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## The Effects of Zeta Potential and Flocculant Molecular Chain Length on the Flocculation of Fines

Kai F. Chiu  
*Western Michigan University*

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THE EFFECTS OF ZETA POTENTIAL  
AND FLOCCULANT MOLECULAR CHAIN LENGTH ON  
THE FLOCCULATION OF FINES

THESIS SUBMITTED TO THE DEPARTMENT OF  
PAPER TECHNOLOGY AT WESTERN MICHIGAN UNIVERSITY  
KALAMAZOO MICHIGAN AS PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE

Kai F. Chiu  
WESTERN MICHIGAN UNIVERSITY  
KALAMAZOO MICHIGAN  
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### ABSTRACT

The factors controlling floc formation and cohesion are discussed in terms of fiber entanglement, electrokinetic potential and fiber-polymer bridging. The methods of measurement of zeta potential and degree of flocculation are also considered. In addition, an experiment is designed to relate zeta potential, molecular weight of synthetic polymers and the degree of flocculation of fines.

It is found that fiber length is the most predominant factor controlling flocculation. The bridging effect of polymer comes next. The higher the molecular weight, the greater the degree of flocculation. The electrokinetic potential effect is only influential if simple electrolytes are used as flocculant, and if no bridging occurs in the system. Under such conditions, the magnitude of the zeta potential becomes significant.



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## INTRODUCTION

In recent years, many serious thoughts have been given and many dramatic actions have been taken in dealing with the enormous water pollution problem. Mainly due to the continuous pressures applied by the State and Federal Governments, the pulp and paper industries become more and more concerned with the stock recovery from save-all and the mill effluent treatment.

Flocculation of the suspended solids is an inevitable step in these processes and its effectiveness determines to a great extent the overall efficiency. In order to have a better knowledge in this area, the factors controlling the flocculation of fines are investigated. Special consideration is given in the use of synthetic polymers as flocculants.

## LITERATURE REVIEW

In the beating or refining of fiber preparation processes, an ~~unavoidably~~ amount of cellulosic and hemi-cellulosic material in a fine state of subdivision is produced mainly as the result of cutting. This portion of the fiber system is considered as "fines." No exact dimensions are agreed upon to define this small fibrous element. Clark (1) selected any fibrous elements having lengths under 0.1 mm. and projected area of under 0.10mm. by 0.01mm. as fines. Ilvessalo (2) considered 0.5mm. as the length limit. In general, any fiber below 0.1 to 0.2mm. in length should be regarded as fines (3).

## FLOCCULATION

The term "flocculation" is used to describe either the process by which randomly distributed, localized aggregates of fibers are formed in a pulp suspension, or the state of being formed. A study of the process of flocculation in fiber suspensions gives us a basic understanding of the flocculation of the fines. The mechanisms controlling fiber flocculation are:-

- (1) Fiber entanglement
- (2) Electrokinetic potential
- (3) Bridging

## FIBER ENTANGLEMENT

Since the extent of fiber flocculation in a suspension is a function of the interactions between fibers, the most obvious explanation to flocculation is that of mechanical fiber entanglement.

Many investigators in this area believe that flocculation is mainly affected by the physical state of the fibers. Mason (4,5) has done extensive theoretical and experimental work concerning the flocculation formation in a fiber suspension from a mechanical entanglement view point. It is shown that mechanical clotting is increased by increased beating of the fibers. It is likely to be due to the increase in fibrillation and fiber flexibility and specific volume. In addition, the gelatinous surface layer of the swollen fiber may also increase interfiber cohesion.

The recent work of Jacquelin (6) shows that there appears to be an intermediate area of optimum fiber flexibility that favors the formation of flocs. It is believed that highly flexible or very rigid fibers could affect flocculation adversely.

From the collision viewpoint, flocculation is affected by fiber length, consistency, shear, temperature and time.

Long fibers favor flocculation formation. It is logical because longer the fiber, greater is the probability for it to come into contact with another fiber when it is

coiling and uncoiling in the aqueous system.

At very low consistencies (below 0.01%), the fibers are isolated from each other and they behave quite independently except for occasional collisions. Each fiber rotates in a well-defined pattern. Mason describes this by defining four types of fiber rotation, depending on the fiber flexibility. At high consistencies, flocculation becomes favorable. It is due to the larger number of fibers available for collision and entanglement. Gray (7) illustrates that there is a critical consistency for uniform dispersion. Recently, Henning (8) and Jacquelin (6) show that there is a certain critical concentration that favors formation. In the case of softwood pulps, this is in the range of 10-17g/liter; for short fibered hardwood pulps, the favored range is 22-30g/liter. It can be seen that the critical concentration value depends on both the type and length of fibers.

Campbell (9) points out fiber flocculation is also caused by eddy currents of low velocity. Chang and Robertson (10) suggested that when a shear gradient is applied to the fiber suspension, the relative motion of fibers brings them into contact and increases the chances of adhesion. At the same time, this shear tends to disperse the flocculations already formed. A dynamic equilibrium can be achieved in which the rate of destruction of existing flocculations by shear stresses is equal to that of the building up of new flocculations by chance collision.

Temperature affects fiber collision in two ways.

First, high temperature reduces the viscosity of the water which allows for an increase in the ease of movement of the fibers and also increases the rate of settling. Secondly, high temperature increases the Brownian movement of the colloidal particles and thus increase the rate of flocculation formation. This is verified by Beasley (11) who shows that a decrease in temperature from 87° to 67°F decreases flocculation.

Flocculation is not an instantaneous process. Time must be allowed for the colloids to grow and the flocculations to form.

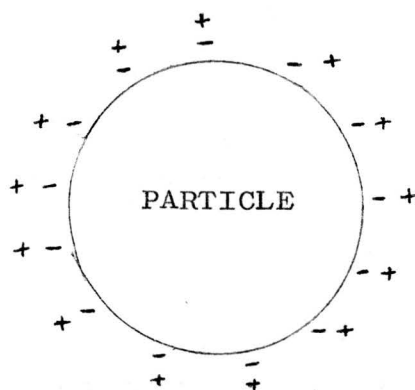
The composition and type of fiber also affect the degree of flocculation (11, 12). Generally, the degree of flocculation in decreasing order is as follows: cotton linters, bleached kraft, unbleached sulfite, bleached sulfite and ground wood. Unbleached fibers usually tend to flocculate more than bleached fibers. Fibers with a lower hemicellulose content tend to flocculate more than fibers with a higher hemicellulose content.

Chang and Robertson (10) summarize flocculation as "a process of fiber entanglement in which fiber length, flexibility and concentration determine the geometry of entanglement, and surface roughness, friction and fiber-colloid properties determine the effectiveness of inter-fiber contacts in the formation of aggregates and in resisting disruptive forces."

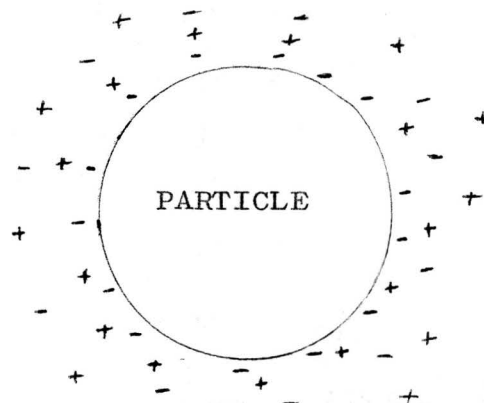
## ELECTROKINETIC POTENTIAL

In distilled water, cellulose fibers acquire a negative charge on their surfaces and behave as negatively charged particles (13). This is the result of selective adsorption of ions, dissociation of electrolytically active groups on the surface or from the orientation of dipoles contained in the liquid phase. Recent work shows that this charge is in the range of -5 to -30 millivolts, depending on the types of fibers used (14).

The purely physical interpretation of this phenomenon is based on the theory of the electrical double layer, originally formulated by H. von Helmholtz (15). In the simplest case, this double layer can be regarded as an electric condenser, the potential of which is termed electrokinetic potential or zeta potential. It is assumed that the layer consists of two parts, one located at monomolecular distance in the liquid surrounding the particle, the other being firmly attached to the surface of the solid. The general concept of the Helmholtz electrical double layer of a particle in contact with a liquid is schematically shown in (FIG.I.)

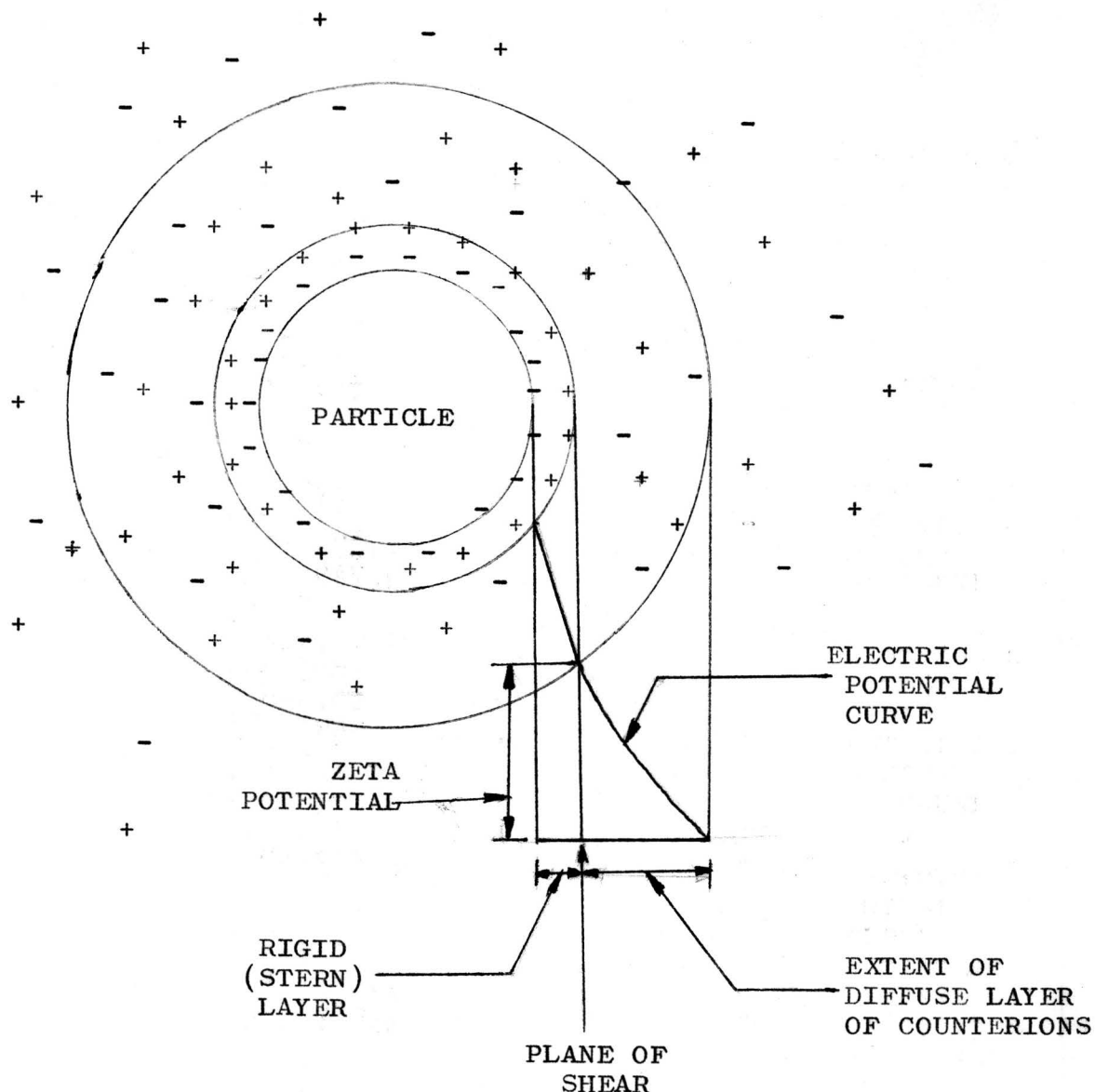


HELMHOLTZ DOUBLE  
LAYER  
FIG.I



GOUY DIFFUSE DOUBLE  
LAYER  
FIG.II

Gouy (16) modified the theory and assumed the potential gradient is not abrupt but diffuses over a short distance (FIG.II). This gives the theory of diffuse double layer. Stern (17) further modified the theory by assuming there is a stationary layer (Stern layer) surrounded by the diffuse double layer. This basic concept is illustrated in (FIG.III)



STERN'S CONCEPT OF ZETA POTENTIAL

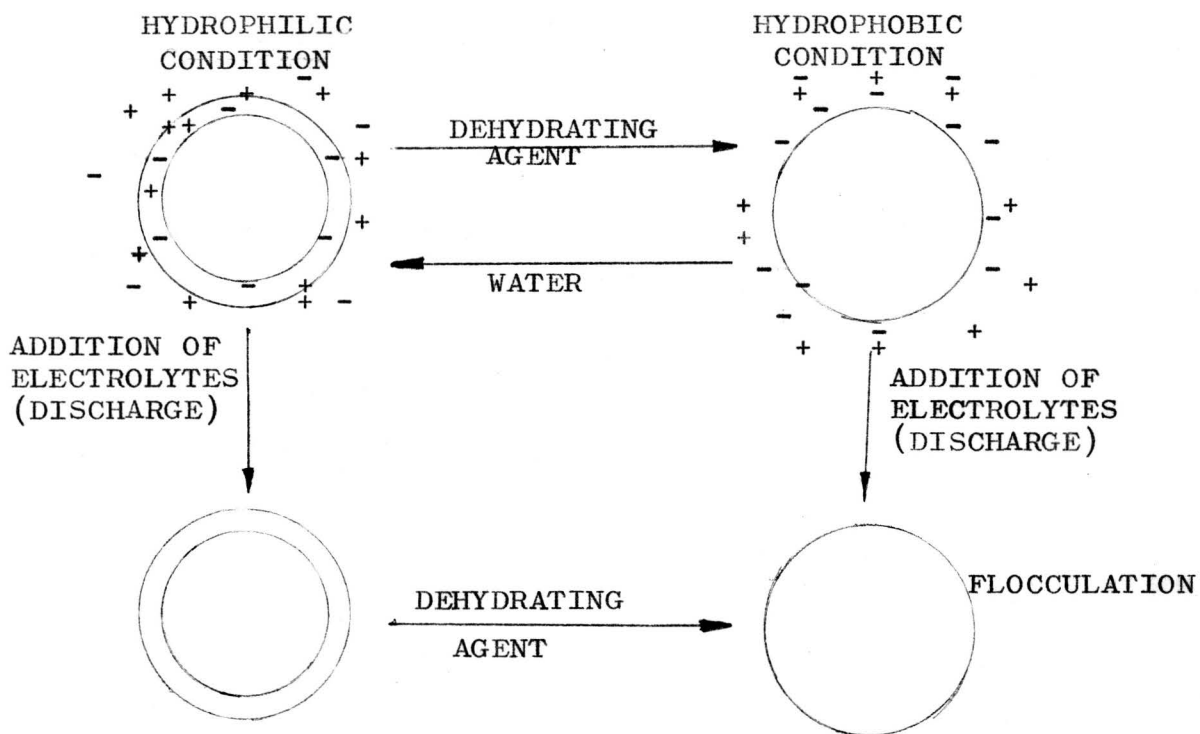
FIG.III.



For a colloidal suspension the particles are kept in stable dispersed state by two factors:-

- (1) a zeta potential, between the particle and the surrounding liquid;
- (2) a layer of adsorbed water molecules on the particles.

Flocculation is most favorable when zeta potential approaches zero and the adsorbed water molecule layer is absent. (FIG.IV) (18).



ELECTRIC NEUTRALIZATION AND DEHYDRATION  
OF COLLOIDAL PARTICLES

FIG.IV.

In water, fines behave as negatively charged colloids and repel each other and before contact can be established, these charges have to be overcome. Ionic materials and

charged colloidal materials are attracted or repelled by the fibers, depending on the sign of the charge. The adsorption of such materials change the surface potential of the fibers and thus change their flocculation behavior. The problem becomes that of stabilizing or destabilizing a dispersion by mutual repulsion or attraction of particles using adsorption of charged ions.

When the electrical repulsion between fibers are neutralized by adsorption of positively charged ions to the isoelectric point, the natural Van der Waal's attractive force becomes significant and eventually causes flocculation. However, if excess positive ions are added, the charge on the fibers are reversed and redispersion will take place (19).

The effectiveness of electrolytes on flocculation is expressed in the Schulze-Harley rule (20) which states that the higher the valence of the precipitating ion, the greater the coagulating power. However, ions of the same valence and sign differ somewhat in their flocculation values depending on the size. This is defined by the Hofmeister series. The effect of valency on zeta potential of cellulose was extensively studied by Briggs (21). This effect of ions on the electrokinetic potential of cellulose was also recently studied by Khripunova (22).

Since pH affects the behavior of electrolytes, it also affects the zeta potential and the degree of flocculation. Alum acts as a dispersing agent in the pH range 4.5 to 9.0 but acts as a flocculating agent outside this region(23).

Erspamer (24) showed that fibers form large stable flocs in benzene because the zeta potential is  $-142\text{mv}$ . He also demonstrated the redispersing effect of pyrophosphate by reversing the electrokinetic charge on fibers previously flocculated by addition of alum.

Cohen (25) suggested that the similarity between the effects produced by dilute solution of electrolytes on the zeta potential of cellulose and on freeness might be related to the electrokinetic properties.

Eklund's (26) work shows that zeta potential is a function of the fineness of pulp fibers. The zeta potential of the fine fraction is higher than that of the coarse fraction, probably by reason of a difference in chemical composition or due to the larger surface charge density.

Vinogradova and Yur'ev (27) conclude in their work that the zeta potential of beaten and dried pulps is lower than that of the initial pulps.

Other investigators dealing with the electrokinetic properties of fibrous suspensions include Sarret (28), and Hästbacka (29).

#### BRIDGING

In a study made by Erspamer (30), it is found that "starch flocculated the pulp fibers, even showing the effect in the absence of alum." The fact that starch, a negatively charged colloid, increases flocculation makes the simple zeta

potential model insufficient.

To explain this phenomenon, La Mer's (31) model of 'bridging' is more applicable. According to this model, a segment of a long polymer is adsorbed on the fiber surface, probably by hydrogen bonds, leaving a portion of the polymer free to be absorbed on another fiber surface. Thus, the polymer forms a bridge between the fibers and acts as an interfiber adhesive. In this model, the zeta potentials of the fibers and the polymer probably control the rate at which the adsorption takes place, but the equilibrium of the adsorption is controlled by chemical interactions. The chemical interactions which operate in flocculation are probably very intense at short range and are of sufficient magnitude to overwhelm the electrostatic repulsion between particles having net charges of the same sign. This bridging action is shown in FIG.V. While only one linkage is shown, it should be realized that in practice, a number of interfiber bridges are formed, linking a number of particles together.

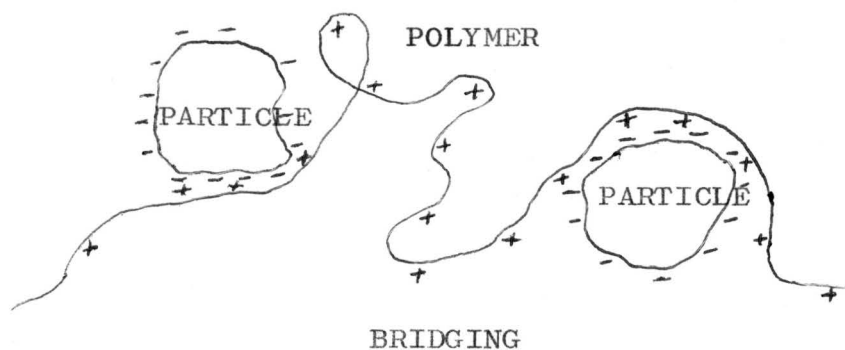


FIG.V.

In a study made by Szwarcasztajn (32), it is postulated that the flocculating effect of starch on cellulose fiber should be related to the cross-linking action of phosphate groups contained in starch.

The addition of starch to a pulp dispersed with alum brings about better flocculation (24). In this case, the formation of the positively charged alumina bridge to the negatively charged fiber increases the efficiency of adsorption of the negatively charged starch.

Polymers made from natural products, such as starch and gums, always restrict the degree of modification that can be put in them by chemical processes. It is not always possible to make the most desirable polymer from these raw materials. Therefore, synthetic polymers are made to suit different end uses. Polyethyleneimines, polyamides, polyacrylates and polyacrylamides are synthetic polymers for flocculation (33).

The flocculating effect of a linear cationic polymer, poly-(1, 2-dimethyl-5-vinyl-pyridinium methyl sulphate) has been studied (34). This polymer in solution is nearly completely adsorbed to cellulose surface until the latter is fully covered. After this, further additions of polymer merely increase the concentration of the polymer in solution with accompanying increases in viscosity but no more adsorption takes place. When the polymer is first added, if the adsorption is of the La Mer type, in which the polymer molecules can provide cross-links between the fibers, flocculation of fiber suspensions is promoted.

The opposite polarities of electric charges at the surface of fiber and polymer presumably favors this effect. However, if the adsorbed polymer lies flat on the surface of the fiber, bridging cannot be expected, and the action of the polymer, like small ionic species, will be to depress the zeta potential of the cellulose.

Agitation greatly affects the effectiveness of polymer in the flocculation process (35). Sufficient mixing should be present at the point where the flocculant solution is added for two reasons. First, the polymer is adsorbed strongly and irreversibly on fiber surfaces and therefore inadequate agitation causes intensive adsorption on fibers around the point of addition leaving fibers unflocculated in other parts of the system. Secondly, mixing gives better probabilities for physical contact of polymers and fibers to form bridges.

Natural movement of fibers is generally insufficient to bring about good flocculation. However, vigorous agitation after the flocs formation causes the flocs to break up in size and the system cannot return to the previous state of flocculation.

From a practical point of view, whenever there is a large amount of colloidal matter in a system, it is preferable to neutralize the negative charges on these particles with an electrolyte such as alum to cause primary coagulation before the addition of the selected polymer to obtain better efficiency. Also, the larger the molecular weight of the polymeric flocculant, the greater the number of sites are available for adsorption.

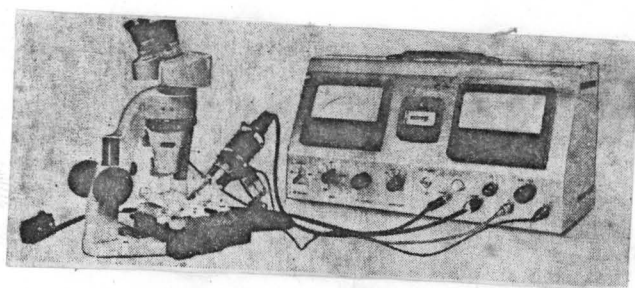
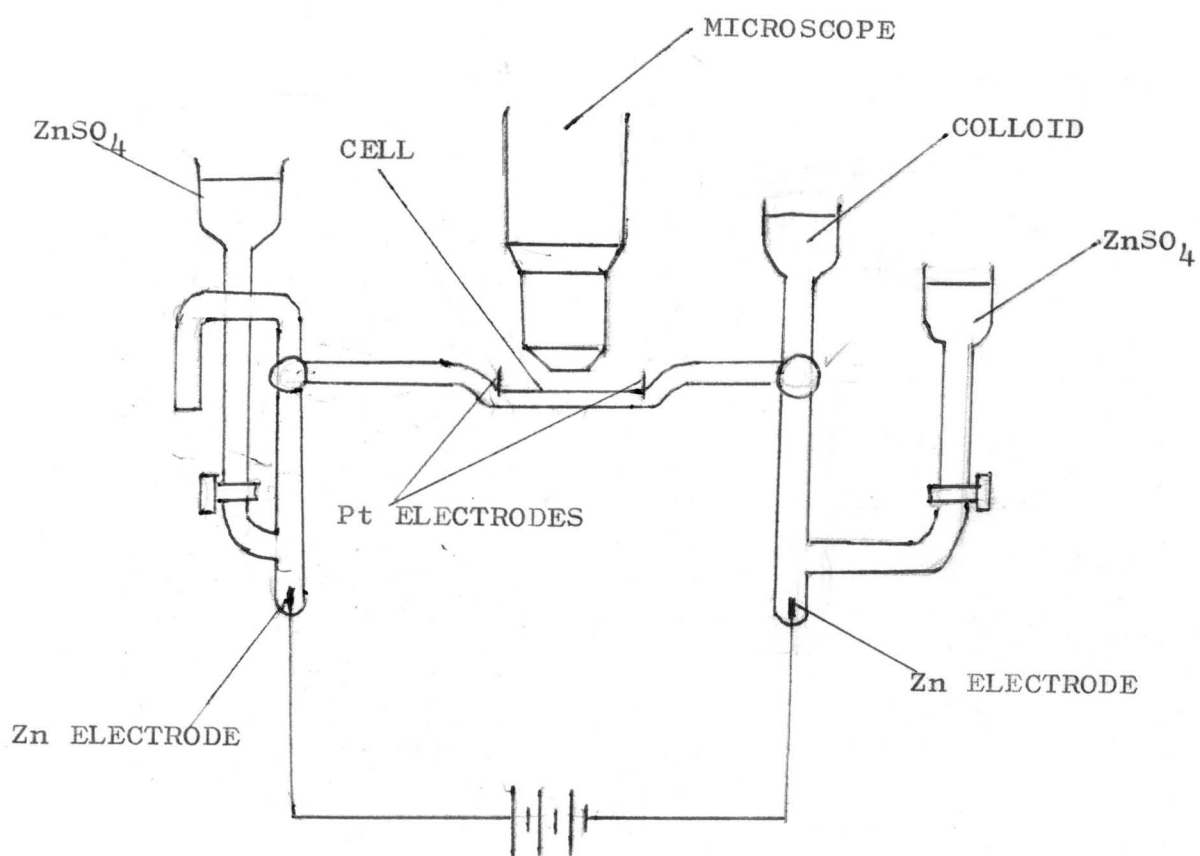
Consequently, the flocs formed are more stable.

Much work has been done in the evaluation of polymers as coagulants or flocculants (36). The National Council for Stream Improvement, Inc. has reported 42 different polyelectrolytes as coagulants for boardmill effluents (37).

#### MEASUREMENT OF ELECTROKINETIC POTENTIAL

There are essentially four types of electrokinetic phenomena based on the fact that although the diffuse double layer is bound to the charged surface by electric forces, it is partially mobile in moving with the liquid phase — electrophoresis, electroosmosis, flow potential and fall potential. In this paper, the measurement of microelectrophoresis using a Zeta Meter is reviewed (14).

The Zeta Meter measures the electrophoretic mobility (converted to zeta potential) of suspended colloids and suspensions, by indirect determination of the ionized or electrokinetic charge surrounding the particles (FIG.VI). In this method, the microscopically visible particles are directly observed as they migrate in an externally applied electric field. Brigg's horizontal flat cell is used. This transparent cell is equipped with platinum electrodes, and there are zinc-zinc sulfate reversible working electrodes connected with a constant voltage supply removed from the cell. There is also a system of tubings and stopcorks for filling and cleaning the cell and electrode compartments. The platinum electrodes are



MICROELECTROPHORESIS MEASUREMENT — ZETA METER

FIG. VI



used only for measuring the potential drops across the cell in which the particles are being observed. The potential gradient is developed by applying a voltage to zinc electrodes further removed from the cell area. The particle zeta potential is calculated from the following equation:-

$$\zeta = \frac{4\pi\eta V}{HD}$$

where:  $\zeta$  = zeta potential

V = particle velocity

H = potential gradient

$\eta$  = viscosity of dispersion medium

D = dielectric constant

One of the sources of error in this measurement is the determination of the stationary level. The linearity of the fine adjustment is therefore a critical factor.

## MEASUREMENT OF FLOCCULATION

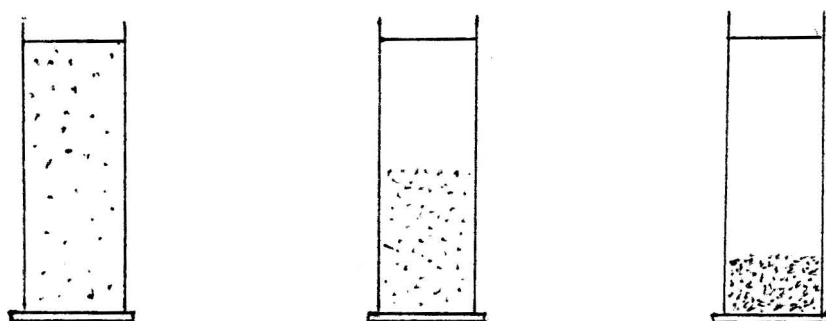
There are indirect and direct methods of measurement of flocculation. The indirect methods used are the sedimentation volume and the filtration rate. They do not measure the degree of flocculation of such but only measure some properties of pulp suspension associated with flocculation. The direct methods include optical transmission and optical scanning. Only the indirect methods are considered here.

The sedimentation volume test (FIG.VII) is usually performed using a 1-liter graduated cylinder. The height of the liquid-solid interface is measured at regular time intervals. From this, the rate of settling and the final sedimentation volume can be obtained. For a typical sedimentation test, the particles settle quite rapidly at first. As the solids are thickened by settling, there is a transition zone which is the result of decreasing velocity and increasing density of the sludge. When the sludge has thickened to the point that the particles do not have room to move, the sludge layer undergoes compression. The rate of settling can be compared with the rate of floc formation and the degree of flocculation.

Filtration rate test (FIG.VIII) is readily accomplished by a buchner funnel technique developed by Coakley (38). In this procedure, a buchner funnel is fitted to a graduated cylinder. A filter paper is put into the buchner funnel and

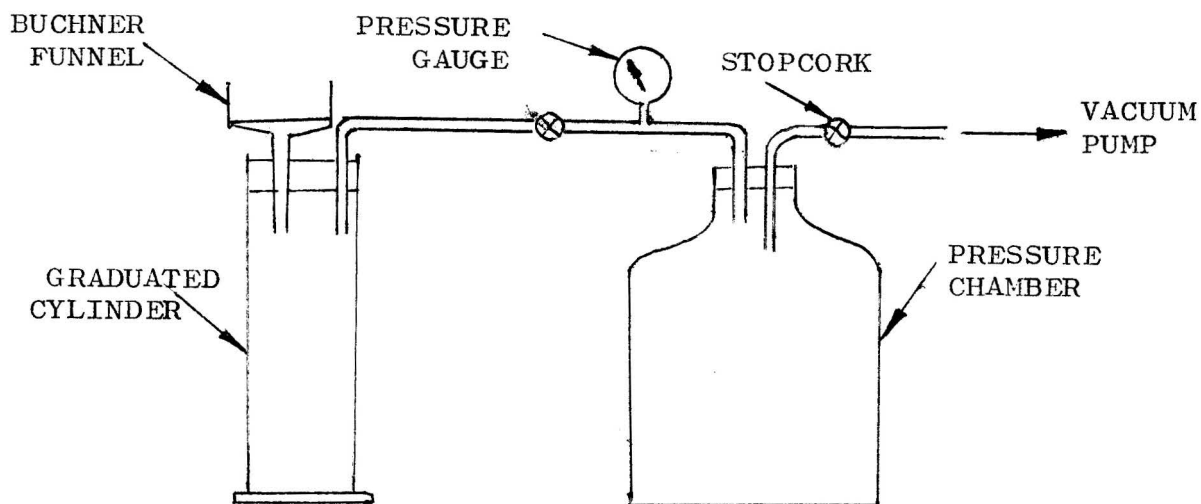
then moistened. A wire screen may be placed under the filter paper to ensure that vacuum is effectively applied to the total area of the filter paper. A sample of sludge is placed in the funnel, and a constant vacuum pressure is applied. At selected time intervals, the volume of filtration is recorded.

The filtration rate increases with the degree of flocculation of sludge.



SEDIMENTATION VOLUME TEST

FIG.VII



FILTRATION RATE TEST

FIG.VIII

## EXPERIMENTAL DESIGN

### MATERIALS USED:-

Pulp - Standard bleached and softwood sulfite  
supplied by Weyerhaeuser Company, Pulp  
Division, Cosmopolis, Washington.

### CHEMICALS:-

- (1) Alum - analytical grade  $Al_2(SO_4)_3 \cdot 14H_2O$
- (2) Polymers - furnished by Dow Chemical Company,  
Midland, Michigan.

IDENTIFICATION	TYPE	MOLECULAR WT.
CP-7	Cationic polyacrylamide	1,000,000gm/mole
PG-5	anionic polyacrylamide	1,500,000gm/mole
PG-2	anionic polyacrylamide	1,000,000gm/mole

NB: PG-5 is identical to PG-2 with  
the exception of molecular  
weight.

- (3) Sodium hydroxide NaOH
- (4) Hydrochloric acid HCl

PROCEDURE:-

PART I - Preparation of fines:-

- (1) Determine moisture content of pulp.
- (2) Weigh out amount of fiber necessary to obtain 1.5% consistency in beater.
- (3) Beat stock to a freeness of 200 C.S.F. using distilled water and with 5500 gram weight on bed plate.
- (4) Fractionate pulp with Clark Classifier. The fraction which passes through the 48 mesh wire is used as fines.

PART II - To compare the effects of zeta potential and fiber length on flocculation using alum as flocculant:-

- (1) Put 1gm. of stock at 200 C.S.F. in a 1-liter measuring cylinder. Dilute to 900ml. mark with distilled water.
- (2) Add alum and adjust to pH4.5 with NaOH and HCl.
- (3) Add distilled water previously adjusted to pH4.5, to 1-liter mark.
- (4) Determine settling rate.
- (5) Determine drainage rate.
- (6) Determine zeta potential.
- (7) Repeat with different dosages of alum.
- (8) Repeat by using fines

PART III - To compare the effects of zeta potential and bridging on flocculation using a cationic polymer:-

- (1) Put 1gm. of fines in a 1-liter measuring cylinder and dilute to 900ml mark.
- (2) Add CP-7 and adjust pH to 7 if necessary, using NaOH and HCl.

- (3) Add distilled water to 1-liter mark.
- (4) Determine settling rate.
- (5) Determine drainage rate.
- (6) Determine zeta potential.
- (7) Repeat with different dosages of CP-7.

PART IV - To compare the effects of bridging and flocculant molecular weight on flocculation using two anionic polymers.

- (1) Put 1gm. of fines in a 1-liter measuring cylinder and dilute to 900ml mark.
- (2) Add 5% alum (based on weight of O.D. fines), adjust to pH<sup>4.5</sup> using NaOH and HCl. Add PG-5 and readjust pH if there is any change.
- (3) Add distilled water previously adjusted to pH<sup>4.5</sup>, to 1-liter mark.
- (4) Determine settling rate.
- (5) Determine drainage rate.
- (6) Determine zeta potential.
- (7) Repeat with different dosages.
- (8) Repeat with PG-2.

When flocculant is added to the testing sample, the following steps are followed:-

- (1) Agitate testing sample with mixer at 250 RPM for 1 minute.
- (2) Add coagulant solution at the point of turbulence and continual mixing at 100 RPM for 1 minute.
- (3) Agitation speed is reduced to 50 RPM and continue mixing for 1 minute.

Sedimentation rate is determined by allowing 1 liter of the sample to stand undisturbed at room temperature. The height of the liquid-solid interface is recorded with settling time. The slope of the height verses time curve gives the sedimentation rate.

Filtration rate is determined by recording the time required for 1 liter of the sample to drain through a Whatman #4 filter paper in a 6" diameter buchner funnel under a constant vacuum pressure of 10" Hg at room temperature.

The zeta potential is measured with a Zeta Meter in the RH room. A detailed description of its use is given in Meersman's thesis (14).

## DISCUSSION OF EXPERIMENTAL DESIGN

This experiment is designed to compare the effects of zeta potential and bridging on the flocculation of fines. The effect of fiber length on flocculation is also touched upon in less detail. The zeta potential is measured with a Zeta Meter. The degree of flocculation is observed by the settling and filtration rate methods.

The flocculation of fines, instead of the whole stock, is studied because of the following reasons.

- (1) In the saveall operation, the primary clarifier process, and retention of fines, we are mainly dealing with the problem of fines, and not the problem of long fibers.
- (2) In the determination of zeta potential using the Zeta Meter, only the fines can be used. It is very doubtful whether the fines fraction is a representative sample of the whole stock. Just studying the flocculation of fines, this sampling problem is avoided, a much more uniform testing sample can be obtained and eventually more reproducible results can be obtained.
- (3) If the whole pulp at 200 C.S.F. is used, the sample flocculates and drains so fast that the simple methods of sedimentation rate determination



with the 1-liter measuring cylinder and the filtration rate determination with the buchner funnel technique become very insensitive.

Distilled water is used to minimize the presence of any foreign ions that may influence the zeta potential of the fines.

The consistency of 0.1% is chosen because preliminary testings showed that a steady, measurable sedimentation rate is best obtained around this consistency.

For filtration, a vacuum pressure of 10"Hg is used because preliminary testings showed that at higher vacuum pressures, it becomes difficult to obtain a reasonable difference in filtration time between samples.

The polymers used are synthetic polyacrylamides. The cationic polymer is a copolymer of acrylamide and a quaternary ammonium type monomer. The anionic polymer is a copolymer of acrylamide and a carboxylic acid. PG-5 and PG-2 are particularly chosen because these two polymers are identical except that of molecular weight. Therefore, the effect of flocculant molecular chain length can be studied.

Cationic polymers, and anionic polymers of different molecular chain lengths are used to determine the effectiveness of flocculation by bridging, with and without the addition of alum. This bridging effect can then be compared with the zeta potential of fines at different dosages of polymer applied.

Because of the amphoteric characteristic of alum, the pH is carefully controlled to a value of 4.5 whenever it is being used. At this pH, the predominant species is the hexahydrated tripositive aluminum ion,  $(\text{Al}(\text{H}_2\text{O})_6)^{+++}$ , which is most effective in suppressing the electrokinetic potential of the negatively charged fines.

The method of addition of polymer is important because agitation has to be great enough to ensure fast and uniform distribution of the polymer throughout the sample and yet gentle enough that any bridge formed will not be broken up by shear.

All these variables, such as pH, particle size of fibers, agitation, consistency, temperature, dispersion medium and concentration, are thus controlled as much as possible. The design of this investigation may lead to a better understanding of the mechanisms involved in the flocculation of fines.

## DATA

The results of the experiments are presented in tables 1 - 5.

The results in table 1 and 2 are plotted in Figure IX. The results in table 3 are plotted in Figure X. The results of table 4 and 5 are plotted in Figure XI.

Figure XII summaries the relationship between the sedimentation rate and the zeta potential for all flocculants used.

TABLE I

Material - 1 gm. 200 C.S.F. stock/liter  
Chemical - alum  
pH - 4.5

ALUM ADDED (PPM)	ZETA POTENTIAL (MV)	SEDIMENTATION RATE (CM/MIN)	FILTRATION RATE (ML/SEC)
0	-10.1	.80	1.39
20	- 3.8	.82	1.40
40	- 1.3	.81	1.44
60	- 1.0	.83	1.44
80	+ 1.4	.81	1.45
100	+ 2.5	.84	1.43
120	+ 5.5	.78	1.42
140	+ 5.4	.82	1.44
160	+ 6.5	.79	1.39
180	+ 7.9	.76	1.42

TABLE 2

Material - 1 gm. fines/liter  
Chemical - alum  
pH - 4.5

ALUM ADDED (PPM)	ZETA POTENTIAL (MV)	SEDIMENTATION RATE (CM/MIN)	FILTRATION RATE (ML/SEC)
0	-11.0	.15	5.0
20	- 5.8	.22	5.3
40	- 4.0	.28	6.0
60	- 2.3	.28	6.2
80	- 2.4	.34	7.0
100	- 1.8	.39	7.8
120	+ 1.4	.38	7.9
140	+ 2.0	.30	6.8
160	+ 3.6	.27	6.3
180	+ 4.0	.26	5.9

TABLE 3

Material - 1 gm. fines/liter  
Chemical - CP-7 a cationic polyacrylamide  
Mol. wt. - 1,000,000 gm/mole  
pH - 7.0

POLYMER ADDED (PPM)	ZETA POTENTIAL (MV)	SEDIMENTATION RATE (CM/MIN)	FILTRATION RATE (ML/SEC)
0	-11.0	.15	5.0
1	- 6.3	.44	8.7
2	- 4.5	.62	10.9
3	- 1.8	.62	10.7
4	- 1.0	.52	10.4
5	+ 1.4	.56	10.6
6	+ 5.0	.52	9.6
8	+ 6.1	.50	8.9
10	+ 9.8	.43	7.5
14	+12.0	.43	6.0
18	+13.8	.40	4.6

TABLE 4

Material - 1 gm. fines/liter  
Chemicals - PG-5, anionic polyacrylamide  
5% alum (based on O.D. weight of fines)  
Mol. wt. - 1,500,000 gm/mole  
pH - 4.5

POLYMER ADDED (PPM)	ZETA POTENTIAL (MV)	SEDIMENTATION RATE (CM/MIN)	FILTRATION RATE (ML/SEC)
0	- 3.0	.28	6.1
2	- 6.0	.52	8.6
4	- 8.5	.60	10.0
6	-10.3	.67	11.5
8	-11.8	.64	11.1
10	-12.0	.60	10.8

TABLE 5

Material - 1 gm. fines/liter

Chemicals - PG-2 anionic polyacrylamide  
5% alum (based on O.D. weight of fines)

Mol. wt. - 1,000,000 gm/mole

pH - 4.5

POLYMER ADDED (PPM)	ZETA POTENTIAL (MV)	SEDIMENTATION RATE (CM/MIN)	FILTRATION RATE (ML/SEC)
0	- 3.0	.28	6.1
2	- 6.8	.42	8.0
4	- 9.3	.51	9.3
6	-11.2	.59	10.5
8	-11.2	.56	10.3
10	-11.6	.50	10.2



FIG. IX  
EFFECT OF ALUM

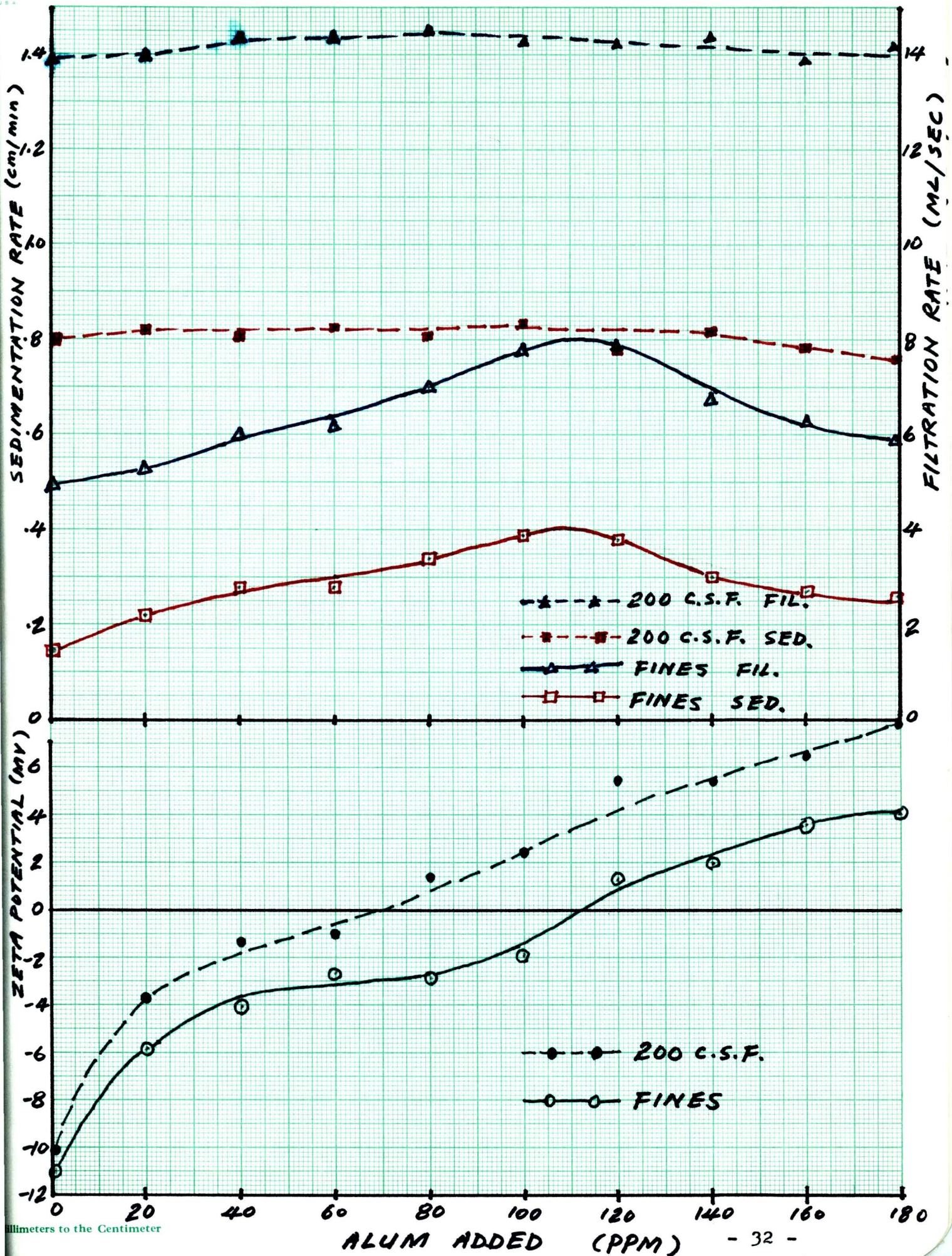




FIG. X  
EFFECT OF CP-7

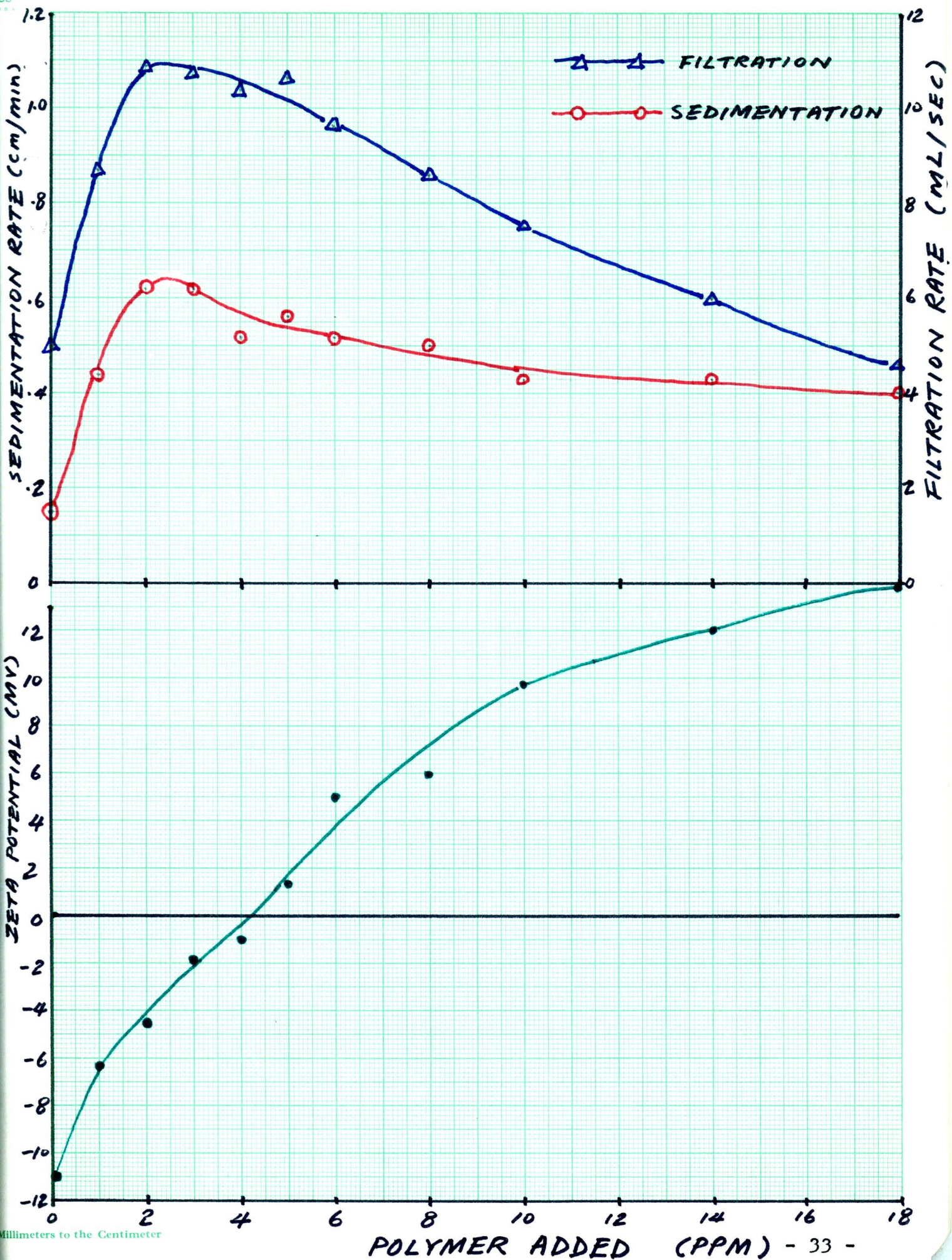




FIG. XI  
EFFECT OF PG-2 VS PG-5

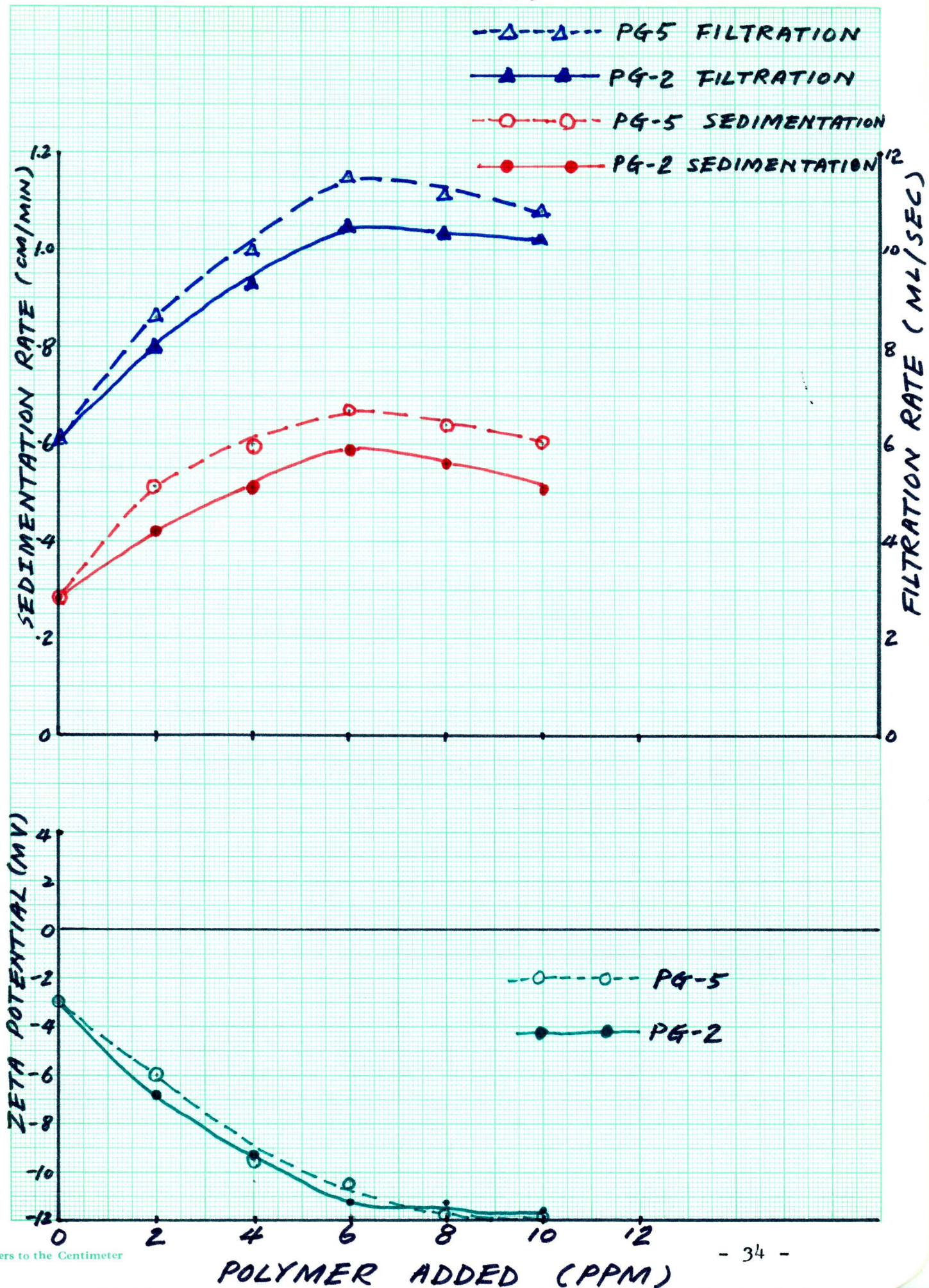
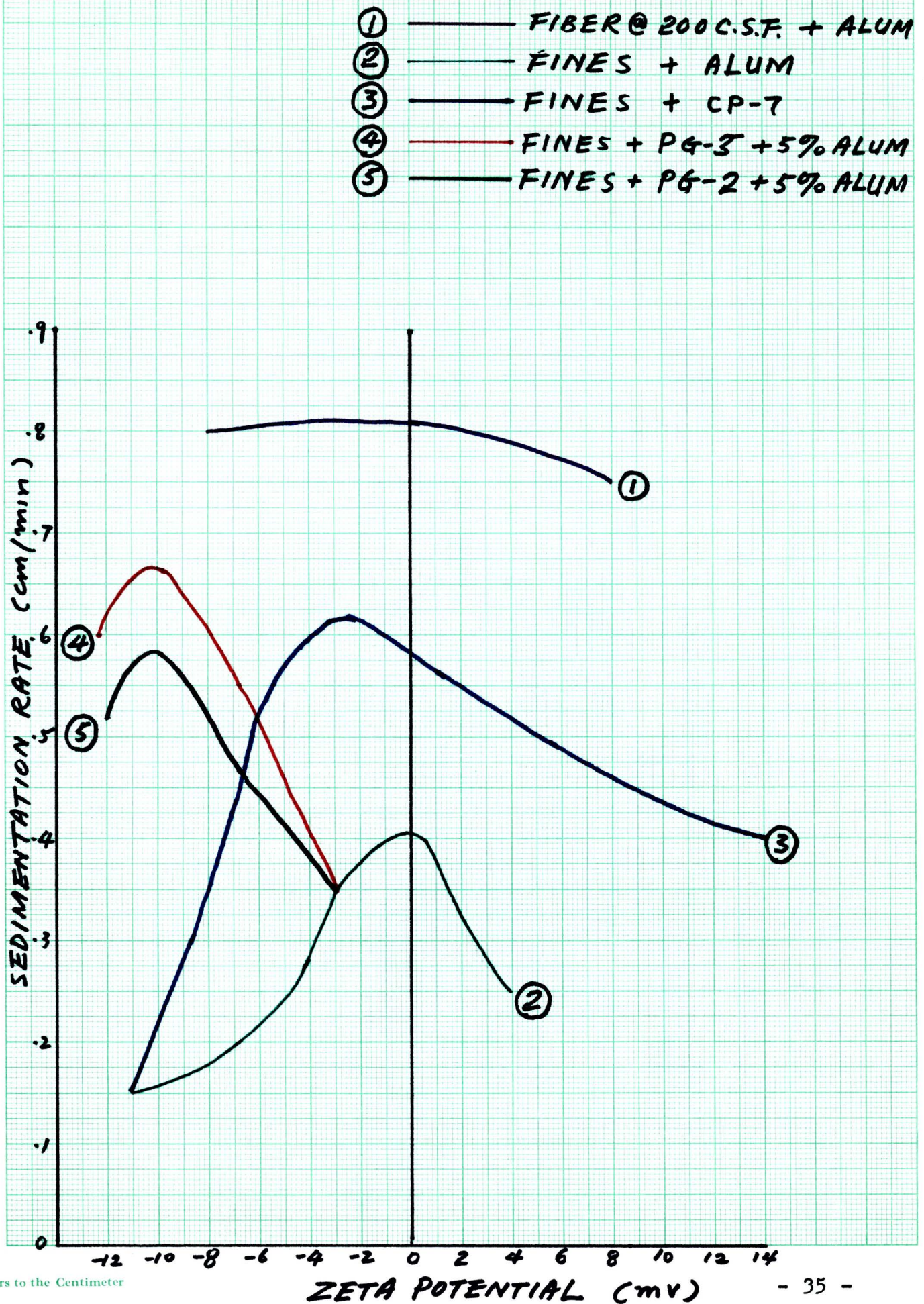




FIG. XII  
ZETA POTENTIAL VS SEDIMENTATION RATE





## DISCUSSION OF RESULTS

In the present investigation, the degree of flocculation is indicated by the sedimentation rate and the filtration rate. Increase of flocculation causes a corresponding increase in these properties.

The experimental results of using alum, cationic, anionic polymers as flocculants are displayed in figures IX to XI. Since the filtration tests and the sedimentation tests follow the same pattern, only the sedimentation rates are used in figure XII to compare the effects of all the different flocculants used.

Figure IX shows the effects of zeta potential and fiber length on flocculation using alum as the flocculating agent. In distilled water, standard bleached sulfite softwood fines acquire a negative charge of -11.0mv. As alum is added at pH<sup>4.5</sup>, the positively charged aluminum ions are adsorbed on the surface of the fines and neutralize some of the negative charges. An isoelectric point (zero mv) is reached with the addition of 110ppm alum. Further alum concentration causes the fines to be positively charged.

Sedimentation rate increases as the zeta potential decreases from -11.0mv towards zero mv. Then it decreases as the zeta potential increases in the positive direction. Maximum sedimentation rate of 0.40cm/min. occurs at the isoelectric point with 110ppm of alum. The filtration curve follows the same

pattern with the maximum of 8.0ml/sec at the isoelectric point. This can be explained by the theory of electrokinetic potential, which predicts maximum flocculation is at isoelectric point. No repulsive forces exist between particles at this point and the van de Waal attraction forces can come into play. When the magnitude of the zeta potential is increased, the increasing repulsive forces between the similarly charged fines keep them apart.

For the whole pulp at 200 C.S.F. the zeta potential decreases from -10.1mv to zero mv. with the addition of 50ppm alum at pH4.5. When compared with 110ppm alum needed for the fines, it is noticed that less alum is required to neutralize all the negative charges on the longer fibers. Since adsorption of ions is a surface phenomenon, this can be explained by the fact that the fines have a much larger specific surface area than the long fibers and thus have more negatively charged sites present to be neutralized by the aluminum ions.

The sedimentation rate and the filtration rate of the whole pulp only increases slightly as it passes the isoelectric point and then decreases slightly as more alum is added. It is very difficult to determine where the maximum is because the whole pulp settles and drains so fast that the simple sedimentation and buchner filtration methods becomes insensitive.

Referring to Figure XII, it is seen that the whole pulp at 200 C.S.F. treated with alum has the highest sedimentation rate, but the change in zeta potential has very little observable effect in improving the degree of flocculation. In other

words, fiber length has a much greater effect on flocculation and it overwhelms the zeta potential effect in a long fiber system.

Figure X shows the flocculating effect of a cationic polyacrylamide, CP-7. The zeta potential of the fines is decreased rapidly from -11.0mv to the isoelectric point at about 4ppm of polymer addition. Further addition of CP-7 increases the positive charges on the surfaces of the fines. The sedimentation rate increases rapidly as the first 2ppm of CP-7 is added. Then, it decreases slowly when more polymer is present. The filtration rate follows the same path except it decreases more rapidly after the maximum is reached. It is probably due to the increase in viscosity as more polymer is present. Sedimentation rate is likely to be less sensitive to viscosity change.

In a system of fines dispersion, if the only determining factor is zeta potential, all flocculants should cause the same degree of flocculation at a given zeta potential value and the maximum should always correspond to the isoelectric point.

Comparing the sedimentation rate curves in Figure XII, CP-7 treated fines has a much higher value than the alum treated fines at any given zeta potential. This can only be explained by the bridging phenomenon. CP-7, a cationic polyacrylamide, has a molecular weight of 1,000,000 and a long molecular chain length. It causes flocculation mainly by cross-linking the fines as a result of surface adsorption. Cross-linking can take place

across a much greater separation distance, and causes a higher degree of flocculation. The depression of the zeta potential only has a secondary effect. The point of maximum flocculation is at a potential value of -3mv instead of zero mv. This again shows that the bridging effect is more influential than the electrokinetic effect. The peak probably corresponds to the condition of optimum bridging across the fines and this is not necessary to be at the isoelectric point.

When too much CP-7 is adsorbed, the optimum bridging condition is destroyed. As the effect of bridging steadily subsides, and as the magnitude of the electrokinetic potential steadily increases, the degree of flocculation decreases.

The effect of bridging is compared with molecular weight of Figure XI. PG-5 and PG-2 are identical anionic polyacrylamides except for the molecular weight. PG-5 has a molecular weight of 1,500,000gm/mole whereas PG-2 has a molecular weight of 1,000,000gm/mole. Since PG-5 has a longer molecular chain length, it can bridge across a greater distance and it is expected to be a better bridging agent than PG-2. The sedimentation rate and filtration rate curves prove this point. In the presence of 5% alum, for equal amount of polymer added, PG-5 always causes a greater degree of flocculation than PG-2. Both polymers reach a maximum at 6ppm polymer addition. Alum is used here to change some of the negative charges on the surfaces of the fines into positive charges so that the anionic polymers can bridge across particles.



The zeta potential reading increase steadily in the negative direction as the polymers added.

Referring to Figure XII again, the fact that the bridging effect can even overshadow the zeta potential effect can be illustrated more clearly by considering the anionic polyacrylamide PG-5. Starting at a sedimentation rate of .15cm/min, and a zeta potential of -11.0mv, the fines are treated with 5% alum which increases the sedimentation rate to .35cm/min while the zeta potential decreases to -3.0mv towards the isoelectric point. Upon the addition of PG-5, the zeta potential is increased negatively again. However, instead of a decrease of sedimentation rate, a steady increase is observed. As the zeta potential is changed from -3.0mv back to -10.0mv, the sedimentation rate increases from .35cm/min to a maximum of .67cm/min. This maximum condition probably indicates again the optimum state for bridging. When more PG-5 are added, the best state for bridging is destroyed and the repulsive forces of the positive charges take over to cause a decline of the sedimentation rate.

PG-2 follows the same trend, except the maximum value is lower than that of PG-5. As it has been stated previously, it is because of the shorter molecular chain length of PG-2.

Although both PG-2 and the CP-5 have the same molecular weight of 1,000,000gm/mole, it is difficult to make an exact comparison of these two flocculants because of their different

monomer structures and thus different molecular chain length. Roughly, their peaks both fall near to the sedimentation rate of .60cm/min.

In general, it is observed that the whole pulp at 200 C.S.F. has the highest degree of flocculation, followed by the polymer treated fines. The alum treated fines shows the lowest degree of flocculation.

## CONCLUSION

The mechanisms controlling the degree of flocculation of a fibrous system is summarized as follows:

- (1) Physical entanglement:- This is the most predominant factor controlling flocculation. Longer the fiber, greater the degree of flocculation.
- (2) Bridging:- When flocculation is caused by bridging of fines with polymers of long molecular chain length, the higher the molecular weight (i.e. the longer the molecular chain length) the greater the degree of flocculation. The effect of bridging can overwhelm the effect of electrokinetic potential and maximum flocculation does not necessarily occur at the isoelectric point.
- (3) Electrokinetic potential:- The effect of zeta potential can only be applied when the flocculant used is a simple electrolyte without any significant bridging effect. In such a case, flocculating is

controlled by:

- a) Magnitude of zeta potential - The smaller the magnitude of the zeta potential of the fines, the smaller is the repulsive force between particles and the greater is the degree of flocculation.
- b) Sign of charge - The flocculant should be of opposite charge to that of the fines to suppress the zeta potential.

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