SOME ASPECTS OF FLOCCULANT USE IN CLARIFICATION AND FILTRATION

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Abstract

Clarification and filtration characteristics of some South African raw juice samples were examined in relation to flocculant usage. The influence of flocculant degree of hydrolysis on the efficiency of these processes is described. The zeta potential of the juice particles was found to modify the choice of flocculant for optimum settling and filtration.

Introduction

The currently utilised process of clarification in South Africa may be described as a destabilisation of the colloidal impurities in cane juice by interaction with a calcium phosphate precipitate followed by settling and removal of the resultant coagulum. This precipitate is obtained after the natural pH of cane juice ($pH \simeq 5,3$) has been raised to a $pH \geq 7,0$ by addition of calcium hydroxide. At this stage the calcium phosphate formed reacts with ionic calcium on the colloid surface to facilitate the defecation process, as described in detail by Bennett and others.[2-6,12]

As the settling characteristics, juice clarity and filtration properties of this system may be unsatisfactory, recourse is made to flocculant addition. The most successfully utilised additives have been based almost exclusively on partially hydrolysed polyacrylamides.[9] With the development of the so-called fast clarifier[10,11] the importance of flocculants has increased considerably and attempts have been made to investigate the fundamental mechanism of flocculant activity with reference to the clarification and mud filtration processes.[9,16] Research has focused on the relationship between the charge characteristics (i.e. zeta potential) of the colloids present in cane juice and the nature of the polyacrylamide flocculant used as defined by its molecular weight and degree of hydrolysis (or degree of anionicity). Whayman[9] suggested that the measurement of juice colloid zeta potential may in the future lead to "fine tuning" of the clarification and filtration processes by allowing the selection of flocculants to be made on a scientific rather than empirical basis.

In view of the importance of these developments, some basic studies have been undertaken at the SMRI to ascertain how flocculant behaviour is modified by the nature and quality of South African juices. The following report is a preliminary account of some of the techniques used and results obtained.

Experimental

(*a*) *Settling tests*

Data on juice quality with reference to initial settling rates and juice clarities were obtained from settling tests. Preliminary settling experiments were performed with a commercial air-heated apparatus, but satisfactory results were not obtained. Convection currents and other spurious effects persisted despite modifications to the design. Hence the air bath was discarded in favour of a more conventional water bath. This settling unit was incorporated into a bench-size clarification apparatus together with a temperature- and pH-controlled stainless steel boiling vessel (5 l) and a glycerol heated pre-heater (see Fig. 1). This assembly ensured that juice at approximately 100°C entered the settling tubes which were immersed in the thermostatically controlled water bath. The tubes were filled with 1,2 l of limed juice to give a settling height of nearly 40 cm. Excellent temperature stability of the water bath ensured the absence of convection currents in the settling tubes.

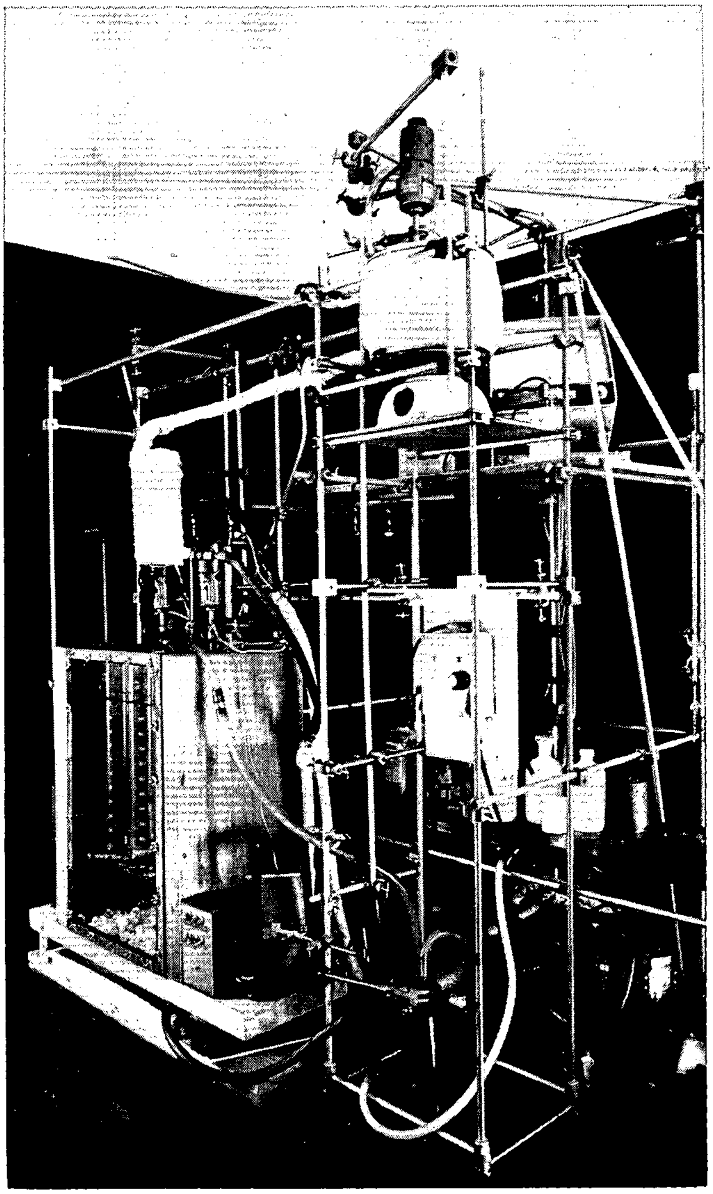


FIGURE 1

(*b*) *Analytical control*

Since the rate of settling has been found to be a function of juice brix[13] all juices were adjusted to yield a clear juice of 14°Bx. Brix values were measured by refractometer (Bausch and Lomb) using juice filtered through kieselguhr.

Inorganic phosphate content was determined by the standard molybdenum blue colorimetric method. Juice deficient in phosphate was made up to 180 ppm of P_2O_5 by addition of phosphoric acid.

Turbidity was determined as the absorbance at 800 nm in a 1 cm cell using a Zeiss PM 4 spectrophotometer.

(*c*) *Electrophoresis*

Colloid zeta potentials were calculated from electrophoretic mobilities measured with a Rank Bros microelectrophoresis apparatus. This unit was operated in the flat cell orientation which enabled observations to be made on particles moving in the vertical plane. Pd electrodes which had previously been charged with hydrogen to obviate gassing at the electrode surface were used. Experiments with reversible Ag/Ag Cl electrodes indicated that they extend slightly the range of field strengths that can be applied before ohmic heating in the sample becomes serious. This advantage was generally outweighed by the ease of maintenance and use of the Pd electrodes. All mobility measurements were made with the cell immersed in a water bath at 25°C.

Particle mobilities were determined in the natural electrolytic medium of the juice. Dilution with water or the addition of buffer was avoided as it has been reported[12] that this can lead to changes in the observed mobilities. Mixed juice was centrifuged at 20 000 rpm for 30 minutes at 20°C and then filtered through a 8,0 μm membrane filter. This produced a suspension readily amenable to laboratory investigation. Clear juice was used without any experimental modification.

The zeta potential was calculated from the Smoluchowski equation[15]

$$\zeta = \frac{4\pi\eta u}{D}$$

where η = juice viscosity
D = dielectric constant and
u = particle mobility.

In calculating the zeta potential, the viscosity and dielectric constant of the juices were found by graphical interpolation of the published values for pure sucrose solutions.[8,14]

(*d*) *Flocculants*

The flocculants used were commercially available partially hydrolysed polyacrylamides. Degree of hydrolysis was determined by nitrogen analysis using the Kjeldahl method. Flocculant additions were confined to the pre-settling stage at 0,05% solution concentration with a dosage rate of 1–4 ppm on limed juice. No flocculant was added to mud prior to mud filtration studies.

(*e*) *Mud filtration*

The percentage of mud after 2,5 hours settling time was taken as the final mud volume. Mud solids were determined by filtering the mud with a Whatman No. 1 filter paper coated with kieselguhr.

Mud filterability was studied using a capillary suction time apparatus.[1] This unit consists of a cylindrical metal reservoir (1,8 cm i.d.) standing on a rectangular piece of absorbent filter paper. The suction applied to the mud sample in the reservoir by the capillary action of the paper causes a water interface to spread out from the base of the cylinder. The time this takes to travel a fixed distance is electronically measured and is known as the capillary suction time (CST). Under the conditions of the experiment, the CST depends on the viscosity of the filtrate (approximately constant in these experiments), the mud solids content and the specific resistance to filtration. It was found that the relationship between mud solids content and CST is linear. Hence all CST values were corrected to 5% mud solids content. Under these conditions, the CST gives a measure of the specific resistance to filtration and has been used to compare filtration properties of clarifier muds. To aid these comparisons, a mud filterability was defined as

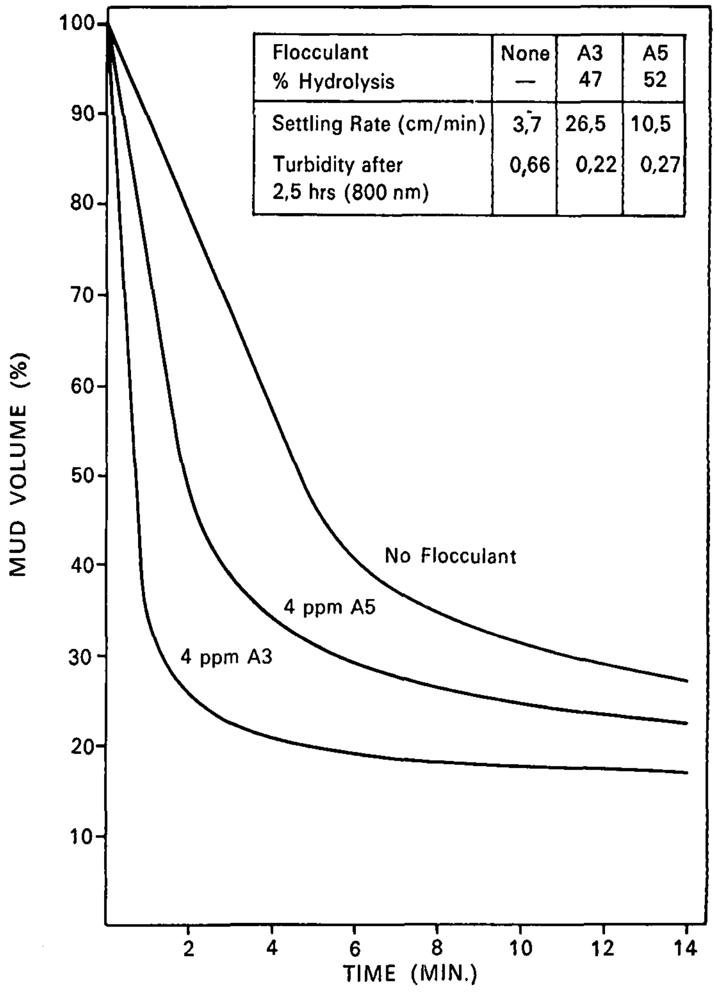
$$f_{mud} = \frac{10^4}{CST} \text{ sec}^{-1}$$

Since these studies were concerned with the influence of the flocculant added at the clarifier, no bagacillo or additional flocculant was added to the muds.

Results and Discussion

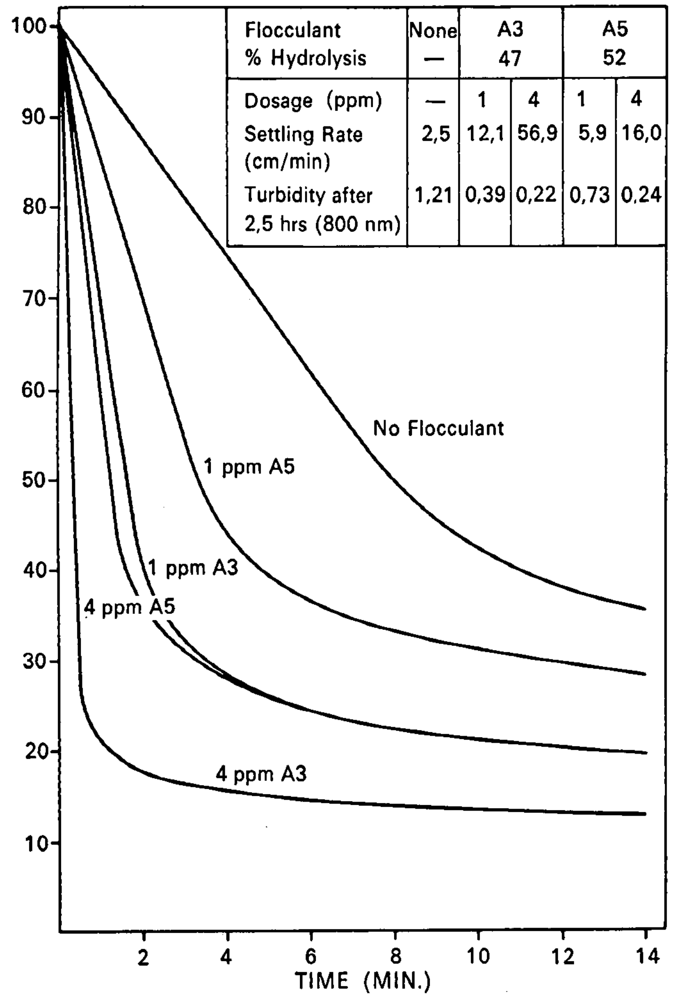
The results discussed in this section cover clarification and filtration measurements using mixed juice samples from a number of South African mills.

Although the batch settling test differs in nature from the operation of a continuous clarifier, the information obtained can be used to predict the settling behaviour of factory juice.[7] In all the settling tests the initial rate has been measured from the settling curve and the final mud volume has been taken as the value after 2,5 hours. Fig. 2 compares the influence of two commercial flocculants on juice settling characteristics. In general the efficiency of any flocculant is assessed in terms of the improved settling properties and of the increased clarity of the clear juice. The initial settling rate (Fig. 2) with Talosep A3 (26,5 cm/min) is far superior to both that of the juices with no flocculant (3,7 cm/min) and also with Talosep A5 (10,5 cm/min), although the turbidities produced by the two flocculants are comparable. The extent of these improvements can be modified by a change in dosage rate: larger doses effect better settling and lower turbidities. For example, the settling curves in Fig. 3 show the overall increase in efficiency by raising the dosage rate from 1 ppm to 4 ppm for two commercial flocculants, Talosep A3 and A5. At the 1 ppm A3 dosage the settling rate is similar to that at 4 ppm A5 dosage, but the ensuing clarity of the latter is far superior for this particular juice.



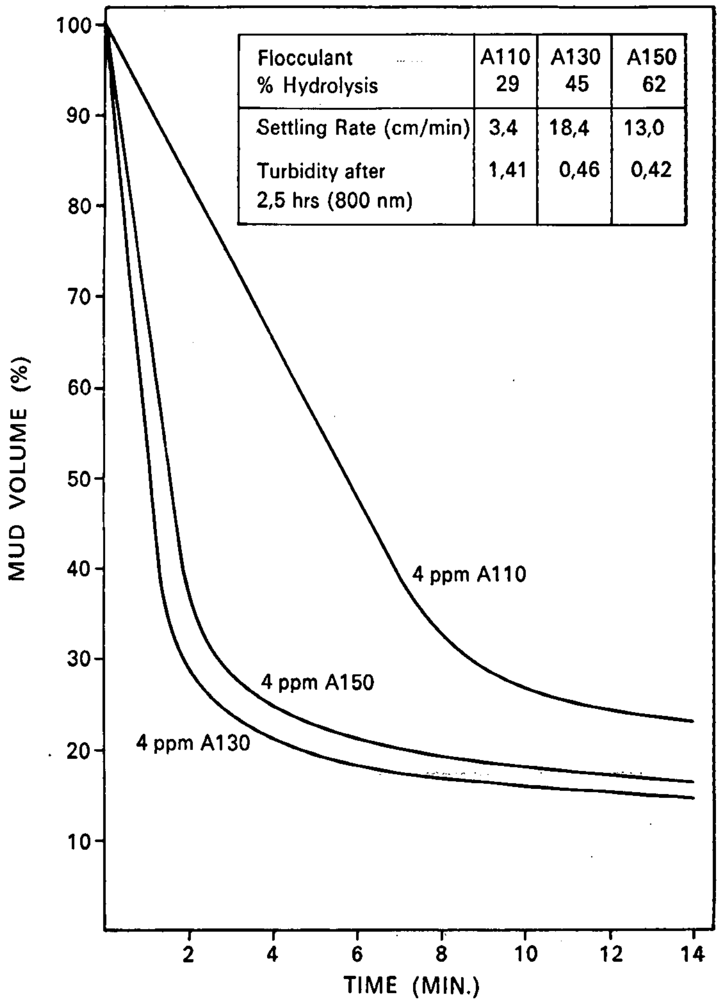
Flocculant % Hydrolysis	None —	A3 47	A5 52
Settling Rate (cm/min)	3,7	26,5	10,5
Turbidity after 2,5 hrs (800 nm)	0,66	0,22	0,27

FIGURE 2 Comparison of different Talosep flocculants on clarification of a raw juice sample from JB.



Flocculant	None	A3		A5	
% Hydrolysis	—	47		52	
Dosage (ppm)	—	1	4	1	4
Settling Rate (cm/min)	2,5	12,1	56,9	5,9	16,0
Turbidity after 2,5 hrs (800 nm)	1,21	0,39	0,22	0,73	0,24

FIGURE 3 Comparison of different dosage rates of two Talosep flocculants on clarification of a raw juice sample from JB.



Flocculant	A110	A130	A150
% Hydrolysis	29	45	62
Settling Rate (cm/min)	3,4	18,4	13,0
Turbidity after 2,5 hrs (800 nm)	1,41	0,46	0,42

FIGURE 4 Comparison of the influence of degree of hydrolysis of different Superfloc flocculants on clarification of a raw juice sample from IL.

In order to understand why the response of a juice to different flocculants can vary so widely, it is necessary to examine more closely the relevant properties of the flocculant as well as its interaction with juice colloid particles.

The flocculants used in sugar milling are very high molecular weight copolymers of acrylamide and sodium acrylate. The latter ionic groups are randomly distributed along the polymer chain and give the flocculant a negative electrical charge in solution. The particles of the limed juice also carry a negative charge and have calcium ions adsorbed to their surface. These ions can bind to the acrylate groups of the flocculant which thus attaches itself to the surface of a juice particle at a number of sites. The remainder of the polymer extends into the bulk of the juice where it can bind to other particles. A large three-dimensional floc structure forms in which the large flocs settle rapidly and having bound together most of the suspended particles leave a clear supernatant liquid.[16]

In relation to this mechanism there are two properties of the polymer which are of importance, namely molecular weight (or chain length) and degree of hydrolysis (percentage of acrylate groups present). A high molecular weight is required for the flocculant to bridge the distance between the particles in the juice. Hence one of the main requirements of a good flocculant[16] is a molecular weight not less than 10^6 but preferably of the order of 10^7. This gives a sufficient chain length for the polymer to efficiently bind together the particles into a good floc structure. The effect of degree of hydrolysis can be seen in Fig. 4 where the settling curves of a low, average and high degree of hydrolysis flocculant are shown. It is found that for any given juice, there exists a degree of hydrolysis which will produce a maximum settling rate. Any hydrolysis above or below this value produces inferior initial rates. Of the three different flocculants shown in Fig. 4, the one with the intermediate degree of hydrolysis (Superfloc A130) yields the best settling rate. Low turbidities are produced by the intermediate and high degree of hydrolysis flocculants, while that given by Superfloc A110 is far inferior. Similar effects have been reported in Australian juices and related to the zeta potential of the particles in the juice.[9,16]

The zeta potential–pH relationship has been determined for a number of S.A. juices clarified over the pH range 5–10. This relationship can vary from week to week. Fig. 5 shows data from two samples of juice dated 19/11/1974 and 25/11/1974 from ME. The slope of the graph for the juice sampled on 19/11/74 indicates a rapid drop in zeta potential as pH increases, whereas the second sample shows little variation in zeta potential over the pH range studied. The significant difference in gradient indicates a fundamental change in the nature of the particle surface, but no information is as yet available on the adsorbed chemical species responsible. It has also been observed that the actual magnitude of the zeta potential of the juice particles at the pH of clear juice can vary. Different samples of juice from IL have shown zeta potentials in the range 0 to —10 mV at a pH of 7.

Fig. 6 summarizes settling, turbidity and filtration data of two IL samples which have zeta potentials which differ greatly, viz. —0,5mV and — 9,4 mV at pH = 7,0. (In fact many of the juice samples studied fall within this mV range.) These juices were clarified in the laboratory using flocculants of

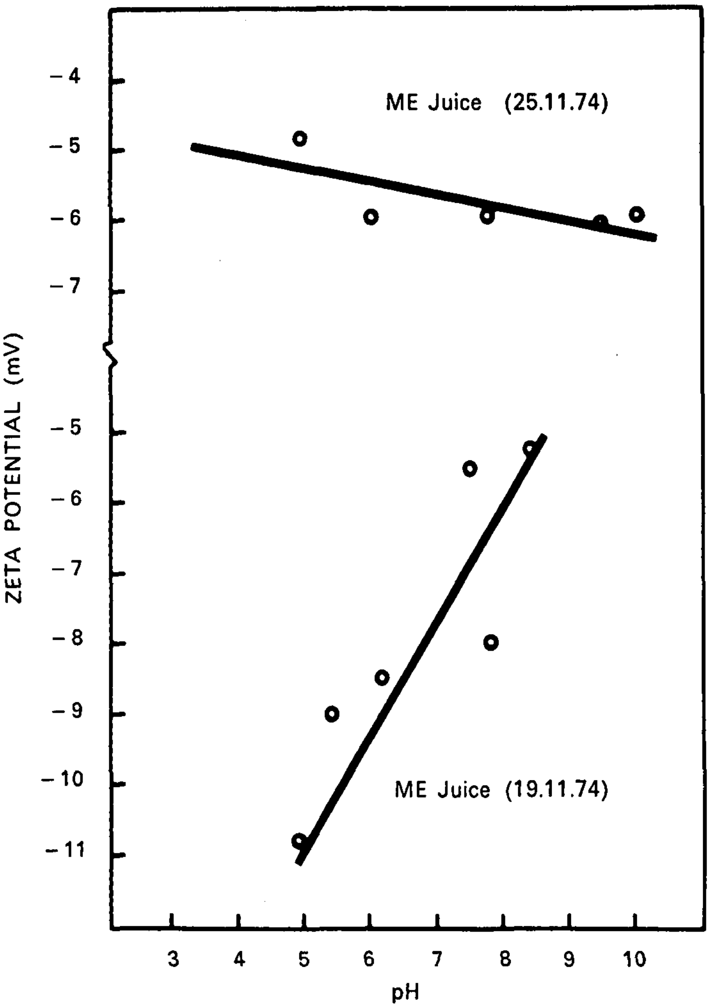


FIGURE 5 Variation of zeta potential with pH for two juice samples from ME.

similar molecular weights (according to the manufacturer) but with a wide range of degree of hydrolyses. The settling rates are plotted on a relative percent basis in which the initial rates are expressed as a percentage of the maximum initial rate observed.

For both juices a maximum in settling rate occurs at a particular degree of hydrolysis, the position of which depends on the zeta potential of the particles in the limed juice. IL juice 2 which has a high negative value of $\zeta = -9,4$ mV requires a much higher degree of hydrolysis (= 52%) than IL juice 1 ($\zeta = -0,5$ mV) which demands a degree of hydrolysis = 40% for optimum settling. In milling practice this would necessitate a change-over from one flocculant to another in order to maintain peak settling performance. The magnitudes of the degree of hydrolyses which are required for optimum settling, i.e. 40%, 52% are considerably greater than those used in Australia[16] where apparently the degree of hydrolysis range is mainly confined to 22%–35%.

The shape of curves a_1 and a_2 (Fig. 6) can be explained in terms of flocculant-particle bonding. At less than optimum hydrolyses the flocculant does not bond strongly enough to the particles due to a deficiency of charged bonding sites on the polymer. At greater than optimum hydrolyses the highly-charged polymer chain becomes bound to the particle at so many sites that the growth of large flocs is hindered. A maximum settling rate is achieved when these two effects are balanced.

The flocculant for optimum settling produces good juice clarities in both examples (curves b_1, b_2) but those with lower hydrolyses give inferior clarities due to their inability to scavenge all the particles during settling. However flocculants with higher hydrolyses will produce slightly better clarities although the corresponding settling rates decrease.

The relationship between mud volumes and flocculant hydrolyses has not been completely established although in curves c_1 and c_2 mud volumes tend to increase as the degree of hydrolysis becomes greater. In some samples studied in the laboratory this increase is masked by an unexplained factor.

With reference to mud filterability the value of f_{mud} shows a maximum for curve d_1 at degree of hydrolysis = 52%; for d_2, a continuous rise was measured over the complete range studied, i.e. up to flocculant degree of hydrolysis = 62%. Other IL juice samples where the zeta potentials lie between the two extreme values of $\zeta = -0,5$ mV and $-9,4$ mV follow an intermediate trend in flocculant degree of hydrolysis. Three significant points have been noted from these results, viz.:

(i) flocculant addition during clarification has a supplementary effect on mud filtration;

(ii) the less negative the juice zeta potential : the better is mud filterability;

(iii) the less negative the juice zeta potential : the lower is the degree of hydrolysis required for optimum filterability.

It has been observed that degree of hydrolyses for optimum f_{mud} values are normally greater than those which provide optimum settling rates. This phenomenon is presently being studied.

Conclusions

At present the basis of selection of flocculants to be used in the industry appears arbitrary. Contrary to this situation the results of this study show that a judicious choice may be made by examining the zeta potential–pH relationship of the cane juice system, and relating this dependence to principally the flocculant degree of hydrolysis. Flocculants added as an aid to clarification are shown also to have a measurable influence on the filterability of the mud formed. Those flocculants which possess a degree of hydrolysis greater than that required for optimum settling may provide better clear juice clarity and superior mud filtering qualities. In addition the results indicate that the zeta potential of mill juice may change markedly necessitating a reassessment of the flocculant requirement if optimum clarification performance is to be maintained.

During the 1975/76 milling season it is intended to apply the techniques used in this basic investigation to study more extensively the clarification and filtration processes as practised in local mills.

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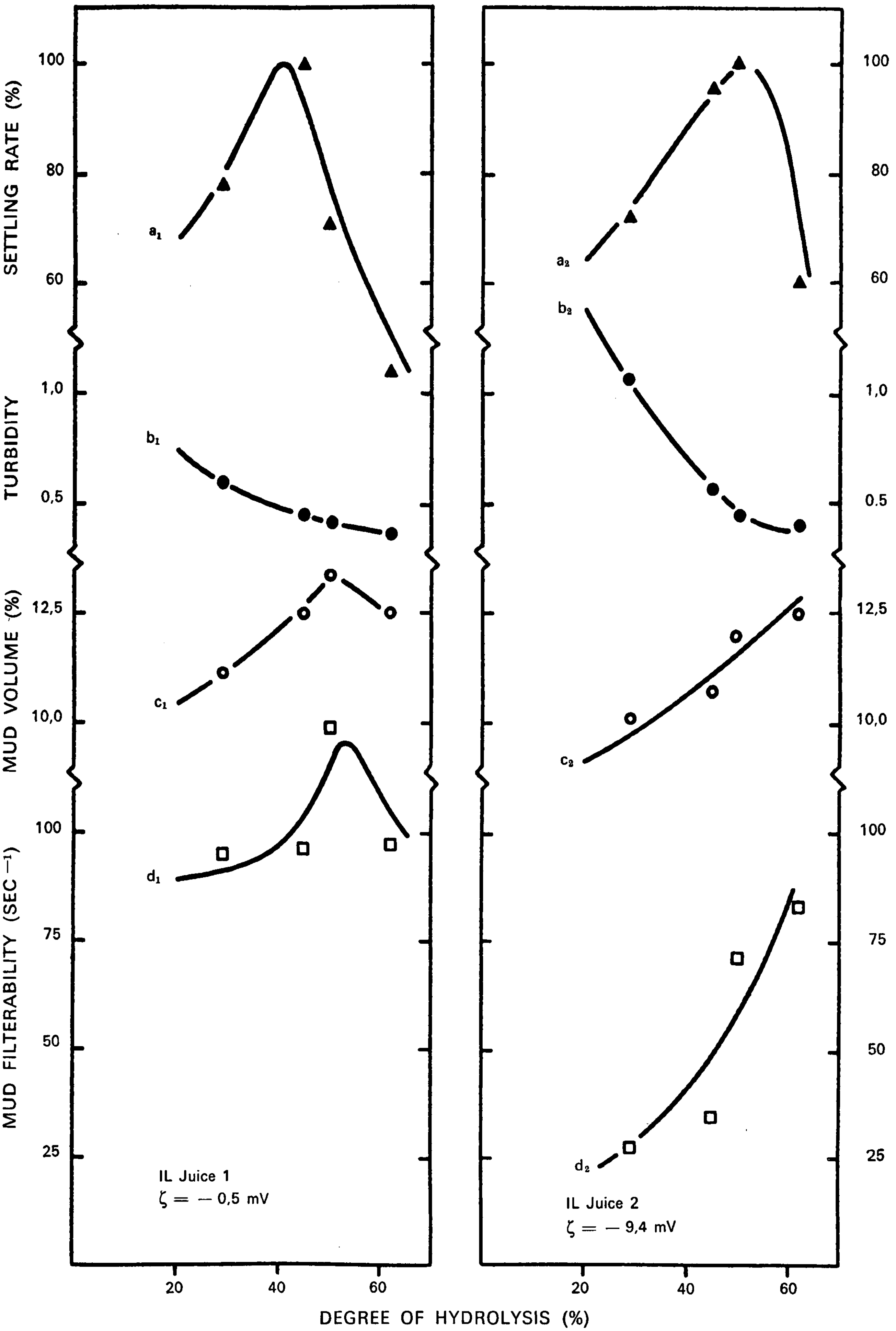

FIGURE 6 Comparison of the influence of degree of hydrolysis of the flocculant on clarification and mud filtration of two IL samples with different zeta potentials.

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