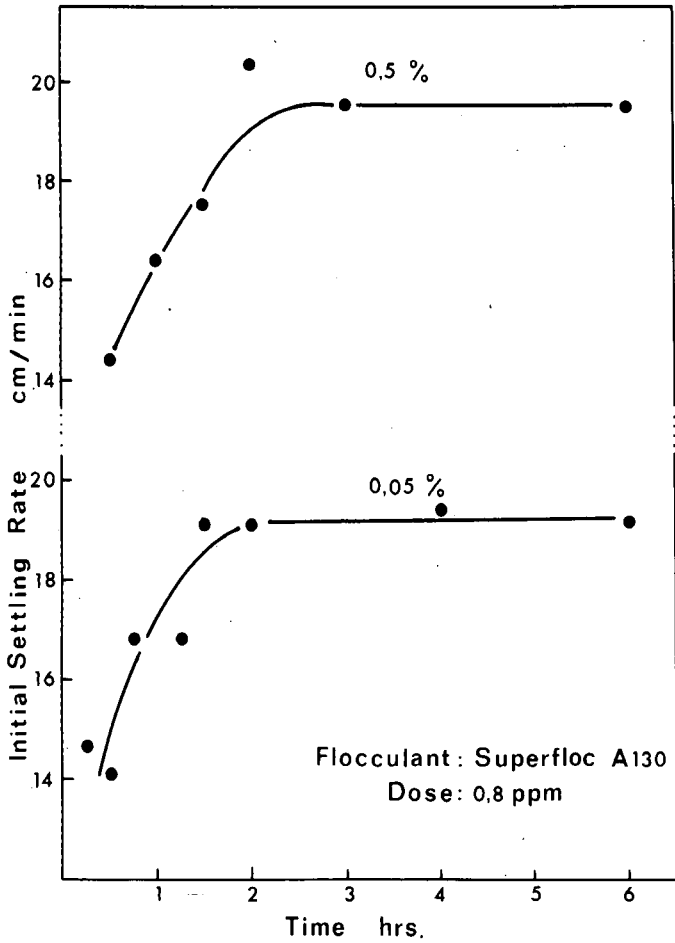


Figure 1: Effect of solution agitation time on settling rate.

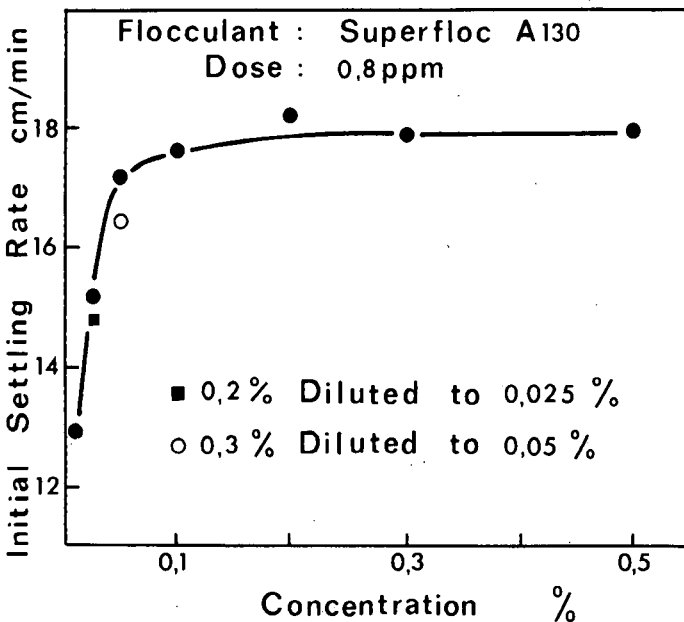


Figure 2: Effect of flocculant solution concentration on settling rate.

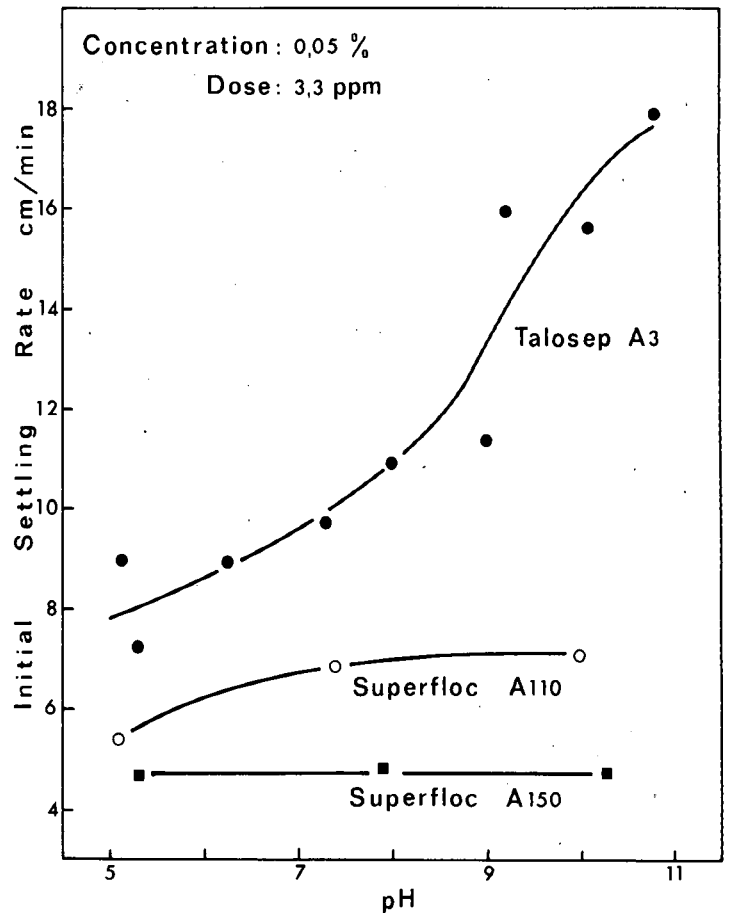


Figure 3: Effect of flocculant solution pH on settling rate.

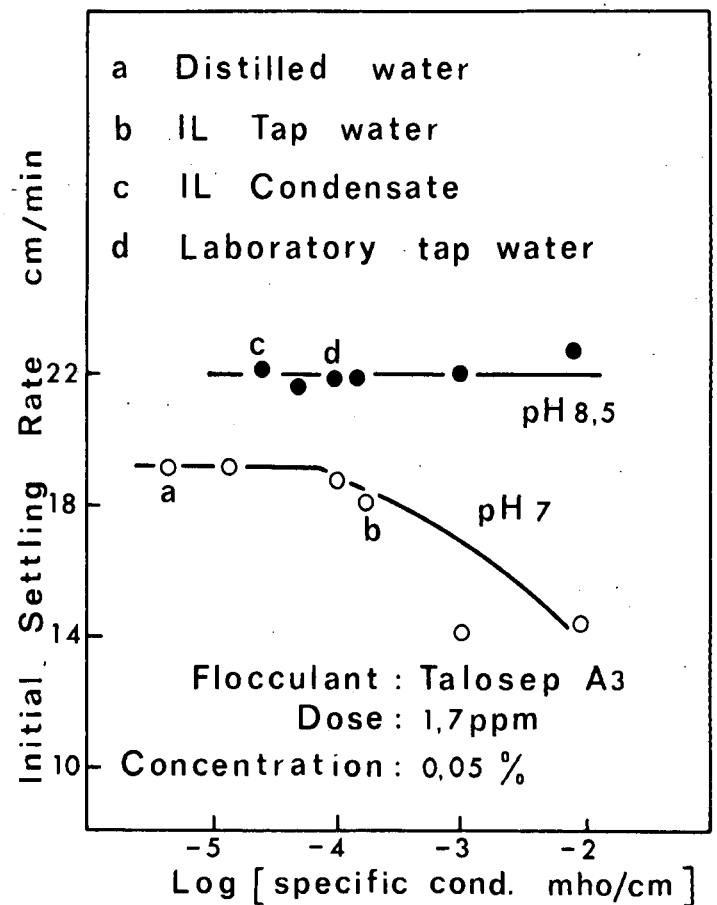


Figure 4: Effect of dissolved salts in the flocculant solution on settling rate.

flocculant preparation water have on settling rates. Solutions at relatively high pH (pH 8,5) are unaffected while those at lower pH (pH 7) show a decline in settling rate at relatively high values of conductivity. The graph indicates that little is gained by using distilled or deionized water in place of tap water as a solvent for these flocculants. It is clear that the amount of dissolved ionic species must be raised considerably before any significant decrease in efficiency is noted.

The above effects relating to flocculant efficiency should be compared with the curves shown in Figure 5 which illustrate the

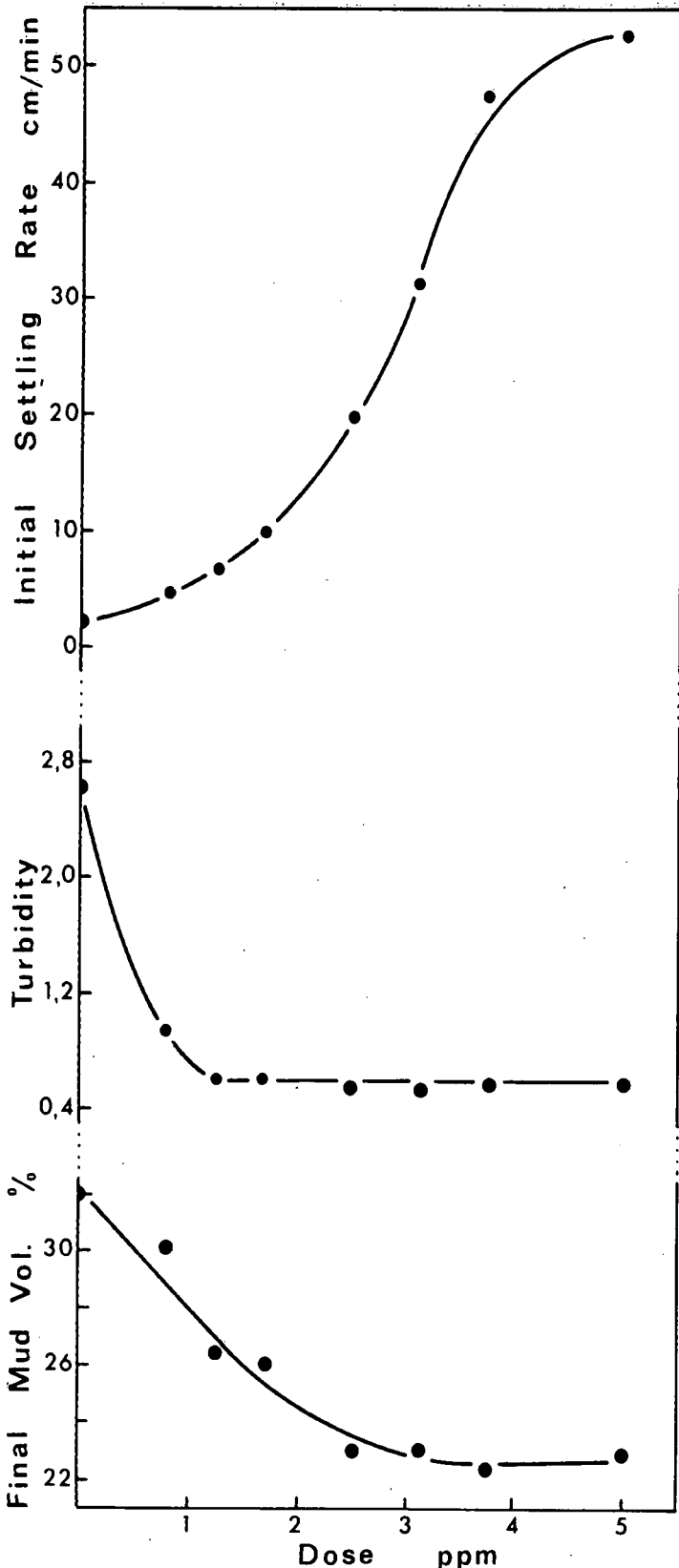


Figure 5: Example of the effect of flocculant dose on clarification.

variation in clarification with flocculant dose. Settling rates are very sensitive to the amount of flocculant used and increase to a maximum level. Turbidity decreases extremely rapidly and reaches an equilibrium value which ever increasing flocculant amounts do not affect. Similarly, final mud volume shows an initial rapid decrease followed by a slow decline. These results show why the settling rate is more sensitive than turbidity or mud volume to changes in the flocculant solution.

The variation of final mud volume, turbidity and initial settling rate for clarification without flocculant aid at increasing P_2O_5 levels in mixed juice (100-400 ppm) and at a constant calcium concentration in clear juice (320 ppm) are shown for a typical juice in Figure 6. The increase in settling rate and clarity obtained by raising the amount of P_2O_5 precipitated are the improvements expected of an increase in the inorganic precipitate^{3, 9} and are achieved at the expense of an increase in final mud volume.

Figure 7 illustrates the behaviour of three polyacrylamide flocculants of varying DH when used to flocculate the limed juice samples shown in Figure 6. The flocculants of low (A110) and intermediate (A130) DH show increases in settling rate with the A130 curve yielding a maximum near 300 ppm P_2O_5 and then decreasing markedly. The curve for the flocculant with low DH appears to rise to a maximum near 400 ppm P_2O_5 . It is clear

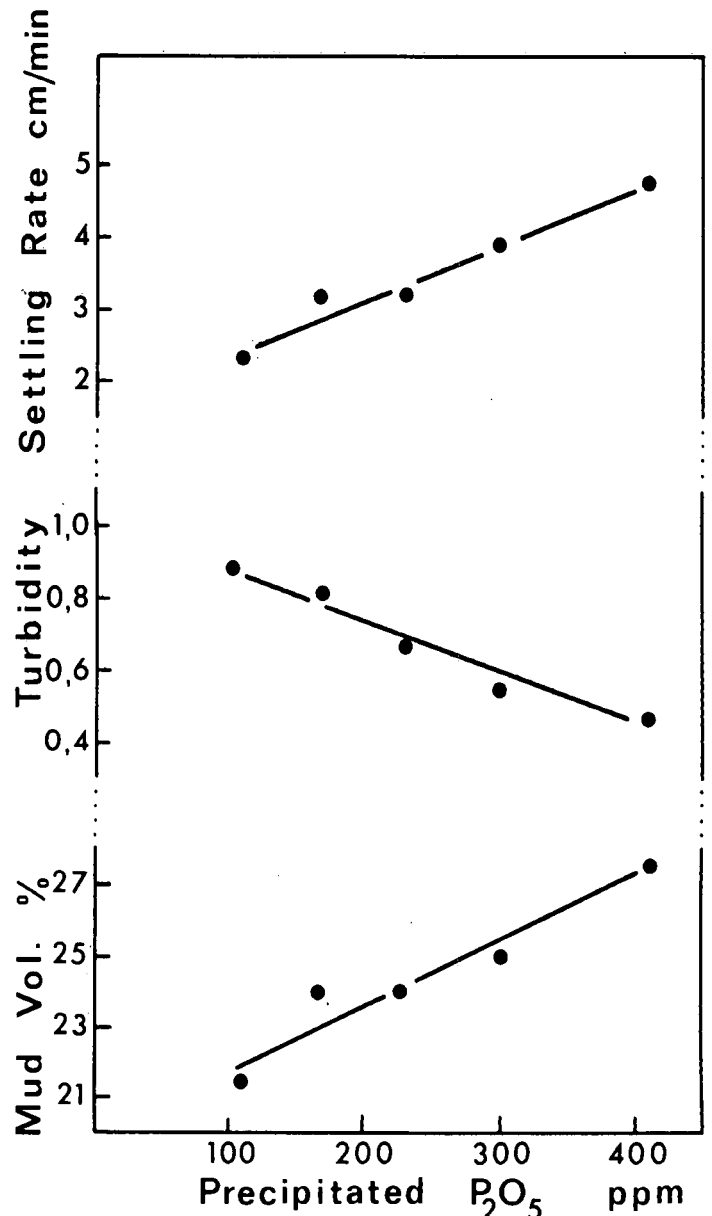


Figure 6: Effect of amount of P_2O_5 precipitated on clarification without flocculant. Amount Ca^{2+} in clear juice was 320 ppm.

that whereas Superfloc A130 is the optimum flocculant at low and intermediate phosphate levels, it is vastly inferior at high P_2O_5 levels. The high DH flocculant (A150) shows only a slight improvement in settling rate. All three flocculants show decreasing turbidity values up to 300 ppm P_2O_5 above which the clarity remains nearly constant. It can be seen that even at high P_2O_5 concentrations, at which stage it yields the best settling rate, the low DH flocculant produces reasonable, but not optimum, clarity. The final mud volume appears to be less sensitive to increases in P_2O_5 concentration in the flocculated case than it is for the unflocculated suspension.

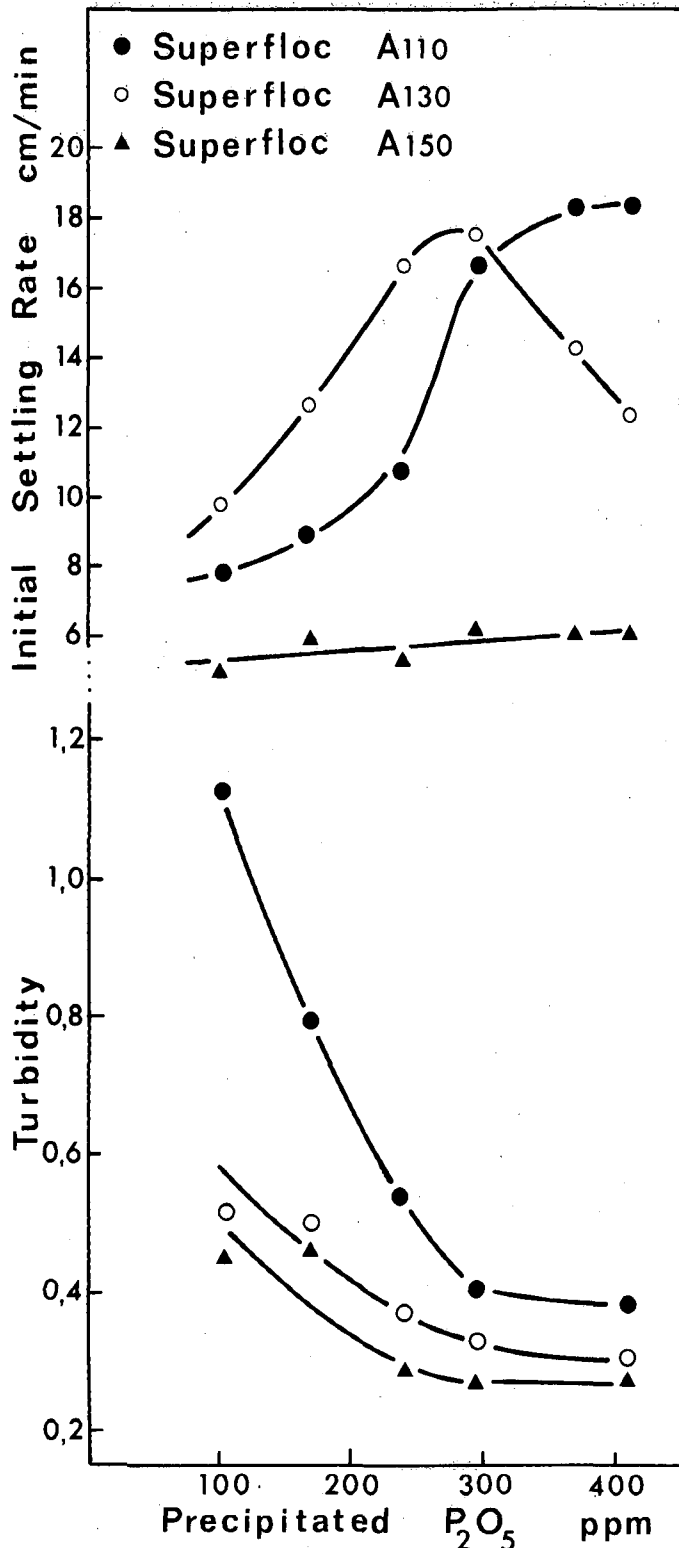


Figure 7: Effect of amount P_2O_5 precipitated on clarification with flocculants of varying degrees of hydrolysis. Amount Ca^{2+} in clear juice was 320 ppm.

The clarification properties of the limed, unflocculated suspension at various calcium concentrations in clear juice are illustrated in Figure 8. Since the quantity of P_2O_5 in mixed juice was held constant at 320 ppm, the initial changes are also affected to some extent by the increasing P_2O_5 precipitation. At 100 ppm Ca^{2+} in clear juice, 75% of the P_2O_5 had been precipitated; at 200 ppm, 85% and at 450 ppm, 90%. The suspension yields a decrease in settling rate as the calcium concentration increases. All the properties change gradually and reach a fixed value between 400 and 500 ppm Ca^{2+} . The experiments shown in Figure 8 were repeated with polyacrylamide flocculants of varying DH and the results with respect to final mud volume and turbidity are shown in Figure 9 and initial settling rate in Figure 10. The former two parameters behave in an analogous manner to the unflocculated suspension although they achieve lower turbidities and lower mud volumes. Figure 10 indicates that the flocculants of intermediate and high DH decrease in activity as the calcium concentration rises, the effect for A130 being quiet substantial. On the other hand, low DH A110 increases the settling rate up to 1 000 ppm Ca^{2+} .

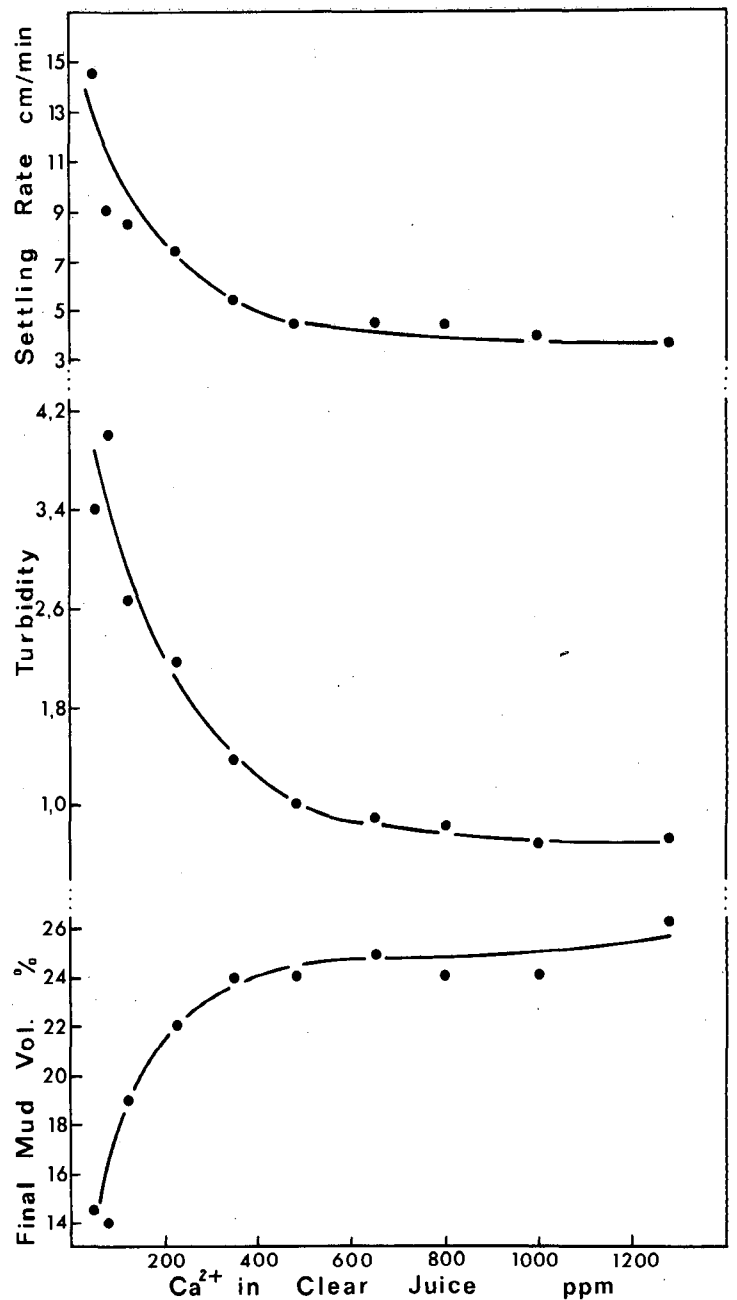


Figure 8: Effect of the quantity of Ca^{2+} in clear juice on clarification without flocculant. Amount P_2O_5 in mixed juice was 320 ppm.

These results indicate that the activity of polyacrylamide flocculants of varying DH depends on the amount of inorganic precipitate formed and on the quantity of calcium remaining in solution. The relative shape and position of the curves shown in Figure 10 are expected to depend on the quantity of phosphate precipitated. Thus for each flocculant there is a family or set of curves, each curve characterizing a particular phosphate level. Similarly the curves shown in Figure 7 will be sensitive to calcium concentration in clear juice. If the respective P_2O_5 and Ca^{2+} concentrations were to be plotted in the X- and Y- directions, then the settling rate obtained with a particular flocculant could be represented as a height above this plane. The result would be a surface in three dimensions indicating the flocculant activity under different conditions.

All the above tests were performed at a liming pH of 7,5 (at 70°C) which generally gave a clear juice of around pH 7,0 (at 25°C). At this level, the precipitation of P_2O_5 had reached its limiting value, maximum precipitation generally being obtained from a liming pH of 7 upwards. Figure 11 indicates the effect liming pH has on clarification at a constant P_2O_5 concentration in mixed juice (320 ppm) and a constant calcium concentration

in clear juice (380 ppm). The curves illustrated can thus be divided into two sections. The first below pH 7 when phosphate precipitation increases and the second above pH 7 when precipitation remains constant and all effects are due to pH changes. As expected, mud volume rises to a maximum at pH 7 and then remains unaltered. Similarly, clarity improves to a maximum but deteriorates at high pH values possibly due to the stabilization of some suspended matter. The behaviour of the flocculants with respect to settling rates is more complicated. The suspension without flocculant appears to be pH insensitive and the flocculant of high DH (A150) shows little variation with pH. The flocculant of low DH (A110) shows a maximum rate at pH 7, 2, corresponding to a minimum produced by the flocculant of intermediate DH (A130). Thus the three dimensional surface representing flocculant activity mentioned above varies according to the pH to which the suspension is raised.

Discussion

The polyacrylamide flocculants used in sugar manufacture are long chain copolymers of acrylamide and sodium acrylate. These long chain compounds are intertwined in the solid phase^{11, 14}. Thus, when a solution is prepared, time must be allowed for the molecules to become hydrated and to disentangle. Figure 1 shows the time required before an effective equilibrium is reached with respect to the clarification properties of the flocculant. Even in this state, a network of entangled polymer molecules exists in solution¹² and has been associated with its flocculant activity⁴. The fall off in flocculant activity at very low concentration (Figure 2) may possibly be explained by a weakening of this network.

The activity of a flocculant is dependent on its conformation in solution. Since these polyacrylamides are required to act as

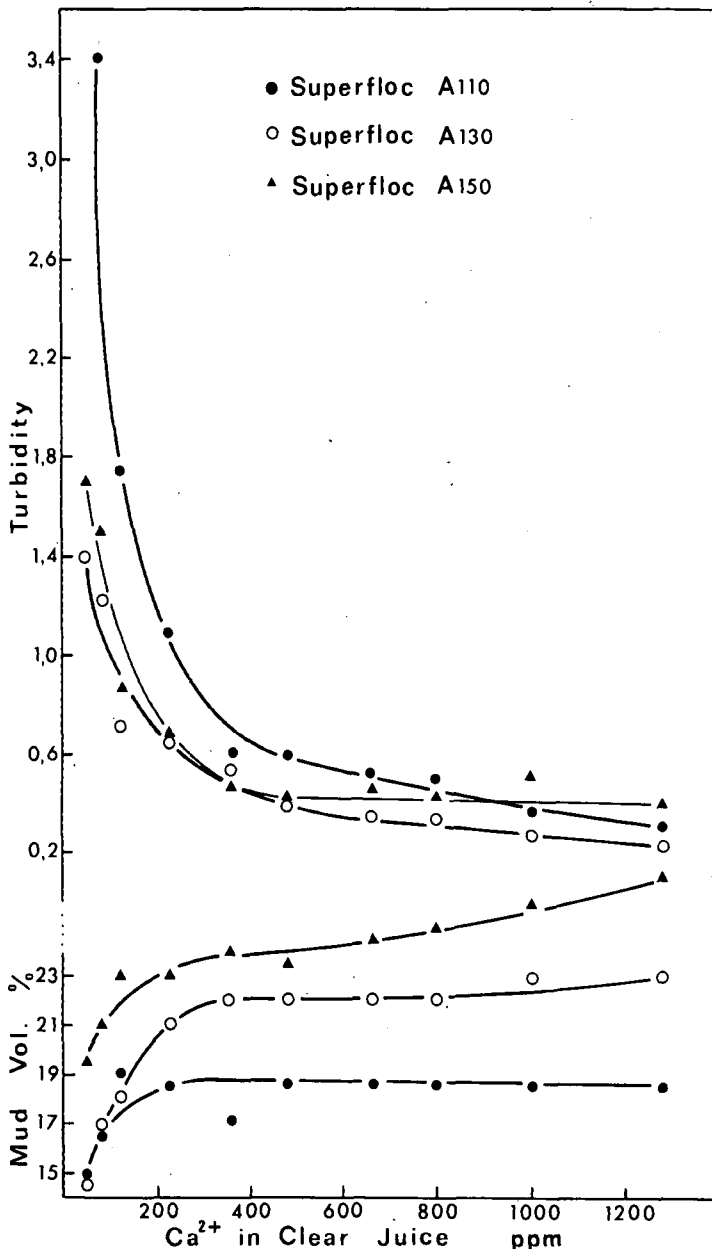


Figure 9: Effect of the quantity of Ca^{2+} in clear juice on clarification with flocculants of varying degrees of hydrolysis. Amount P_2O_5 in mixed juice was 320 ppm.

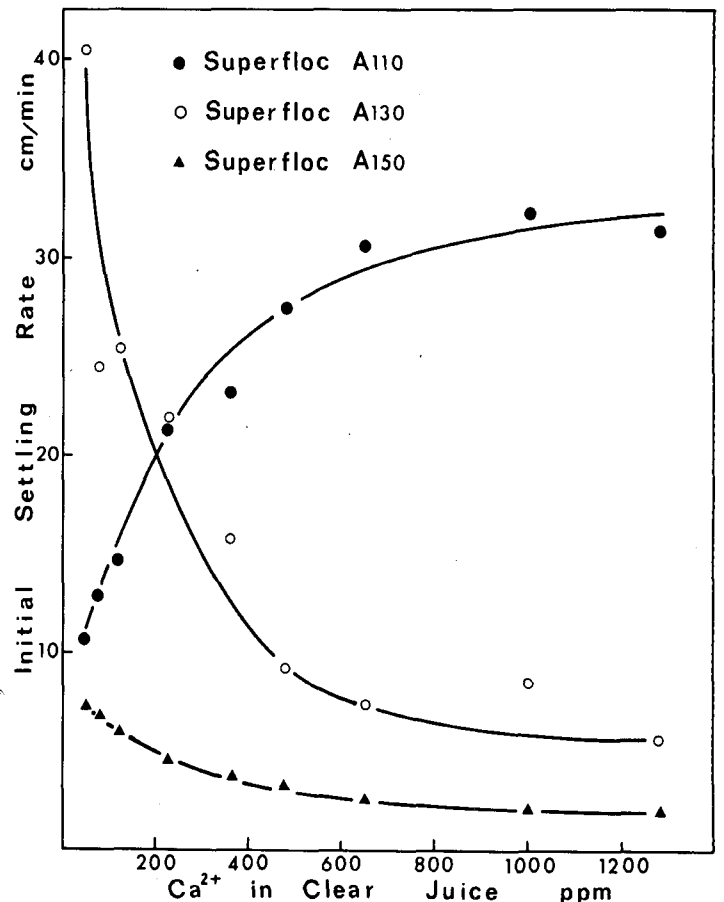
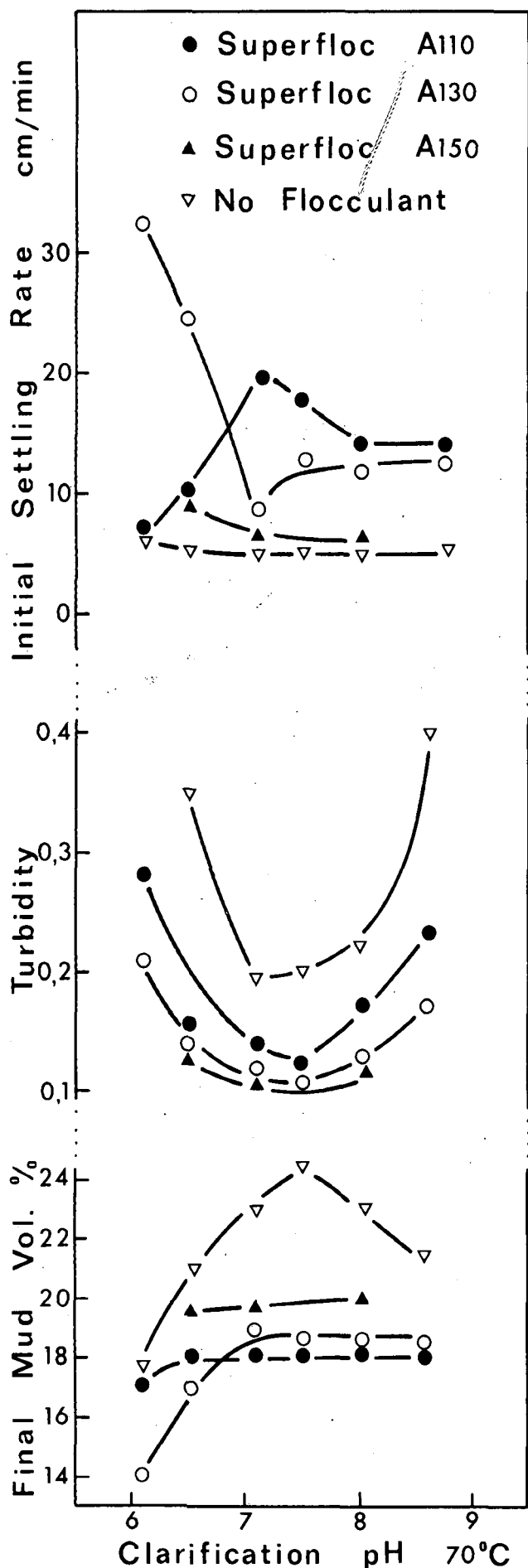


Figure 10: Effect of the quantity of Ca^{2+} in clear juice on settling rates using flocculants of varying degrees of hydrolysis. Amount P_2O_5 in mixed juice was 320 ppm.



bridges between impurity particles during floc formation, they have their best performance when the polymer chain is at its maximum extension. This extended conformation is caused by the presence of intra-molecular repulsive forces generated by the ionization of the acrylate groups along the chain. This dissociation is pH dependent, reaching its maximum at high pH and corresponds to the enhanced activity of the flocculants shown in Figure 3. The extension of the polymer in solution is also affected by the ionic content of the solvent. At high ionic concentrations, the anionic centres on the molecules gather around themselves a sufficient ionic atmosphere of counter-charge to become neutralized to a certain degree and the long polymer does not achieve such a favourable extended conformation.

The results in Figure 5 indicate that the flocculant first scavenges all the particles to which it can adsorb and rapidly achieves an optimum clarity. With increasing amounts of flocculant larger flocs are formed but little of the residual turbidity is removed.

The physico-chemical mechanism of juice clarification depends on the precipitation of calcium phosphate in a primary flocculation⁴ in which the impurities are bound into the floc. The action of the polyacrylamide is to produce a secondary flocculation, the extent of which depends on the DH of the polymer^{6,10}. The presence of an optimum DH has been explained in terms of a balance between particle-flocculant bonding and the need for the flocculant to extend into the solution and act as a bridging agent¹⁵. It is already known³ that an increase in the amount of phosphate precipitated leads to the formation of larger flocs and a more extensive primary flocculation. The overall result is an increase in settling rate and clarity of clear juice (Figure 6). Similar trends are observed with polyacrylamides (Figure 7), although the presence of a maximum in settling rate suggests that the interaction between particle and flocculant is dependent on particle size. Thus as the primary floc size increases, the individual area available for polymer adsorption also enlarges with the result that the flocculant of intermediate DH with its relatively large proportion of carboxylate groups passes into the overbound condition. Similarly, the previously ineffective low DH flocculant with its smaller proportion of carboxylate groups becomes the optimum flocculant at high amounts of precipitated phosphate.

Since both primary and secondary flocculation mechanisms rely on the adsorption of calcium ions² onto impurity particles, an increase in calcium concentration aids flocculation and thus leads to an improved clarity (Figures 8 and 9). Superimposed on this is an increase in P₂O₅ precipitate of 40-50 ppm and a change in Ca : PO₄ ratio in the precipitate of 1.0 to 1.6 which occurs over the concentration range 100 to 400 ppm Ca²⁺ in clear juice. The increase in impurity removal and inorganic precipitate explains the observed increases in mud volume. The rapid improvement in primary flocculation indicated by the rapid decrease in turbidity suggests that increasing amounts of organic impurity are being flocculated with only this small increase in the amount of inorganic precipitate. The primary flocs will thus probably become smaller in size leading to the decrease in settling rate. The variation of settling rate with Ca²⁺ concentration observed with the use of polyacrylamides appears to be related to the specific interaction between polyacrylamide and adsorbed Ca²⁺ ions rather than to changes in primary floc size. Whereas the high DH flocculant remains in the overbound condition even at relatively low Ca²⁺ concentrations, the intermediate DH flocculant tends to this state with increasing Ca²⁺ concentration and the low DH flocculant achieves optimum efficiency when the increase in adsorbed Ca²⁺ ions produces stronger particle-flocculant binding.

Raising the pH of a mixed juice suspension at constant Ca²⁺ concentration in clear juice produces changes in a number of parameters and it is thus difficult to assign exact causes to the various effects noted (Figure 11). As the pH is raised increasing

Figure 11: Effect of liming pH on clarification of a sample with fixed quantity P₂O₅ in mixed juice (320 ppm) and fixed quantity of Ca²⁺ in clear juice (380 ppm).

amounts of calcium phosphate are precipitated and the extent of Ca^{2+} adsorption also increases². The similarity of the settling curves below pH 7 to those produced with increasing Ca^{2+} concentration suggest that this is the primary cause behind the changes in flocculant behaviour. Above pH 7 the increasingly alkaline medium might render some of the adsorbed calcium inactive and a reverse in behaviour is noted. It is, however, clear that the behaviour of the suspension in respect of the pH will be very much dependent on the exact calcium and phosphate concentrations.

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