A STUDY ON THE TREATMENT OF WHITE WATER EFFLUENT STREAM OF A PAPER MILL :

By

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ABSTRACT

The problem of separation of suspended solids present in the effluent stream of a paper mill has been investigated. The separation process considered in this study is chemical flocculation followed by sedimentation. The present investigation includes an analysis of the problem leading to the establishment of important parameters that determine the cost of separation, the experimental evaluation of the determining factors, and the evaluation of the cost items. In this context, the sedimentation behaviour of the flocculated suspensions of individual constituents of the waste namely, TiO_2, clay and the paper fines has been studied and compared with that of actual waste from a paper mill. Alum and Super Floc-330 (an organic polyelectrolyte) are the flocculants used for the study. Electrolytic process has also been investigated.

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NOMENCLATURE

A	area.
A_1	activation energy.
a	unit cost of chemicals, \$/lb.
b	unit cost of electricity.
c_1	unit capital cost of the flocculation unit, \$/gal.
c_2	unit capital cost of the sedimentation unit, \$/gal.
D	diffusion coefficient, cm^2/sec.
d	diameter of the particle.
E	energy state.
E_b	height of the energy barrier.
G	root mean square velocity gradient.
K	proportionality constant.
k	Boltzman constant.
L	overflow rate, $gal/day.ft^2$.
m	amount of flocculant required per unit weight of solid.
N	particle count, $number/cm^3$.
n	rate of stirring, rpm.
P	power dissipation per unit volume.
Q	volume rate of flow, gal/day.
R	radius of the particle.
S	total cost of the treatment..
T	temperature ^oK.
T_x	torque.
u	velocity of the particle.
u_e	electrophoretic velocity of the particle.

V	volume.
v_s	settling velocity.
x	concentration of the suspension.
y	rate of capital depreciation.
z	distance.

GREEK LETTERS

β	attachment coefficient of collision.
ψ	void fraction of the aggregates formed.
ϕ	volume of the suspended solids per unit volume of the medium.
ε	dielectric constant of the medium.
η	viscosity of the medium.
ρ	density.
θ	time.
τ	retention time.
ζ	zeta potential
ξ	fraction of solids remaining in the suspension.

ABBREVIATIONS

mg	milligrams.
mgd	million gallons per day.
ppm	parts per million
rpm	revolutions per minute.

1. INTRODUCTION

Paper mills use 10,000 to 50,000 gallons of water per ton of paper produced. The waste water containing suspended solids, bio-degradable materials and the dissolved solids is drained into the river causing pollution problem. The main ingredients of the suspended solids are titanium dioxide (TiO_2), clay and the paper fines. Starch and other bio-degradable materials used in the paper processing cause biological pollution and is measured in terms of Biological Oxygen Demand (B.O.D). A list of ingredients used in the paper processing from which the effluent stream originates, is presented in Appendix I.

The amount of suspended solids and B.O.D. vary from mill to mill and also fluctuates during the operation of the mill. Published reports[1,2] show that the concentrations of the suspended solids vary vetween 100 to 1000 ppm. The concentrations of the suspended solids and B.O.D. are usually around 300 ppm. Other impurities present in the effluent stream are in the form of dissolved solids, whose concentrations are usually twice that of the suspended solids. A medium size paper mill producing 200 tons per day of paper drains several tons of chemicals and biological pollution materials per day. The present regulation restricts the permissible level of suspended solids in the effluent stream to 50 ppm. This could be further lowered by the demand of the government.

The present study is restricted to the removal of suspended solids from the effluent stream. The suspended particles in the waste stream are in the colloidal form. Titanium dioxide particles are between 0.2 to 1 micron, clay particles are between 1 to 5 microns and the paper fines are mostly below 100 microns in length and several microns in diameter. These particles cause difficulties in all the separation processes, whether it is filtration, floatation or sedimentation. It is necessary to use some pretreatment by which these particles could grow bigger before any such process is possible.

The separation process for such a suspension consists of two distinct independent processes,

i) the process by which the particles could grow bigger and form aggregates,

ii) the process by which the aggregates separate out from the fluid medium.

The usual way of achieving particle growth is by adding an electrolyte and the process is called flocculation. Flocculation followed by the sedimentation of the flocs formed is called chemical treatment and is considered to be standard practice for the removal of suspended solids from waste water.

The pollution abatement usually means a non returnable expenditure for the industry and its cost frequently determines the acceptability of process. The important cost items of the treatment process which are functions of process parameters, are the capital cost determined by the size of the units, and the cost of chemicals. The size of the units is determined by the rate of individual process such as flocculation and sedimentation. The selection basis of any electrolyte is often the overall cost of separation. It is necessary to evaluate the factors that determine the cost of separation. Therefore, an experimental study has been planned to investigate the flocculating and sedimentation behaviour of the paper mill effluent stream as a function of flocculant dosage using different flocculants. It is realized that, due to the presence of a large number of different chemicals in the paper mill effluent stream, understanding of the problem will be difficult. By studying the flocculating and sedimentation behaviour of the individual constituents, namely the TiO_2, clay and paper fines separately, it may be possible to identify the nature of the problem. Therefore, in this study most of the experiments have been performed using the individual constituents, and their results are compared with that of an actual paper mill effluent stream.

Electrolytic process has also been investigated as an alternative for the particle growth process and the results are compared with that of the chemical flocculation process. In the experimental study, only TiO_2 suspensions have been used.

2. LITERATURE SURVEY

The treatment of paper mill effluent streams has drawn a considerable interest on the grounds of pollution abatement, fibre recovery and water economy. Since 1970, government's initiative has led to the formation of a joint government-industry committee known as the Coordinating Committee for the Water Pollution Abatement Research for Canadian pulp and paper operation. The research is being conducted at the Ontario Research Foundation under the title "Separation, Handling and Utilization of Paper Fines", and is aimed at reducing the pollution caused by pulp and paper mill effluent streams. A survey of all the related works done till 1971, is presented in their published report[1]. A literature review[3] has also appeared prior to this. The reviewed literature covers almost every aspect of the treatment, such as its problems, different methods of the treatment and their suitabilities. Although, most of the reported literatures are dealing with the treatment of combined pulp and paper mill effluent streams, where the problem is much more complex than that of white water, some of them are worth mentioning in order to present an idea about the nature of work done in this field.

McFarlane[4] (1962) reviewed the methods for the treatment of pulp and paper mill effluent streams other than spent cooking liquor. The treatment problems of the pulp and paper mill effluent streams has been discussed by Bhootta[5] (1966), and a suggestion has been made for the reuse of the treated paper mill waste. Raus[6] (1969) suggested the use of separate treatment processes for each of pulp and paper mil instead of one combined. The treatment problems and the disposal of the treated Kraft Mill waste water into a classified inland water were discussed by Vickerman[7] (1967). Billing and DeHass[8] (1971). discussed the pollution control methods of the pulp and paper mill effluent streams. Besides these, the treatment methods for the paper board effluent[9], and for the paper and allied products effluent [10] are of interest. The problem of fibre recovery, and water economy in paper mill have been discussed by Klemm[11] (1961). Leitner [12] (1970), and Biddiker[13] (1971) discussed the waste utilization and the reclaiming of waste water.

It is apparent from the literature study that the chemical treatment has been given most serious consideration. The treatment process consisted of adding an electrolyte to induce a particle growth and separating the aggregates formed. A review of the chemical flocculant used for the treatment of the paper mill effluent streams have been present by Shunas [14]. It appears that a wide variety of chemicals (inorganic and organic) have been used for the treatment.

Among them alum is one of the most frequently used chemical. Being one of the ingredients used in the paper making process it has obvious advantage over others, when one considers the reuse of the separated solids. It has been reported also, that the amount of alum required for the treatment could be considerably reduced by adjusting the pH value of the medium. In many cases, ferric sulphate has been used and found to be more effective than alum, specially if the medium is alkaline. A combination of chemicals providing mixed cations, such as Fe^{+++}, Al^{+++} and solid materials which have a strong adsorbent property like activated silica, fly ash and short fibred asbestos have also been used in some cases. A huge number of organic poly-electrolytes, synthetic or natural, are reported of being used in the treatment process. Among them, poly ethylene amine, synthetic quaternary ammonium, sulphonium, phosphonium poly-electrolytes, and cationic starch are most common. In some cases, a combination of inorganic and organic electrolytes have been used. Commercial poly-electrolytes belonging to the class mentioned above, are available in the market under different trade names. Their merits and demerits are discussed in a number of papers[15, 16]. It has been mentioned that sometimes the cost of chemicals can be prohibitive, and due to this, practical implementation has been very limited.

The separation processes considered were sedimentation, floatation and filtration. In most cases sedimentation were used. In some cases, chemical treatment have been used for a partial separation prior to biological treatment which remove most of the

B.O.D and the dissolved solids. Before arriving at the treatment process it may be worth while to investigate the nature of the problem. The basic problem of particle growth is due to the colloid behaviour. An enormous volume of literature has been published on the behaviour of the colloids and on the kinetics of particle growth, since early this century. A basic concept about the problem could be obtained from a number of text book on colloid and particulate chemistry,[17, 18, 19] and from a few recently published literature on the subject[20, 21, 22, 23, 24, 25, 26, 27]. In the next few sections of this chapter, attempts will be made to identify the basic problems in the separation of colloids and bring out the important process parameters that control the rate of particle growth and sedimentation, citing all the relevant literature, as it will be helpful in formulating this research study.

2.1 Basic Problem :

The problem of particle growth in a colloidal suspension has been discussed by Kruyt[17], Clyde Orr[18] and van Olphen[9]. The basic problem is due to the presence of an electric charge on the surface of the colloid, which creates an electrical double layer at the interface between the particles and the medium in which they are suspended. The growth of the particles take place due to the van der Waal's force of attraction between them, whereas the electrical double layer prevents them from coming in contact with each other.

2.1.1. Origin of Electric Charge :

The electric charge on the surface of a colloid particle may result from one of the following reasons depending on the chemistry of the substance concerned.

i) At the phase boundary of solid surfaces, the charge may result from an isomorphic replacement within the lattice and by the lattice imperfections. Clay offers a representative example of this nature. The acquisation of a negative charge at the phase boundary is due to the replacement of sillicon atoms by aluminium atoms in $Si0_2$ tetrahedron and due to the replacement of Al atoms by magnesium atoms in aluminium oxide octahedrons. $Ti0_2$ particles also belong to this class.

ii) On chemically inert materials, such charges are established due to the adsorption of certain ionic species such as $0H^-$ ions from the solutions.

iii) The primary charge of colloidal particles may result from an ionization of a complex ionogenic group on the surface of the dispersed particles. Many natural colloidal impurities contain ionizable functional groups such as hydroxyl, carboxylic, phosphato and sulphato groups. Their charge depends on the degree of ionization and may be either positive or negative depending on the pH value of the solutions. Examples of such cases are :

a) the electrical state of a protein, or the charge on the surface of a micro-organism,

b) the ionizable carboxylic and hydroxylic group in a natural color, and

c) the ionizable carboxylic, phosphato and sulphato groups in the starch and the cellulose derivatives.

2.1.2 Electrical Double Layer -

These charges are compensated by an equal amount of counter charge forming an electrical double layer, which keeps the whole assembly electrically neutral. This is schematically represented in Figure-1[18] Particles are surrounded by a highly compressed positively charged layer, defined as Stern's layer. This is followed by a diffuse layer called Gouy's layer. The potential difference between the shear plane and that of the solution is called Zeta potential.

There are two types of colloids, the hydrophobic and the hydrophyllic. The hydrophobic colloids repel water and there is a distinct phase boundary between the colloid particles and the medium. Inherent charge on the surface of the particle establishes the double layer with the help of counter ions from the solutions. Clay, TiO_2 and many other inorganic chemicals are examples of this type of colloid. On the other hand, the hydrophyllic colloids attract water. In many cases, they are present in true solution as a single molecule or as a cluster. A distinct phase boundary does not exist in this case. The double layer formation in such a case is due to the presence of a hydration layer and the counter ions from the solutions. Starch, gums and color complexes used in the paper processing are examples of this type of colloids.

2.1.3 Force of Repulsion

When two particles approach each other owing to their Brownian movement or due to an induced velocity gradient, their diffuse counter ion atmospheres begin to interfere. This difference leads to a change in distribution of ions in a double layer, which involves in an increase in the free energy of the system, or in other words there will be repulsion between the particles. Repulsive force prevents the particles from coming in contact with each other. It is a function of surface charge density on the particle and decreases approximately

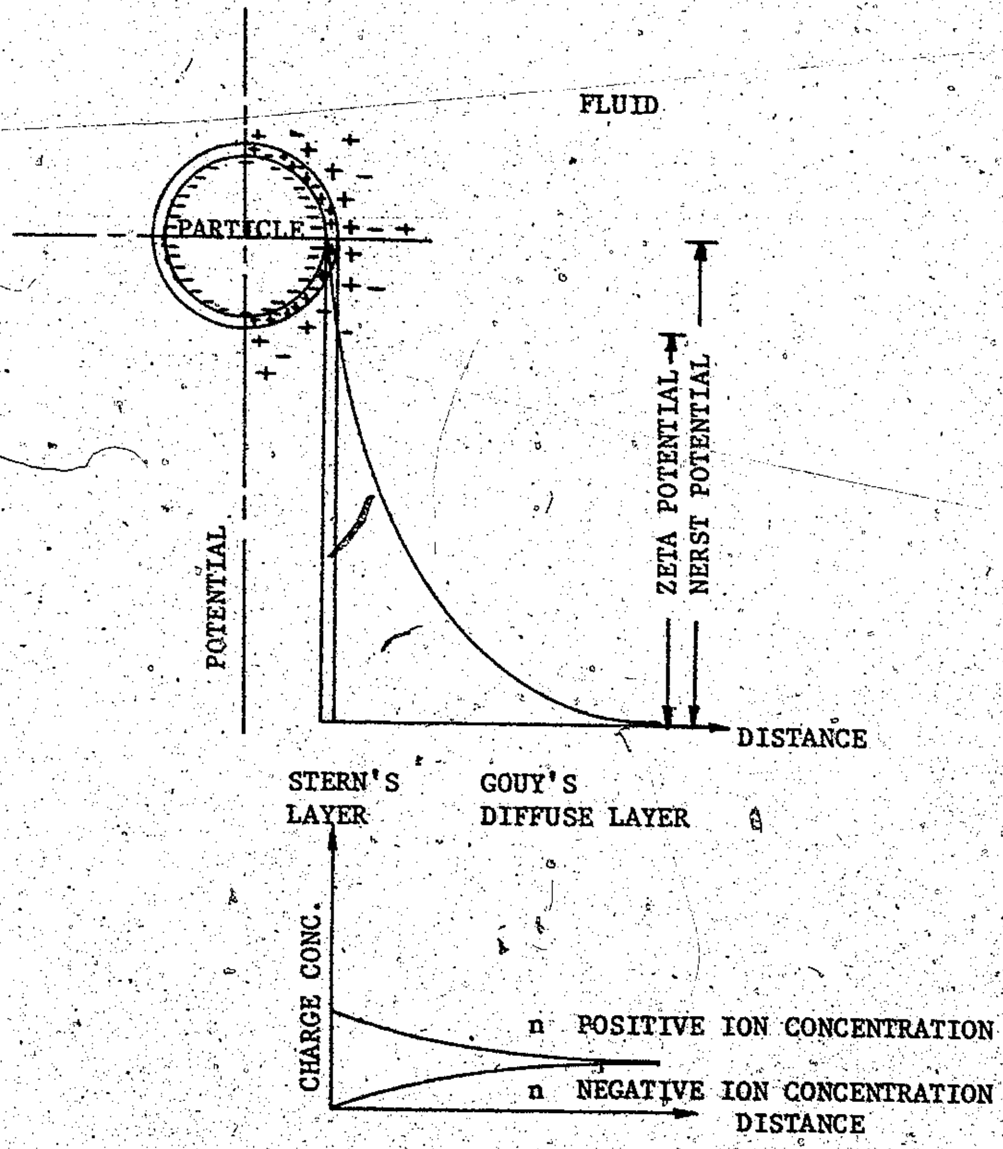


FIGURE-1 : POTENTIAL DISTRIBUTION CURVE IN AN ELECTRICAL DOUBLE LAYER exponentially with an increase in the separation distance between the particles.

2.1.4. The van der Waal's Attraction Force.

Particle growth takes place because of the van der Waal's force of attraction between two particles. For an atom pair, the van der Waal's attractive force is inversely proportional to the seventh power of the distance, (or to the sixth power for the attractive energy). For two spherical particles however, the force is inversely proportional to the third power of the distance between the surface, and the attractive energy therefore to the second power of the distance.[19] This is because, van der Waal's attraction force between the atom pair is additive. The total attraction between two particles containing large number of atoms is equal to the sum of all the attractive force between every atoms of one particle to every atoms of the other particles. The summation leads not only to a large total force but also to a less rapid decay with increasing distance.

If the particle is surrounded by a shell of absorbed molecule of either solvent or the solute, the density of atoms packing the shell is less than the particles itself with a reduction of effective attraction force. The shape of the particle and the position of mutual approach also play a role.

2.1.5. Energy Barrier and the Stability of the Colloids:

The resultant of the van der Waal's attractive force and the force of repulsion is actually the net force acting on the particle. The potential energies due to these forces are shown as a function of the distance from the particle surface in Fig-2[19]. The curves A, R and S represent the van der Waal's attractive force, the repulsive force and the resultant, respectively.

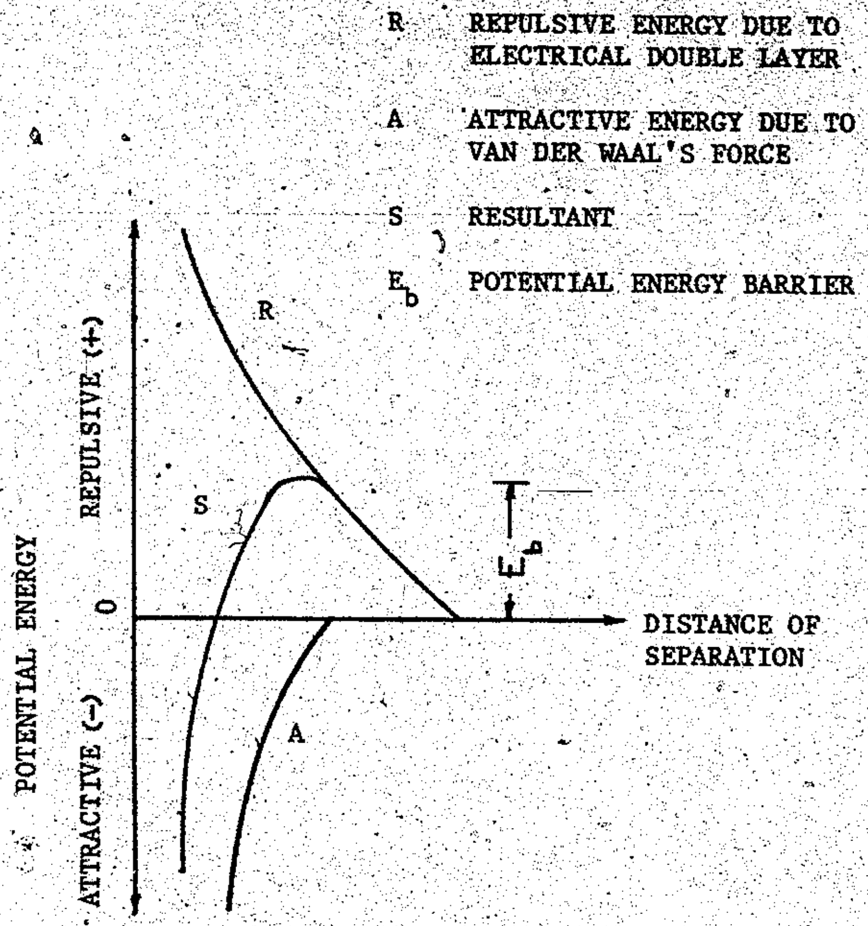


FIGURE-2 : A POTENTIAL ENERGY DIAGRAM IN THE VICINITY OF A CHARGED COLLOID PARTICLE

The nature of the curve S suggests that the particles will have to climb and energy hill E_b before the force of attraction come into play. Particles which overcome the energy hill make contact to each other. This energy barrier represents the stability of the colloid. At a particular distance, the force of attraction is a constant quantity. Where as, the repulsive force is a variable one, determined by the charge density on the surface of the colloid. This makes the energy barrier a variable quantity and its value for a stable suspension is of the order of 15-25 kT.

2.1.6. Destabilization of the Colloid :

The energy barrier is a measure of the colloid stability and is strongly dependent on the electrolytic concentrations of the medium.

If the double layer is created by the absorption of potential determining ions from the solutions, the electrical potential is determined by the concentrations of these ions. Therefore, the energy barrier could be changed by changing the electrolytic concentrations of the medium.

If the double layer results from an interior lattice imperfection, the charge per unit area is a fixed quantity determined by the imperfection of the crystal lattice. In this case, a decrease in surface charge may be brought by the charge neutralization due to the absorption of certain ionic species from the solution, or the diffuse double layer may be compressed with an increasing electrolytic concentration. In either case, there will be a change in the shape of the net interaction curve.

The effect is shown in Fig-3[19], in which the curves I, II and III represent the net potential energy for medium and high electrolytic concentrations, respectively. At a high electrolytic concentration, the

CURVES I, II & III ARE FOR THE ELECTROLYTIC CONCENTRATIONS OF THE MEDIUM IN INCREASING ORDERS.

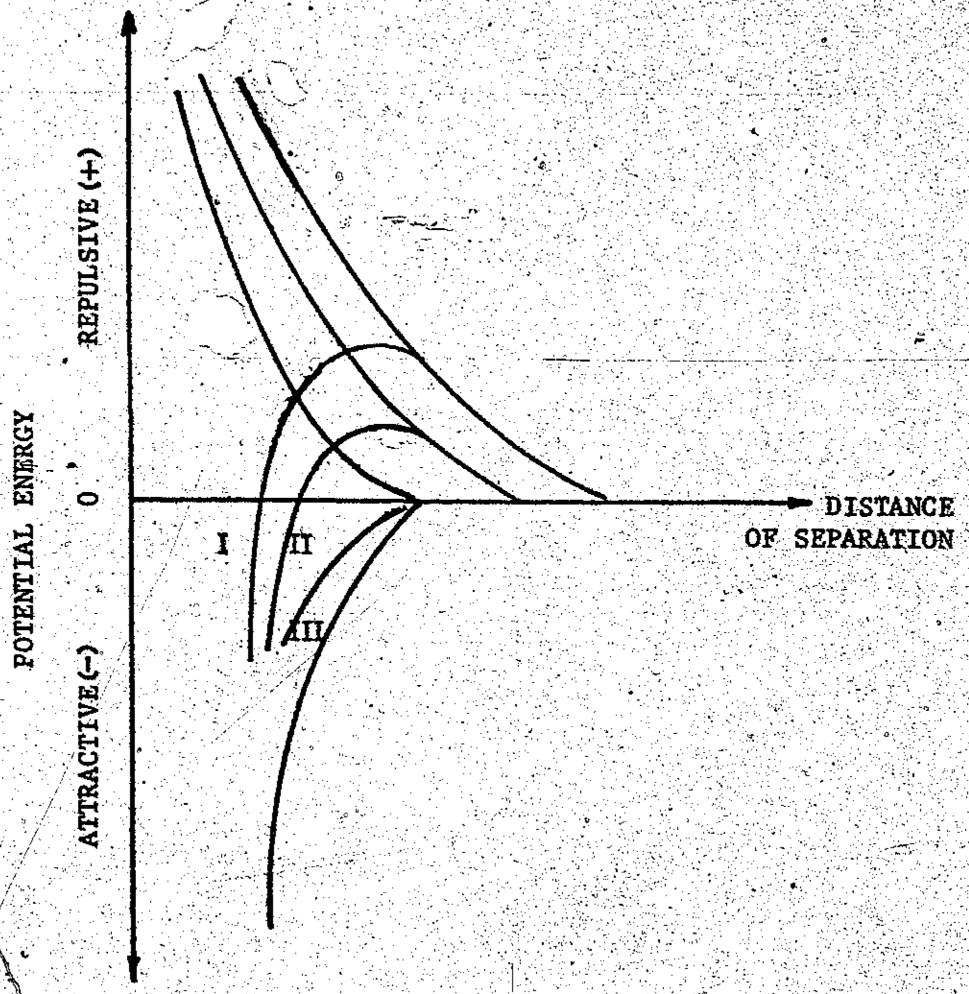


FIGURE-3 : A DIAGRAM SHOWING THE EFFECT OF CONCENTRATION OF THE ELECTROLYTE ADDED, ON THE POTENTIAL ENERGY DIAGRAM IN THE VICINITY OF A CHARGED PARTICLE.

potential energy curve III does not show a repulsion at any distance and the particle agglomeration takes place very rapidly. At an intermediate electrolytic concentration (curve II), the long range repulsion restricts the particle agglomeration. At a very low concentration (curve-I), the long range repulsion restricts the agglomeration to such an extent that it takes weeks or even months to show any noticeable effect.

The process by which the energy barrier is lowered, is called destabilization. Most of the naturally occurring colloids have negative surface charge. Any positively charged ion, which can get absorbed on the surface, will cause charge neutralization. Schultz Hardy Rule[19] predicts that the higher the valency of the ion, the greater will be its power of destabilization. Thus, the destabilization power of Fe^{+++} or Al^{+++} is much greater than that of Ca^{++} or Mg^{++}, which again is higher than that of monovalent ion Na^{+} or K^{+}. For this reason, ferric sulphate and aluminium sulphate have proved to be effective destabilization agents.

It is to be noted that the coagulating power of alum and ferric sulphate is extremely sensative to the pH value of the medium and a very high coagulating power is attributed to the polymeric hydroxide complex formation in some pH range.[28,29,30] For alum flocculation the pH range in which polymeric hydroxide complex forms is 5 to 9. Organic poly-electrolytes which provide a large number of cations in a single chain, likewise become very effective. Destabilization can be brought simply by increasing the acidity or alkalinity of the medium. In case of a hydrophyllic colloid, where the stability of the colloid is due to the presence of a hydration layer, destabilization is brought only after dehydration .

The factors that determine the potential energy barrier after destabilization are as follows :

i) the initial surface charge,
ii) the ability of an electrolyte for charge neutralization.
iii) the concentration of the electrolyte,
iv) the adsorption equilibrium of the added electrolyte between the solid and the liquid phase.

As the amount of surface charge is proportional to the total surface area, the extent of destabilization will be a function of the amount of electrolyte added per unit surface area of the colloid or, in other words, the amount of electrolyte required is proportional to the surface area concentration of the colloid.

2.2. Theory of Particle Growth :

The colloid particles suspended in a medium move around either due to the Brownian motion or due a mechanically induced velocity gradient. The potential energy barrier surrounding the particle prevents them from coming close to one another. Those particles, which overcome the energy barrier make contact with each other forming aggregates. The process is called coagulation. As discussed earlier the energy barrier may be lowered by adding an electrolyte. If the coagulation results in complex particle aggregates with the association of molecules of electrolyte , the process is defined as flocculation.

Coagulation or flocculation could be either perikinetic or orthokinetic depending on whether it takes place due to Brownian motion or due to a mechanically induced velocity gradient.

The rate equations of peri - and orthokinetic coagulation were developed by Smolochowsky[17] in 1918 . The equations were based on the following simplified assumptions :

i) the particles are non-interacting spheroids of equal sizes, having no potential energy barrier between them.

ii) the particles move either due to the Brownian motion or due to a mechanically induced velocity gradient and collide with each other forming multiplets of an equivalent diameter.

iii) the particles are randomly oriented and the volume of the dispersed phase is negligibly small as compared with the liquid.

iv) All Collisions lead to attachment.

2. 2. 1. Smolochowsky's Perikinetic Rate Equation :

The collision frequency J, in numbers per second, of the particle of radius R with $\bar{N}$ other spheres of equal size is given by

$$J = 4\pi D N R \qquad (1)$$

where,

D = diffusion coefficient of Brownian movement, cm^2/Sec

R = Radius, cm.

N = Particle density, Number/cm^3

If all the particles participate, the rate at which the particles disappear, can be expressed by Equation 2,

$$\frac{dN}{d\theta} = -4\pi D N^2 R \qquad (2)$$

where θ = flocculation time, secs.

and D = diffusion coefficient, cm^2/sec.

The value of D is given by the Stoke's - Einstein's expression[17].

$$D = \frac{kT}{6\pi\eta R} \tag{3}$$

where,

k = Boltzman's constant,

T = Temperature °K,

and η = Viscosity of the medium.

Combining Equations 2 and 3 yields,

$$\frac{dN}{d\theta} = -\frac{2}{3}\frac{kT}{\eta}N^2 \tag{4}$$

$$= -KN^2 \tag{5}$$

Where,

K = rate constant = $\frac{2}{3}\frac{kT}{\eta}$

Integrating Equation 5, we obtain,

$$\frac{1}{N} - \frac{1}{N_o} = K\theta \tag{6}$$

Where,

N_o = initial particle concentration

and N = final particle concentration

2.2.2. Smolochowsky's Orthokinetic Rate Equation :

The rate equation of orthokinetic coagulation or flocculation is given by

$$\frac{dN}{d\theta} = -4\frac{du}{dz} \cdot \frac{\varphi}{\pi} \cdot N \tag{7}$$

Where,-

φ = volume fraction of the suspended particle

$\frac{du}{dz}$ = local velocity gradient in which the particles are exposed within the fluid.

Integrating Equation 7 yields

$$\ln \frac{N}{N_0} = - 4 \frac{du}{dz} \frac{\varphi}{\pi} \theta = - K \theta \qquad (8)$$

where K is the flocculation constant and is equal to

$$\frac{4}{\pi} \frac{du}{dz} \varphi .$$

Expressing the root mean square velocity gradient as G, we obtain :

$$K = \frac{4}{\pi} G \varphi \qquad (9)$$

The equation of orthokinetic flocculation (Equation 8) could be written as :

$$\ln \frac{N}{N_0} = - K' G \varphi \theta \qquad (10)$$

However, this is a very simplified form, based on two important assumptions as follows:

i) all collisions lead to attachment,

and ii) the particles are uniform to start with.

The concept of attachment efficiency was introduced by Victor Lamer[20]. The rate of flocculation is given by

Rate of flocculation = Rate of collision X Attachment efficiency (θ).

The attachment efficiency is defined as the rate of attachment collision to the total number of collisions taking place.

In this case, the flocculation constant K' becomes a function of the attachment efficiency.

The rate of collision could be calculated from the kinetic theory of colloid particles, but the attachment efficiency is an unpredictable factor, and is determined by the energy barrier and the mechanism of the attachment process.

The degree of destabilization depends on the amount of electrolyte added, thereby varying the energy barrier and the attachment coefficient. In other words, K' is a function of the amount of electrolyte added.

2. 2. 3. The Effect of Addition of an Electrolyte on the Rate Equation :

It has been observed that the rate of flocculation increases initially with the increase in the dosage of the electrolyte. It goes through an optimum value attaining a highest rate, and then starts decreasing with further increase in the dosage. Whether it is an inorganic or an organic polyelectrolyte, the flocculation takes place only within a limited range of dosage. With increase in the dosage, a reversal of charge takes place at the surface of the colloid bringing a stability to the colloid. The mechanism has been discussed in the literature both for inorganic electrolytes such as alum and ferric sulphate, and for organic polyelectrolytes. Lamer and Healy[25] proposed a mathematical model in order to explain this phenomenon in the case of organic polyelectrolyte. According to this model the rate of flocculation is expressed as follows :

$$- \frac{dN}{d\theta} = K \; N^2 \; p(1-p) \qquad (11)$$

where,

K = rate constant,

N = the particle count

p = the fraction of the colloid surface covered by an electrolyte,

1-p = the fraction of the colloid surface that remains uncovered.

Equation 11 suggests that the optimum rate will be obtained when p is 0.5. The equation could be analysed by means of the following boundary conditions :

i) when $p = 0$ (i.e. no electrolytes are added),

$$-\frac{dN}{d\theta} = 0 \;;$$

ii) when $p = 1$ (i.e. surface saturation is attained),

$$\frac{dN}{d\theta} = 0 \;;$$

iii) when $p = 0.5$.

$$-\frac{dN}{d\theta} = \text{maximum}$$

In terms of a charge neutralization, the value of $p = 0.5$ represents complete neutralization. Between $p = 0.5$ and 1, the opposite charge builds up bringing a stability to the colloid.

Lamer and Healy[30] explained the process of flocculation in terms of an energy model shown in Figure 4. According to this, there are following four steps in flocculation.

i) $\text{P(polymer)} + \text{S (solid)} \longrightarrow \text{PS (unit floc)}$

ii) $n\ \text{PS} \longrightarrow \text{(PS)}n$ (macro floc

iii) $\text{(PS)}n \longrightarrow n\ \text{PS}$

iv) $\text{PS} + \text{P} \longrightarrow \text{PSP}$

The final step leads to surface saturation resulting in the formation of a double layer of opposite charge.

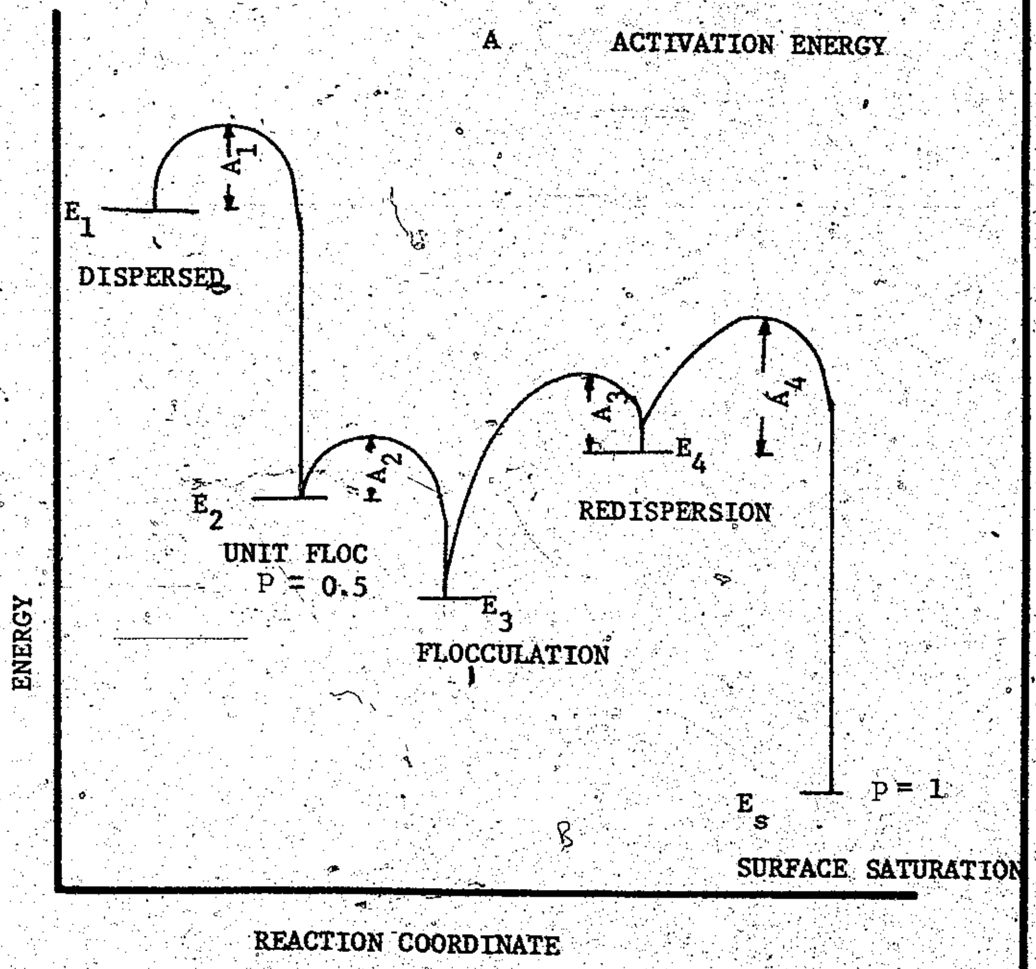


FIGURE-4: ENERGY LEVEL DIAGRAM OF FLOCCULATION

Each step of the process is associated with an activation energy requirement, A_1, A_2, A_3 and A_4. The flocculation state is a meta-stable equilibrium condition, and the equilibrium point is determined by the shear rate. It is possible to switch from state 2 to state 4 by providing sufficient energy such that the state of flocculation will be by-passed.

2.2.4. Rate Equations for Simultaneous Ortho- and Peri-Kinetic Flocculation :

When the movement of the particle is due to a combined effect of the Brownian movement and the shear rate introduced, Friedlander[23] has presented the following rate equation :

$$\frac{dN}{d\theta} = -4\,\frac{du}{dz}\cdot\beta_2\,\frac{\varphi}{\pi}\,N - 4\,\frac{KT}{3\eta}\,\beta_1\,N^2 \qquad (12)$$

where, β_1 and β_2 are the attachment efficiency of collision for the respective processes. He has shown that for a moderate shear rate prevailing in a flocculator, the effect due to the Brownian motion constitutes a negligible part of the effect of shear rate introduced. It means that for all practical purpose Equation 10 represent the basic equation of flocculation.

2.2.5. Methods of Study :

The flocculation kinetics have been studied either by using Coulter counter[31] or by studying the sedimentation behavior of the flocculated suspensions[32].

2.2.5.1. Coulter Counter Technique :

In this method, a dilute sample is allowed to pass through a small aperture. The electrical resistance across the orifice

The results have been expressed in terms of flocculation half life and rate constants. A method of analysis of the data using a digital counter has been developed by Akhira[33]. It has been possible to evaluate the value of attachment efficiency using this technique. This method has revealed many intricate details of the process. It is found that the efficiency is a function of the particle size, meaning bigger particles grow faster and there is a limit of growth determined by the floc strength, after which the redispersion overwhelms the flocculation.

2.2.5.2. Sedimentation Characteristics as a Tool of Study :

The flocculation process has also been studied by the sedimentation characteristics of the flocculated suspensions. The particle size distribution is determined by following the settling rates. This method of determination of the particle size is indirect, and may not be accurate. However, it is able to provide a comparative information about two systems. Cahn Instrument has developed a sophisticated technique of determining the sedimentation characteristics with the help of an electrobalance . The amount of sediment collected in a pan remaining suspended in the medium with the help of a fine wire, is weighed continuously with the help of an electrobalance. The technique has been discussed in detail in Cahn's Technical Bulletin.[34]

2.2.5.3. Zeta Potential Technique :

Besides these two techniques for obtaining the quantitative informations about the flocculation rate, there is another technique (Zeta potential determination), which has been very useful in determining the utility of any chemical as a flocculant and in evaluating its optimum dosage requirement.

The electrical charge on the surface of the particle is the barrier for the particle growth. The amount of charge and the thickness of the electrical double layer determine the zeta potential, which is again a measure of the colloid stability. It has been reported[35] that the value of zeta potential for a stable colloid should be above ± 25 millivolts. The flocculation proces takes place at an appreciable rate when the value of the zeta potential is lowered down to the range of ± 15 millivolts. The rate increases with a decrease in the value of zeta potential, and as its value approaches zero, the rate of flocculation attains a maximum value. The value of zeta potential should be between ± 5 millivolts for a rapid rate of flocculation. But, any correlation of the flocculation rate with the zeta potential is lacking.

2. 3. Theory of Sedimentation

The basic rate equation of sedimentation is given by the Stoke's law. The settling velocity of a particle, settling freely in a medium is given by :

$$v = \frac{2g}{9\eta}(\rho_s - \rho_w) R^2 \qquad (13)$$

where,

v = the settling velocity,
g = the acceleration due to gravity,
ρ_s = the density of the particle,
ρ_w = the density of the medium,
R = the radius of the particle,
η = viscosity of the medium.

This is based on the following assumptions :

i) concentration of the dispersed phase is negligible, so that the particles can settle freely,

ii) particles are spherical,

iii) particles are non-interacting,

iv) the medium through which the particles are failing is of infinite dimension.

The basic equation of settling was extended further to accomodate the effect of non-spherical particles[36], to allow for the deviation from the free settling condition[37], and to allow for the wall effect for settling in a container[37].

The first general study of flocculated suspensions was done by Coe and Clevenger[38], who described the various concentration zones existing within the settling suspensions. Wadsworth and Cutler[39] studied the effect of the flocculating agent upon the settling rate of kaolin suspensions. Hoak and Bramer[40] studied the sedimentation of flocculated suspensions.. A mathematical model for the treatment of kaolin suspensions was presented by Michelis and Bolger[41]. According to this model the basic flow unit is the small clusters with enclosed water. The settling velocity of such an unit, developed from the Stoke's law is given by :

$$v = \frac{2g}{9\eta} (\rho_A - \rho_w) R_A^2 \psi^{4.65} \qquad (14)$$

where,

ρ_A = density of the aggregates formed,

R_A = radius of the aggregate formed,

ψ = void fraction .

Boadman[42] studied the settling characteristics of the flocculated TiO_2 and kaolin suspensions and interpreted their experimental data using the above mentioned model.

2.4. Electrolytic Process :

The electrolytic method has drawn a considerable interest for the study of the colloid behaviour and as a separation process since late 19th century. History of its development as a separation process has been presented by Knipe and Muller[43].

It was first observed that on application of a D. C. potential across a pair of electrodes immersed in a suspension, the particles move due to their charges. The negatively charged ones moved towards the anode and the positively charged ones move towards the cathode. This separation process is called electrophoresis. Most naturally occurring colloids are negatively charged particles enclosed in a shell of positively charged ions in such a manner that particles along with the double layer is electrically neutral. Any potential difference causes a disbalance of the charge situation causing the negatively charged colloid to move towards the anode inspite of the positively charged sheath around it. The electrophoretic velocity of the particle is given by :

$$u_e = \frac{\varepsilon \zeta}{4 \pi \eta} \qquad (15)$$

where, u_e = Electrophoretic velocity,

ζ = Zeta potential,

ε = Dielectric constant of the medium,

η = Viscosity of the medium.

The electrophoretic mobility of the particle is however very small and the application of electrophoresis as a separation process is rather limited. It has been mainly used for obtaining information about the electrical property of the colloid.

The method was seriously considered for the treatment of municipal waste in later 19th century. A method using an electric current was developed and patented by William Webster in 1889[44]. The main feature of the process was based on the principle of providing metallic ions needed for the destabilization, in addition to the effect of electricity. The metallic ions were introduced, either by anodic dissolution or by the addition of an electrolyte. Since then, a considerable development of the process occured, which is noticeable from the huge number of patents available on the process. Plants were built for the treatment of domestic sewage and reported to be quite successful at the beginning in removing the suspended solids, B.O.D., and odor. However, they were closed down on the ground that electricity could not do anything that could not be done by chemicals alone, but in a cheaper way. Besides, the cost of electricity was exhorbitant in those days. In recent years, the interest on the process has been renewed, because of the decrease in the cost of electricity.

A detailed cost estimate of the electrolytic process has been presented by Knipe and Muller[43]. Wide varieties of electrode materials were used for the purpose of providing metallic ions needed for de-stabilization. It has been pointed out that the method still remains incompetitive to other coventional methods of treatment such as the chemical flocculation. The electrolytic method has been used by Basu[45] for the treatment of sulphite pulp mill effluent.

It has been mentioned that the electrolytic treatment, applying a potential difference of 200 volts (d. c.) for a period of 5 minutes the suspended solid and B. O. D. concentration could be reduced by 80%. This method has also been used for the removal of lignin from the Kraft mill waste[46]. Aluminium electrodes were used in order to provide Al^{+++} ions[46]. A. C current was used in order to avoid surface anodization.

2. 5. Economic Considerations :

The removal of suspended solids from an effluent stream for the abatement of pollution involves the following three important steps:

i) the destabilization of the colloid,

ii) the growth of the colloidal particles to form flocs or aggregates.

and, iii) the separation of the aggregates by settling.

A schematic diagram of the entire process is shown in Fig- 5.

Destabilization is brought by adding chemicals in a mixer, usually called Flash Mixer, where the colloidal particles are intimately mixed with the chemicals. The destabilized suspension is then sent to the flocculator, where the particle aggregation takes place under carefully controlled agitation. Finally, the flocculated suspension is sent to a sedimentation basin, where the floc aggregates are separated out from the fluid medium in the form of sludge and the effluent stream becomes ready for disposal.

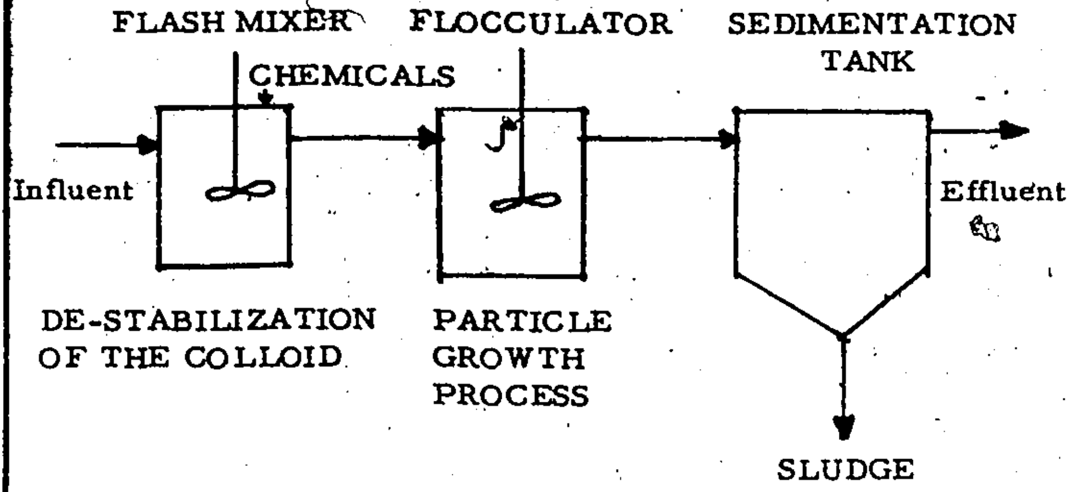


FIGURE-5:
A SCHEMATIC DIAGRAM OF THE TREATMENT PROCESS

As the acceptability of a method for the abatement of pollution depends on its cost, an attempt has been made to analyse the important cost factors of the process.

The cost of treatment could be expressed as:

TOTAL COST = COST OF CHEMICALS
+ COST OF ELECTRICAL ENERGY
+ CAPITAL COST.

Other cost items such as the land site cost and the maintenance cost have not been considered.

i) COST OF CHEMICALS:

For the treatment of Q gallons / day, the requirement of chemicals is $Q.x.m$

where,

x = weight concentration of solids in the suspension,
m = amount of chemicals required per unit weight of solids

Then the cost of chemicals in $Q.x.m.a$ and a is the unit cost of the chemicals.

ii) COST OF ELECTRICAL ENERGY :

The energy requirement is given by $\eta G^2 V$,[47] in which:

η = viscosity of the medium,
G = root mean square velocity gradient or shear rate
V = volume of the unit.

Since the volume of the unit is $Q.\tau$ and the quantity τ is the retention time, the cost of electrical energy is given by $Q\,\tau\,\eta G^2 b$ in which b is the unit cost of the electrical energy.

Therefore, the total cost of electrical energy is given by

$$Q\,\eta\,b\,(G_1^2\,\tau_{F.M} + G_2^2\,\tau_F)\ ,$$

where,

G_1 = shear rate in the flash mixer

G_2 = shear rate in the flocculator

$\tau_{F.M}$ = retention time in the flash mixer

τ_F = retention time in the flocculator.

iii) CAPITAL COST :

The capital cost is given by: $c y V$, in which, V is the volume of the unit and is equal to τQ, c is the unit cost of the unit and y is the rate of depreciation.

Therefore, the total capital cost is given by : $y Q (c_1 \tau_{F.M} + c_2 \tau_F + c_3 \tau_S)$, in which, c_1, c_2, and c_3 are the unit cost of the flash mixer, the flocculator, and the sedimentation basin, respectively. $\tau_{F.M}$, τ_F and τ_S are their respective retention time.

RETENTION TIME, τ :

i) $\tau_{F.M}$ and τ_F :

The flocculation time θ as expressed by Equation 10 represent the total time taken for the growth of the particle from its initial condition, and obviously it also includes the time taken for the destabilization. It has been shown both theoretically and experimentally by Agraman[47], that, if the flocculation is carried on in stages, the total time is less than that required for a single stage. The purpose of introducing a flash mixer is to reduce the total time taken for the particle growth to take place. The quantity

$\tau_{F.M}$ represent a small fraction of the total time $\tau_{F.M} + \tau_F$. Hence for simplification θ could be expressed as equal to τ_F.

As the ratio $\frac{N}{N_0}$ could be approximately expressed as the fraction of the solids (ξ) remaining in the suspension, τ_F could be expressed, after modifying Equation 10, as :

$$\tau_F = - \frac{\ln \xi}{K' G \varphi} \qquad (16)$$

ii) τ_S :

The retention time of the sedimentation unit is given by :

$$\tau_S = \frac{\text{Volume of the unit}}{\text{Volume rate of flow}}$$

$$= \frac{\text{Area x Height}}{\text{Area x Overflow rate}}$$

$$= \frac{\text{Height}}{\text{Overflow rate}}$$

$$= \frac{\text{Height}}{\text{Settling velocity } v_s}$$

The performance of the sedimentation tank is independent of its height. The minimum height requirement is set by the engineering design limitations.

Hence, τ_S could be expressed as :

$$\tau_S = \frac{K^*}{v_s} \qquad (17)$$

The quantity K^* in Equation 17 can be treated as constant for the sedimentation unit. It includes the efficiency factor associated with a particular value of the fraction of solids removal desired.

The total cost S could be expressed as :

$$S = Q\,x\,m\,a + Q\,\eta\,b\,(G^2\,\tau_F) + Q\,y(c_2\,\tau_F + c_3\,\tau_S) \quad (18)\,,$$

On the basis of this, the cost of separation per unit volume of flow could be expressed as :

$$\frac{S}{Q} = x\,m\,a + \eta\,b\,G^2\,\frac{\ln \xi}{K'GQ} + y c_2\,\frac{\ln \xi}{K'GQ} + y c_3\,\frac{K^*}{v_s} \quad (19)$$

The cost of power requirement, as will be revealed later , constitute a negligible fraction of the total cost. Hence, for all practical purpose could be neglected.

So, the unit total cost could be expressed as :

$$\frac{S}{Q} = x\,m\,a + y\,c_2\,\frac{\ln \xi}{K'GQ} + y\,c_3\,\frac{K^*}{v_s} \quad (20)$$

3. EXPERIMENTAL

3. 1. Planning of the Experimental Work and the Scope of The Study :

This study is restricted to the removal of suspended solids from the effluent stream. The separation process considered is chemical flocculation followed by sedimentation of the flocculated suspensions. The cost factors of the separation process, such as : i) m, the ratio of the flocculant to the amount of solids, ii) τ_F, the retention time of the flocculator and, iii) τ_S, the retention time of the sedimentation unit, are experimentally evaluated in order to determine the cost of separation.

Experimental study is planned to express the flocculation time θ, as a function of : i) m, ii) G, the shear rate, iii) ϕ the concentration of suspension and, iv) the fraction of solids remaining in the suspension. The relation between θ and the settling property of the flocculated suspension expressed as weight fraction of solids having more than settling velocity v_s is determined. From these results τ_F, τ_S are computed. The study is conducted with titanium dioxide suspension using the flocculants : 1) alum, an inorganic electrolyte extensively used in the paper industry and, 2) Super Floc - 330, an organic polyelectrolyte developed by American cynamide, Inc. .

Flocculation and the sedimentation behaviour of other ingredients of the paper mill effluent stream such as clay and paper fines and that of the effluent stream of a paper mill are investigated.

As an alternate means of particle growth, electrolytic process has been considered. Sedimentation characteristics of the electrolytically (D. C) treated suspensions are studied. Investigated parameters are : the applied potential, the duration of the passage of electric current and, the concentration of suspended solids. Titanium dioxide suspensions are investigated in this study.

3. 2. Apparatus Used :

3.2. 1. Chemical Flocculation :

Experiments on flocculation were conducted using a standard jar test apparatus as shown in Figure-6. The set-up consisted of six stirrers, the speed of rotation of which could be varied between 0-100 rpm. Using this set-up, it was possible to carry on six experiments at a constant stirring rate, varying other parameters such as the flocculation time, the dosage of flocculant and the concentration of the suspensions. 600 ml beakers were used as containers for flocculation.

3.2.2. Electrolytic Process :

The experimental set-up consisted of an electrolytic cell having a pair of parallel stainless steel electrodes connected across a Sorenson d. c. power supply (constant voltage 0-150 volts, constant current 0-2.5 amperes), in series with an ammeter. Two different types of cells were used for this study, one of which was designed for the visual observation of the effect (cell-A), and the other for obtaining a quantitative data on the kinetics of the electrolytic process (cell-B) .

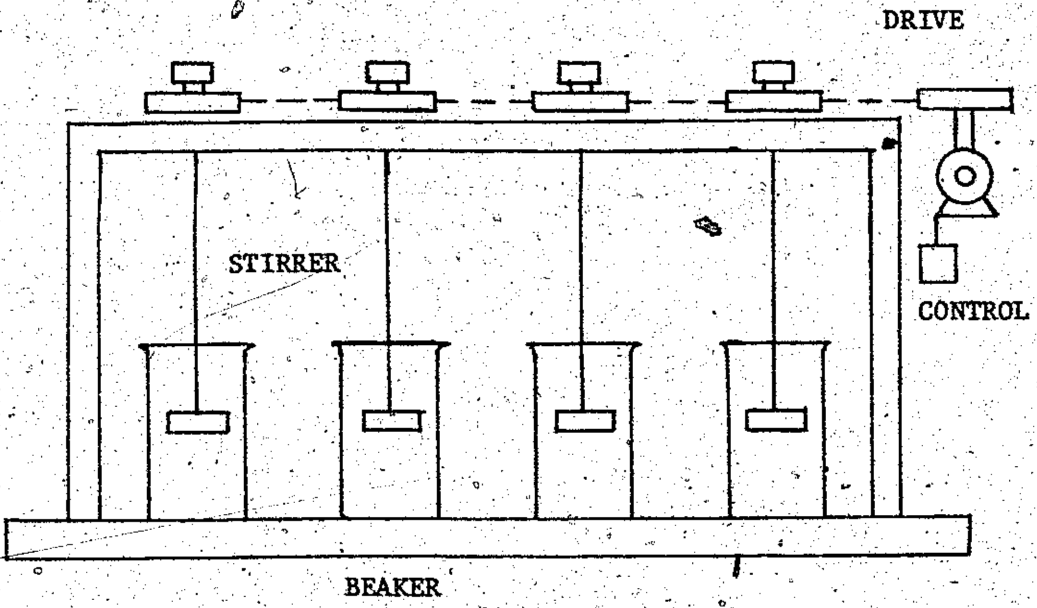


FIGURE-6 : AN APPARATUS FOR THE STUDY ON FLOCCULATION (JAR TEST APPARATUS)

Cell-A

It consisted of a rectangular plastic container, approximately 40 cm^3 in volume. Stainless steel electrodes were placed parallel in slots at 1 cm apart. The transparent wall permitted the observation and the measurement of the settling rates while the suspensions were treated electrolytically in the cell. A schematic diagram of the set-up is shown in Figure-7A.

Cell-B

It consisted of a rectangular container with an open buttom. The pair of electrodes were placed in slots at 2 cms apart. The cell was placed in a beaker containing the suspensions which was kept well stirred during an experiment with the help of a magnetic stirrer.

The experimental set-up is shown in Figure 7B.

3.2.3. Sedimentation characteristics :

A series of 600 ml beakers were used for the determination of sedimentation characteristics. In order to reduce the wall effect as much as possible, beakers were preferred over graduated cylinders.

3. 3 Materials Used :

3.3.1. Suspensions And Their Preparation Technique :

The following materials were used for the preparation of suspensions.

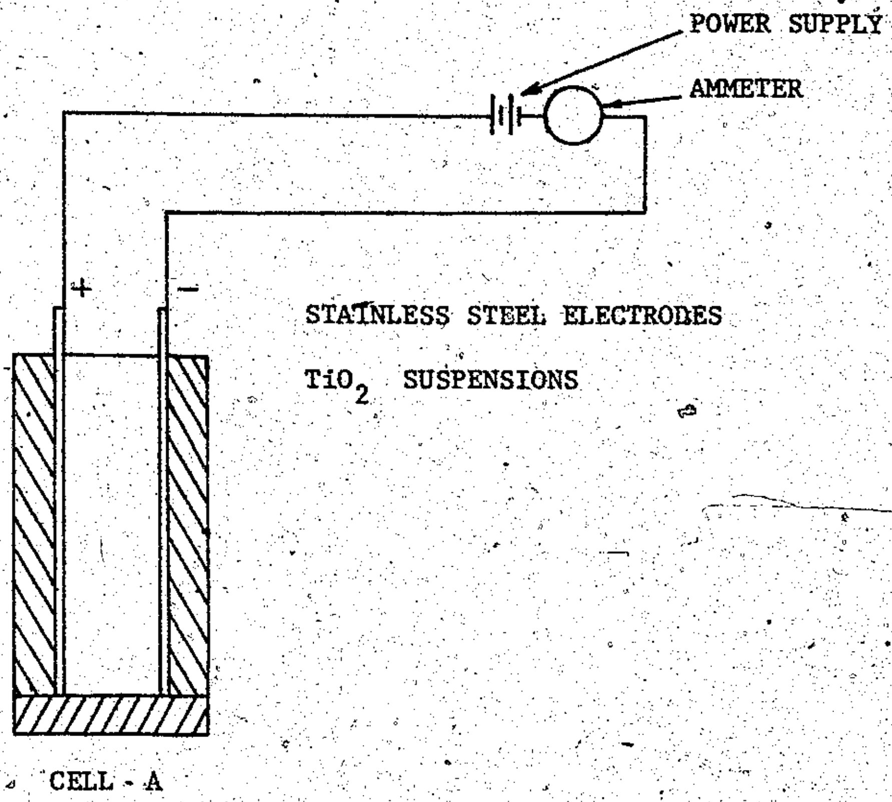


FIGURE-7A: AN EXPERIMENTAL SET-UP FOR THE VISUAL OBSERVATION OF THE PARTICLE GROWTH PROCESS INDUCED BY A D. C. FIELD.

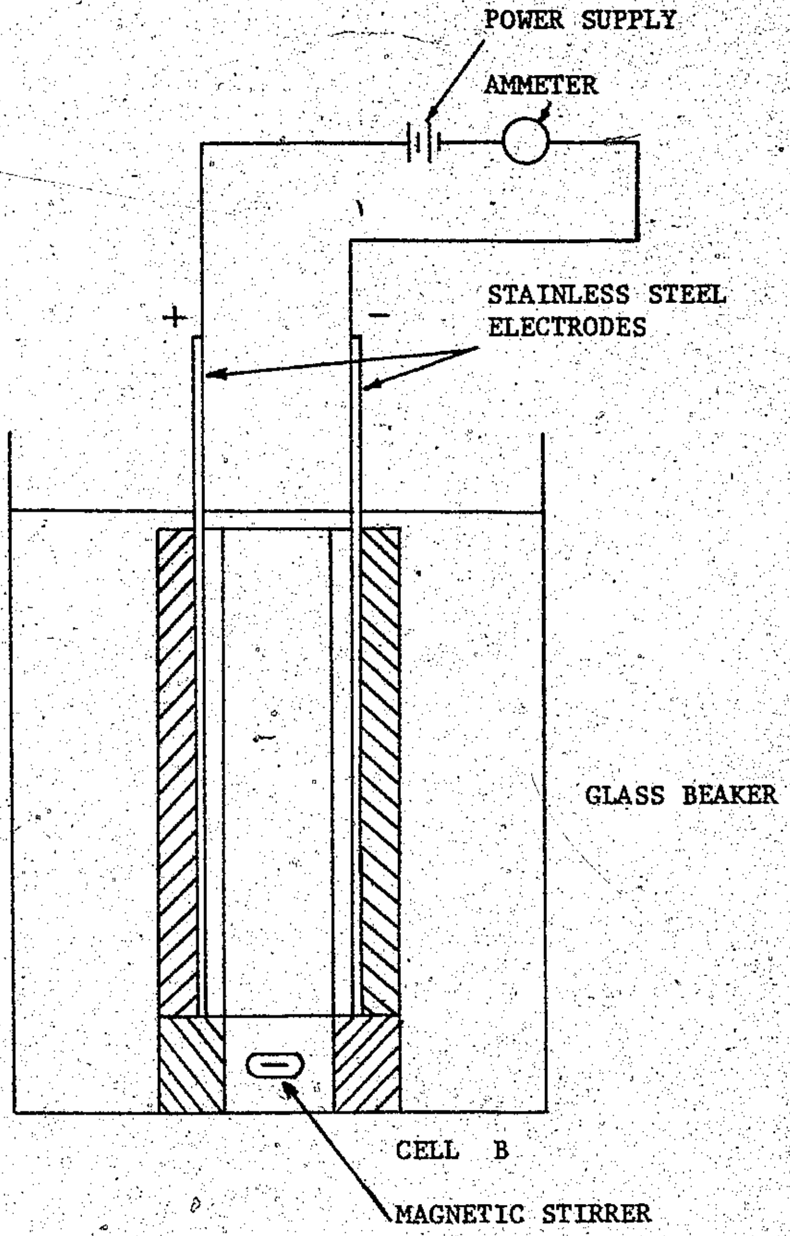


FIGURE-7B: AN EXPERIMENTAL SET-UP FOR THE STUDY ON KINETICS OF THE ELECTROLYTIC PROCESS

i) Titanium dioxide - A pigment grade TiO_2 supplied by E.I. Dupont Nemour Inc., in antase form was used for this study. The particles size were reported to be around 0.2 micron.

Approximately 3 grams of TiO_2 were dispersed in a litre of distilled water using a high speed blender. The suspension so made was filtered through a filter paper (Whatman No-41) and the filtrate was blended further for several minutes and was stored as the stock suspension. The concentration of solids in the suspension was determined accurately by filtering through membrane filter and weighing the residue after an overnight drying at room temperature. The concentration of the suspension was adjusted to any known value and was blended further before use, so that the particles remain in well dispersed condition at the time of experiment. The concentration of the suspension was determined before performing any experiment.

ii) Clay - Industrial clay used for the paper making was chosen. The particle sizes were reported to be between 1-5 microns.

Approximately 5 grams of industrial clay were dispersed in a litre of distilled water using a high speed blender. The suspension so made was allowed to settle in order to remove any coarser particles. This was necessary because the effluent stream contains only the finer particles. Most of the larger particles are usually used up in the paper making process. The decanted solution containing the finer clay particles in suspension was blended further. The concentration of the suspension was determined by filtering a known volume of the suspension through a membrane filter and weighing the residue after drying. It was then stored as stock suspension. Prior to any experiment the suspension was diluted to a required value of concentration and was blended further. The concentration of the suspension was determined before performing any experiment.

iii) Paper Fines - Industrial grade hard wood pulp was used.

10 grams of hard wood pulp were soaked in distilled water for an hour. The sample was then blended using a high speed blender for several minutes. The blended sample was diluted by adding distilled water to a final volume of 1 litre, and was blended further. Its concentration was determined and was stored as stock solution Prior to any experiment the suspension was diluted to any known value and was blended further. The concentration of the suspension was determined before performing any experiment.

3.3.2. Flocculants :

The following chemicals were used as the flocculants :

i) Alum $Al_2(SO_4)_3$, $16\ H_2O$: The reagent grade alum was used for this study. An aqueous solution containing 20 gms / litre was prepared and was used as the stock solution.

ii) Super Floc-330 : An organic poly-electrolyte manufactured by American Cyramide was used in this study. An aqueous solution containing 600 milligram of Super Floc-330 per litre of solution was used as the stock solution.

3.3.3. Other Chemicals :

In order to adjust the pH of the medium 1N NaOH solution and 1N HCl were used.

3.4. Experimental Procedure and Results :

In this investigation, 400 mls of solutions with known concentration of suspension were taken in a series of beaker 600 mls beakers and the flocculation experiments were carried out by varying the dosage of chemicals , flocculation time, stirring rate, and the concentration of the suspensions. The sedimentation characteristics of the flocculated suspensions were obtained using the following procedure.

Determination of the Sedimentation Characteristics :

The flocculated suspension was poured into a beaker and was allowed to settle. After a definite interval of time, the supernenant liquid was carefully decanted off and was allowed to settle further for a longer duration of time, and the sediments were collected. The amount of solids in all the sediments collected separately and a mass balance was made after determining the amount of solids in the final supernenant liquid. The amount of solids was determined by weighing, after filtering the settled solids along with its wash, through a membrane filter, followed by drying overnight at room temperature. The cumulative weight fraction of the settled solids was determined as a function of time.

3.4.1. A Study on the Flocculating and the Sedimentation Behavior of the Flocculated TiO_2 Suspensions Using Polymer Electrolyte (Super Floc-330) As the Flocculant.

The objective of this study was to determine the residence time required for the flocculator, as a function of the concentration of the suspension, the shear rate, and the settling behavior of the flocculated suspensions.

3.4.1.1 Preliminary Experiments :

In order to determine the approximate range of the flocculant dosage required for the treatment, a series of preliminary experiments was conducted using suspension containing 900 milligrams of TiO_2 per litre. 400 ml of freshly dispersed suspensions were taken in each of the six test jars. 100 millilitres of the stock solution containing 600 milligrams of Super Floc-330 per litre were diluted to a litre by adding distilled water. 4, 5, 6, 7, 8, 10 and 12 ml of the diluted Super Floc solution containing 60 mg/litre were added to the suspensions, successively. The suspensions were kept well stirred with the help of magnetic stirrer. The control knob of the stirrer was maintained at a definite position for all the samples, so that all six were stirred uniformly. Suspensions were flocculated for a period of 15 minutes and the sedimentation characteristics of the flocculated suspensions were determined.

The experimental data are presented in Table-1. The sedimentation characteristics of the flocculated suspensions are shown in Figure-8. The cumulative weight fraction of the solid settled is plotted against the settling time in minutes, and the dosage of flocculant as the variable parameter. Curves I, II, III, IV, and V of Figure 8 represent the flocculant dosage of 0.66, 0.83, 1.0, 1.16 and 1.33, respectively.

The concentration of TiO_2 remaining in the suspension after an hour of settling is plotted in Figure-9 as a function of the flocculant dosage. It appears from this figure that the process is associated with an optimum dose requirement, and its value is approximately 1.5 mg /gm of TiO_2. It is noted that the curve in Fig-9 is comparatively flat between a dosage of 1.3 to 1.7 mg / gm, and a very little advantage is expected if the dosage is more than 1.3 mg/gm. of TiO_2.

A general trend is observed in the sedimentation characteristics that most of the agglomerates formed are above certain sizes and the remainders are in the dispersed phase, instead of being equally distributed over the entire range. The equal size distribution is marked by a gradual change in slope of the sedimentation curve instead of a sharp change as observed.

3.4.1.2 The Effect of Varying the Speed of Rotation of the Stirrer:

The flocculant dosage was maintained constant at 1.3 mg/gm of TiO_2. Experiments were conducted by varying the rotating speed of the stirrer of the jar test apparatus, maintaining the flocculation time constant at 15 minutes. The experimental results are shown in Table 2 and 3 for the suspension having 900 and 190 ppm of TiO_2, respectively. The sedimentation characteristics are shown in Figure-10 and Figure-11, for the respective cases. The curves I, II, III and IV

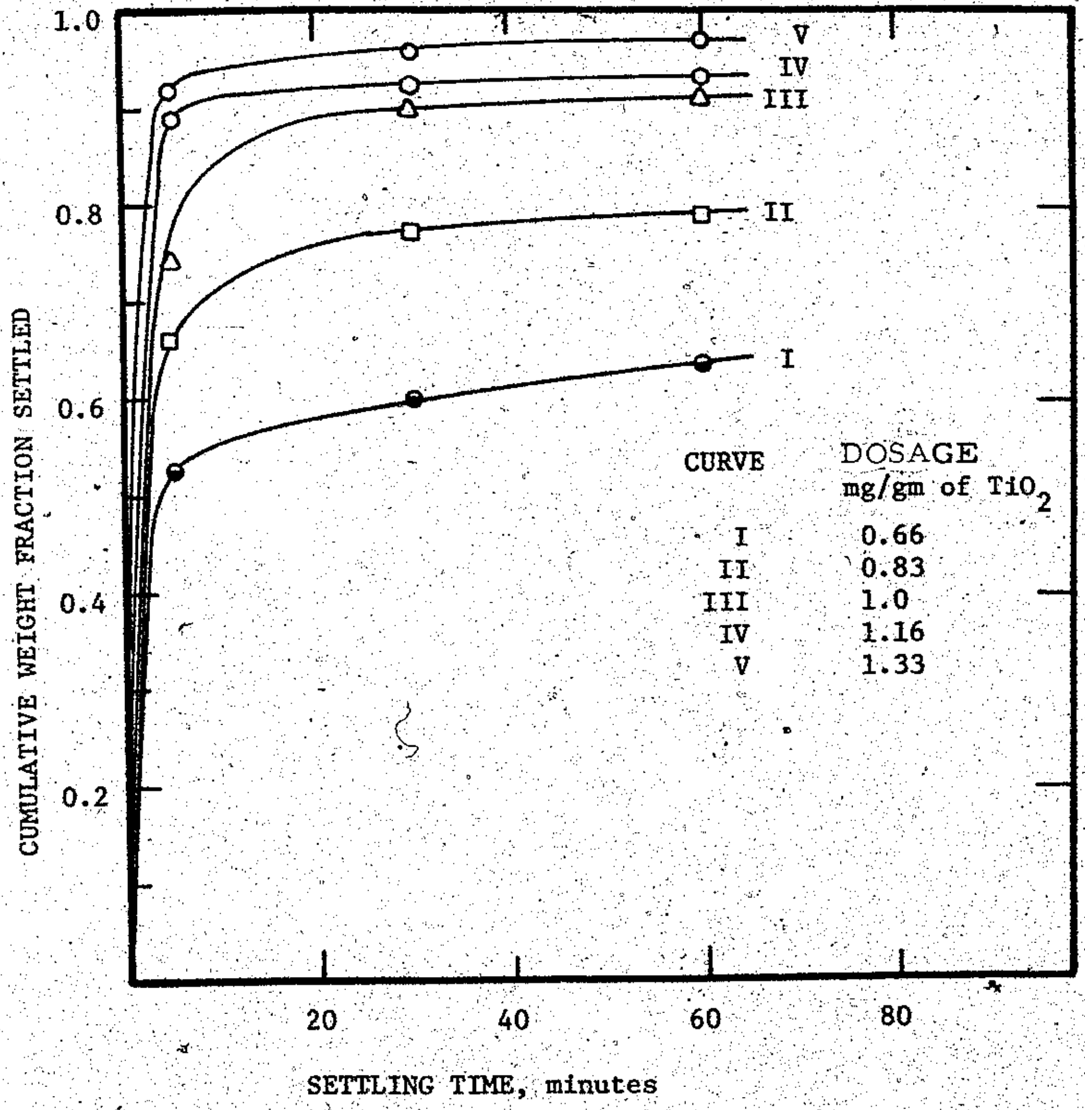

FLOCCULATION TIME- 15 minutes
STIRRING RATE- CONSTANT

FIGURE-8: SEDIMENTATION CHARACTERISTICS OF THE FLOCCULATED TiO_2 SUSPENSIONS OF 900 ppm CONCENTRATION AS A FUNCTION OF THE DOSAGE OF FLOCCULANT (SUPER-FLOC)

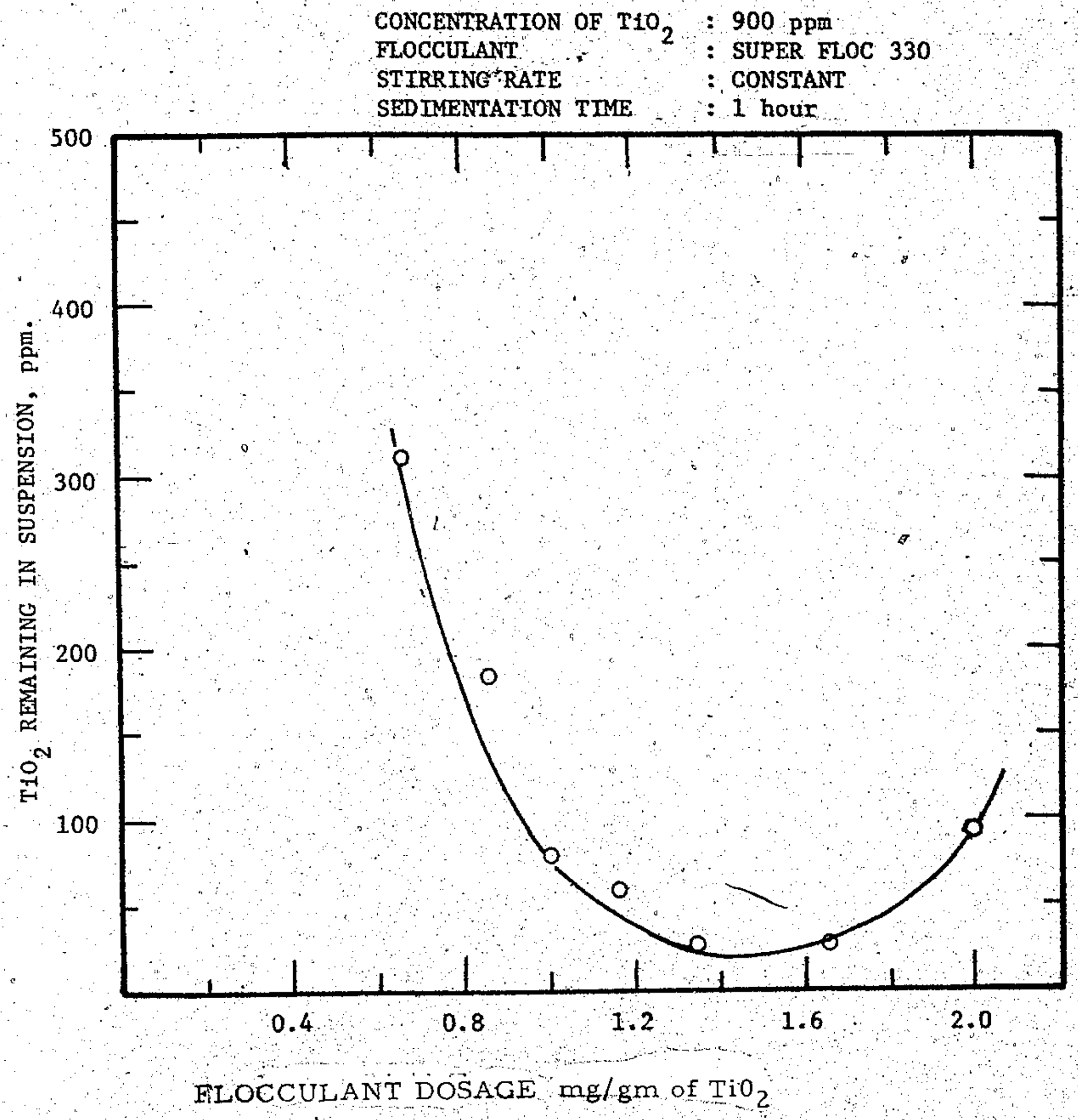


FIGURE-9: FINAL CONCENTRATION OF TiO_2 REMAINING IN SUSPENSION AS A FUNCTION OF THE DOSAGE OF FLOCCULANT.

CONCENTRATION OF TiO_2 : 900 ppm
FLOCCULANT : SUPER FLOC
FLOCCULATION TIME : 15 minutes
FLOCCULANT DOSAGE : 1.3 mg/gm of TiO_2

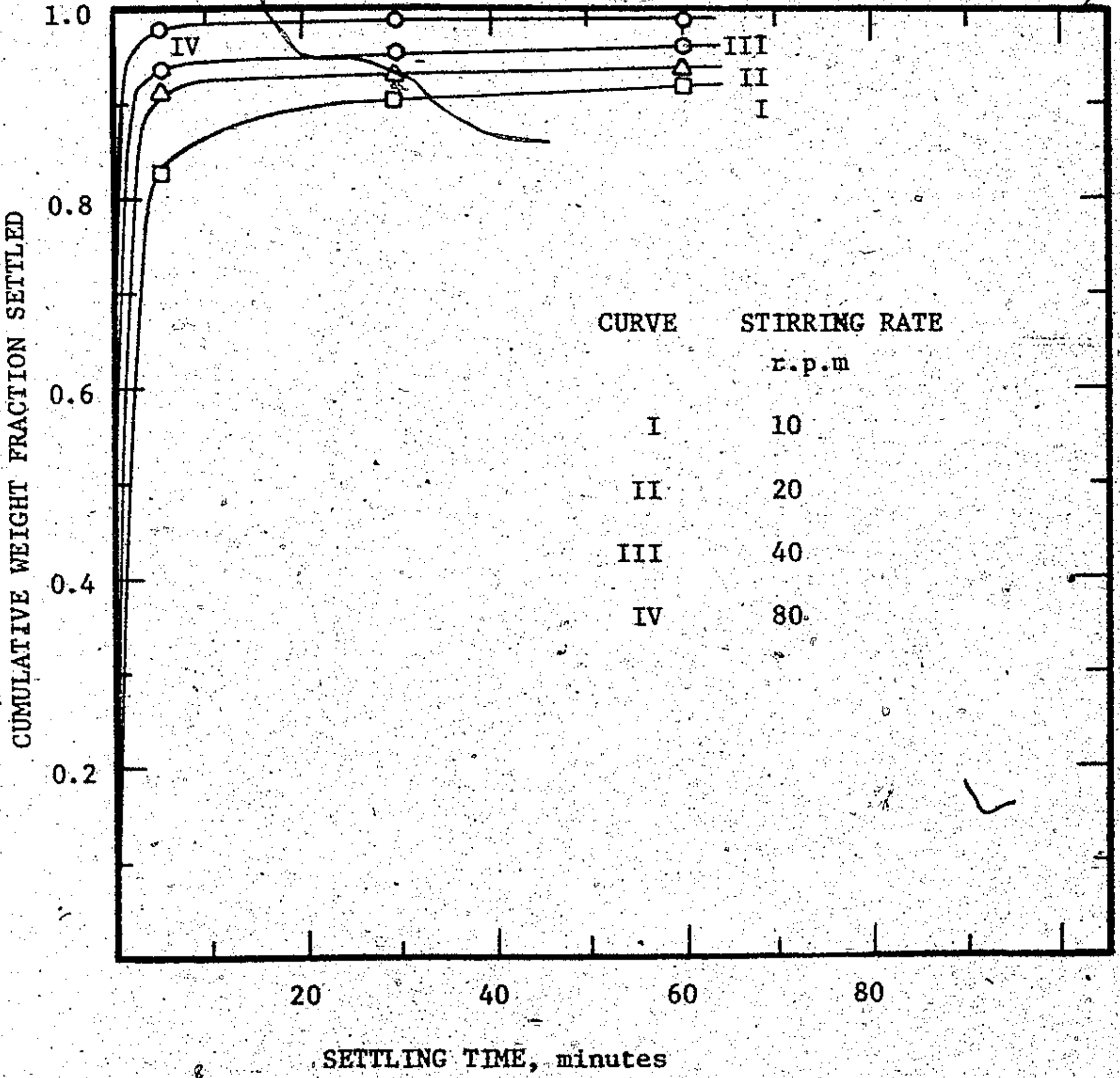
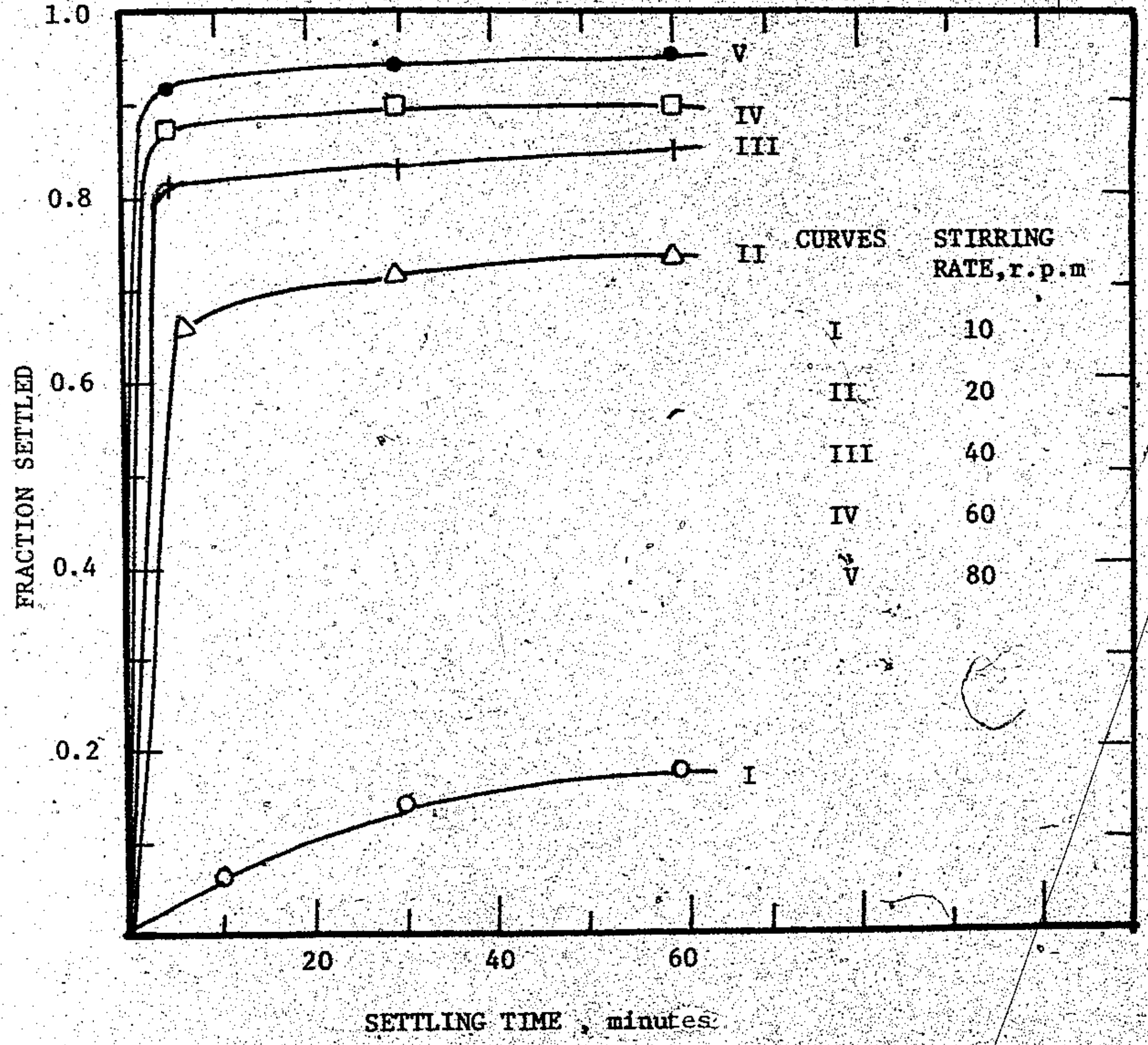


FIGURE-10: SEDIMENTATION CHARACTERISTICS OF THE FLOCCULATED TiO_2 SUSPENSIONS, STIRRING RATE AS THE PARAMETER



FLOCCULANT SUPER FLOC 330
FLOCCULATION TIME 15 minutes
FLOCCULANT DOSAGE 1.3 mg/gm

FIGURE-11: SEDIMENTATION CHARACTERISTICS OF THE FLOCCULATED TiO_2 SUSPENSIONS OF 193 ppm CONCENTRATION AS A FUNCTION OF THE STIRRING RATE.

in Figure-10 represent the stirring rates of 10,20,40 and 80 rpm, respectively, and the curves I to V in Figure 11 represent similarly the stirring rates of 10, 20, 40, 60 and 80 rpm.

3.4.1.3 The Effect of Varying the Flocculation Time:

Experiments were conducted at a constant flocculant dosage of 1.3 mg/gm of TiO_2. The flocculation time was varied, while the rotating speed of the stirrer and the concentration of the suspensions were maintained constant. Experimental results are presented in Table 4 and 5 for 900 ppm and 190 ppm TiO_2 suspensions, respectively. The sedimentation characteristics of the flocculated TiO_2 suspensions are shown in Figure-12 & 13 respectively. The curves I, II, and III in Figure-12 represent the flocculation time of 5, 10 and 20 minutes, respectively, and the curves I, II, III, IV and V in Fig-13 represent similarly the flocculation time of 15, 30, 45, 60 and 105 minutes.

3.4.1.4 The Effect of Varying the Concentration of TiO_2 Suspensions :

The suspensions containing 200, 400, 600 and 900 ppm of TiO_2 were flocculated while all other parameters were kept constant. The speed of rotation of the stirrer, the dosage of chemicals and the flocculation time were maintained constant at 10 rpm, 1.3 mg/gm of TiO_2 and 15 minutes, respectively. Experimental results are presented in Table-6. The sedimentation characteristics of the flocculated suspensions are shown in Fig-14. The curves I, II, III and IV represent the ~~concentrations~~ of 200, 400, 600 and 900 ppm, respectively.

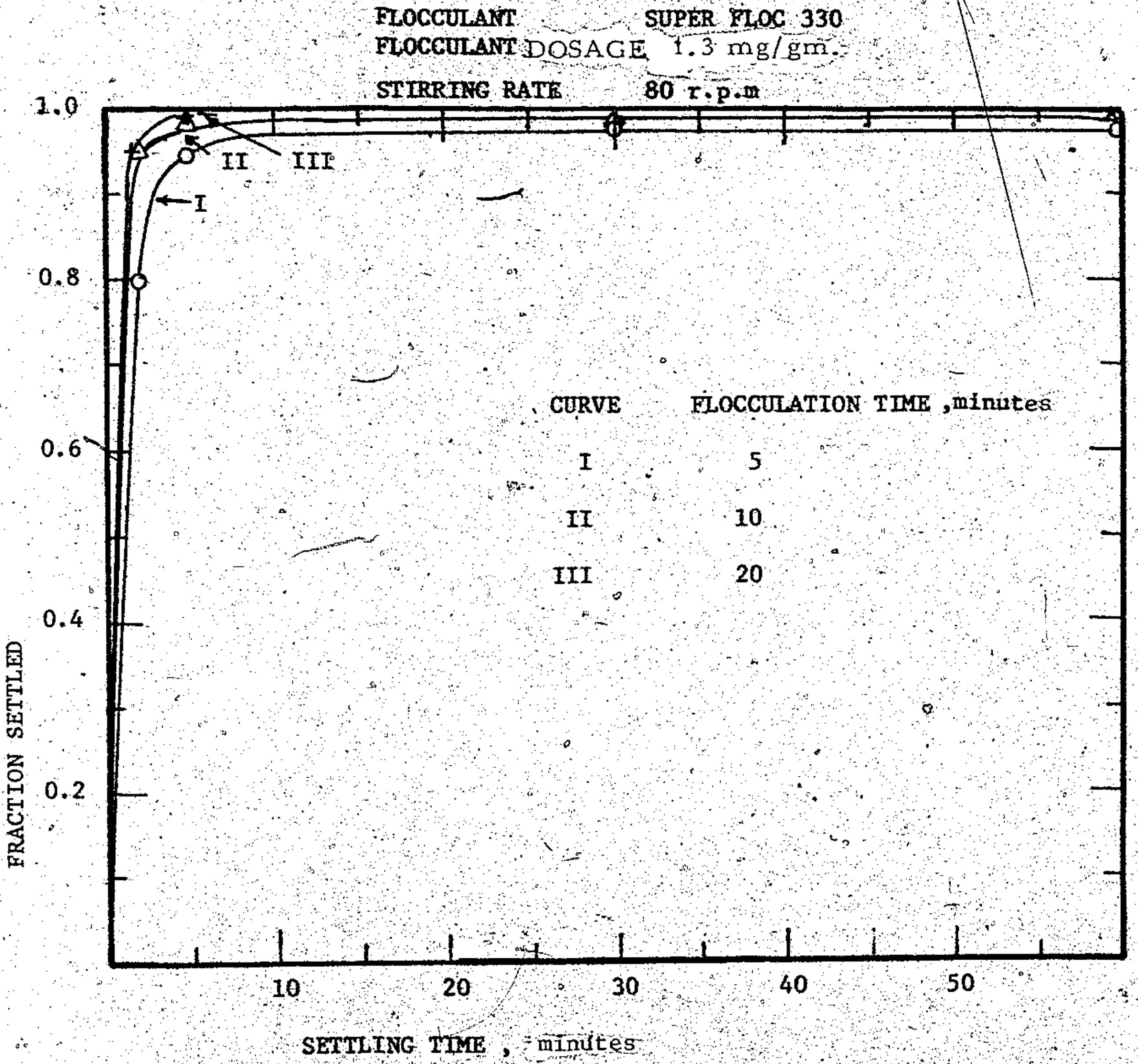


FIGURE -12 : SEDIMENTATION CHARACTERISTICS OF THE FLOCCULATED TiO_2 SUSPENSION OF 900 ppm AS A FUNCTION OF THE FLOCCULATION TIME.

FLOCCULANT SUPER FLOC 330

FLOCCULANT DOSAGE 1.3 mg/gm.

STIRRING RATE 10 r.p.m

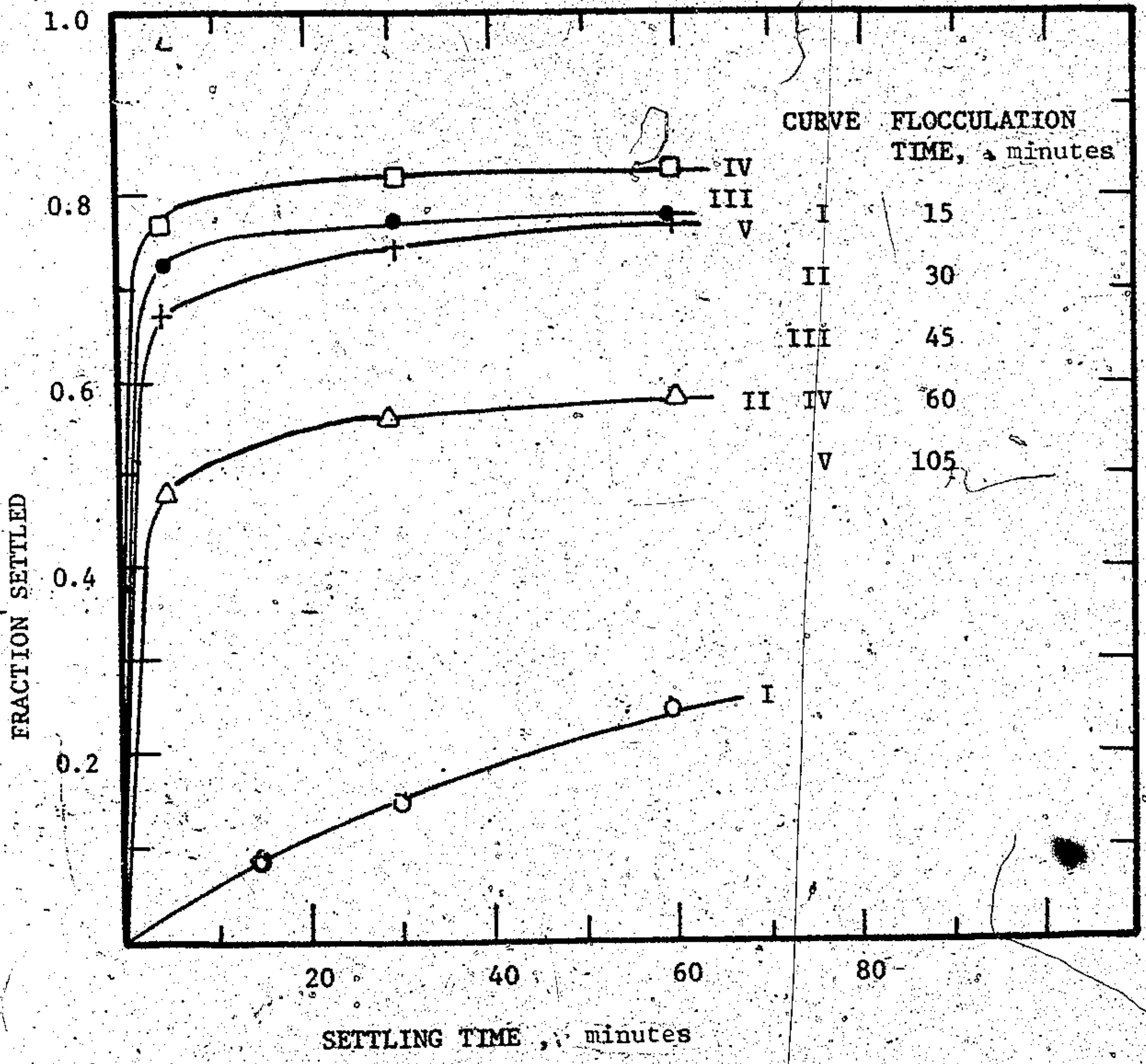


FIGURE -13: SEDIMENTATION CHARACTERISTICS OF THE FLOCCULATED TiO_2 SUSPENSIONS OF 193 ppm AS A FUNCTION OF THE FLOCCULATION TIME

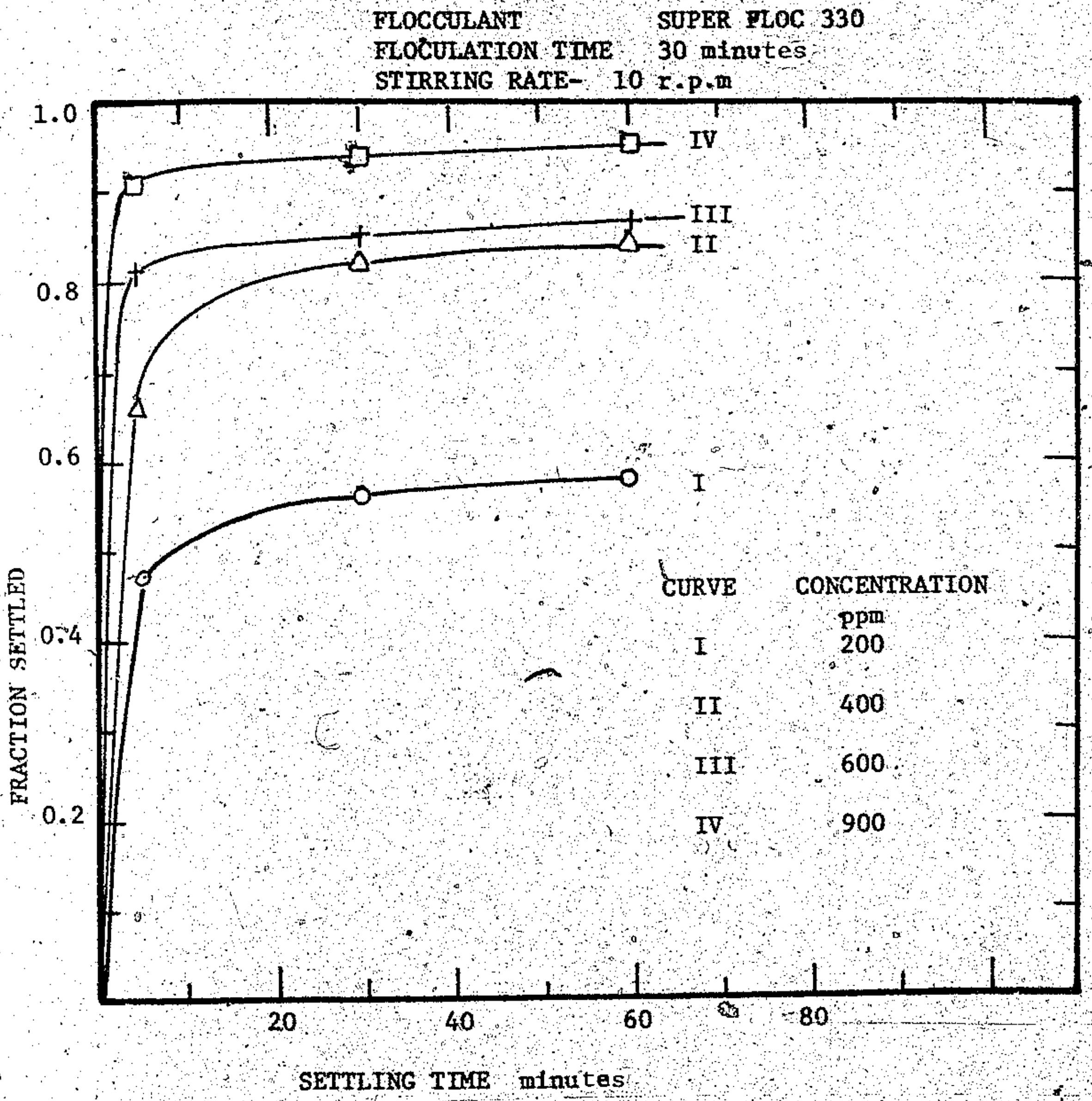


FIGURE 14: SEDIMENTATION CHARACTERISTICS OF THE FLOCCULATED TiO_2 SUSPENSIONS AS A FUNCTION OF THE TiO_2 CONCENTRATION.

3.4.1.5. Determination of the Optimum Dosage :

In the determination of the optimum dosage of polymer, the parameters n, θ are maintained constant at 80 rpm and 15 minutes, respectively. The fractions of solids remaining suspended is plotted as a function of the flocculant dosage m in in Figure-15. The results are presented in Table-7.

3.4.1.6 Determination of the Flocculation Time θ, as a Function of G, φ and m, and the Evaluation of the Flocculation Constant K' :

Experiments were conducted with Super Floc dosage of 1.0, 1.3 and 2.1 mg/gm of TiO_2, while varying the speed of rotation of the stirrer between 10 - 100 rpm, the concentration of TiO_2 in the suspension between 190 to 900 ppm, and the flocculation time between 2 to 105 minutes. Experimental results showing the fraction of solids remaining in the suspension, for different values of G, θ, φ and m are presented in Table-8. The values of the flocculation constant K' are also presented. Flocculation constant K' is calculated on the basis of Equation 10. The speed of rotation of the stirrer is expressed as G_{ave} (sec^{-1}). The values of G_{ave} have been evaluated by Camp for an identical set-up with the same blade dimension 3" x 1" and are presented in Table-9 as a function of n, the speed of rotation of the stirrer.

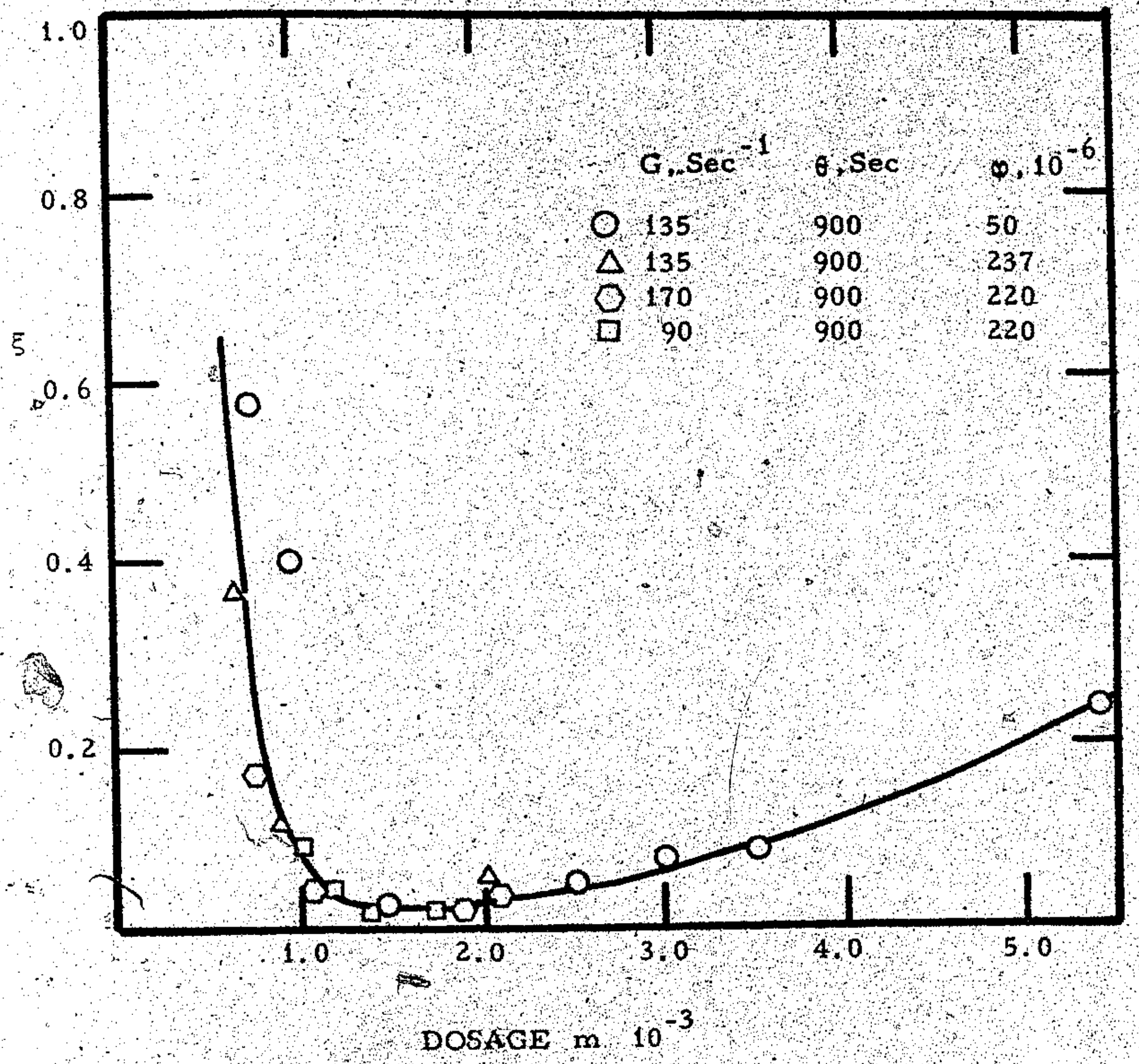


FIG-15 : A PLOT OF ξ VS m FOR SUPER FLOC.

The volume concentration φ is calculated from the weight concentration x assuming the specific gravity to be 3.82 The fraction of the solids remaining in suspension is presented on a log-log plot as a function of the dimensionless product $G\theta\varphi$ in Fig-16. The parameter is m. The curves I, II and III are for the values of m, 1.3, 1.0 and 2.1 mg/gm of TiO_2, respectively. It appears from the Table 8 that the value of the flocculation constant K' changes with θ and G. The value of K' is plotted as a function θ for four different experimental series in Fig-17. In Fig-18, K' is plotted as a function of G, while θ was kept constant at 15 minutes.

3.4.1.7. Expressing the Settling Velocity (v_s) as a Function of the Flocculation Time θ:

The sedimentation characteristics of the flocculated suspensions indicate that the size of the particles are not uniform As a result, it becomes more meaningful to express the settling characteristics in terms of the fractions of solids having settling velocity more than certain value v_s.

A plot of the settling velocity v_s against the fraction of solids having settling velocity more than certain value v_s, flocculation time θ as the parameter is shown Fig-19. Experimental results are presented in Table-10. The method of calculation of the settling velocity is presented in Appendix II.

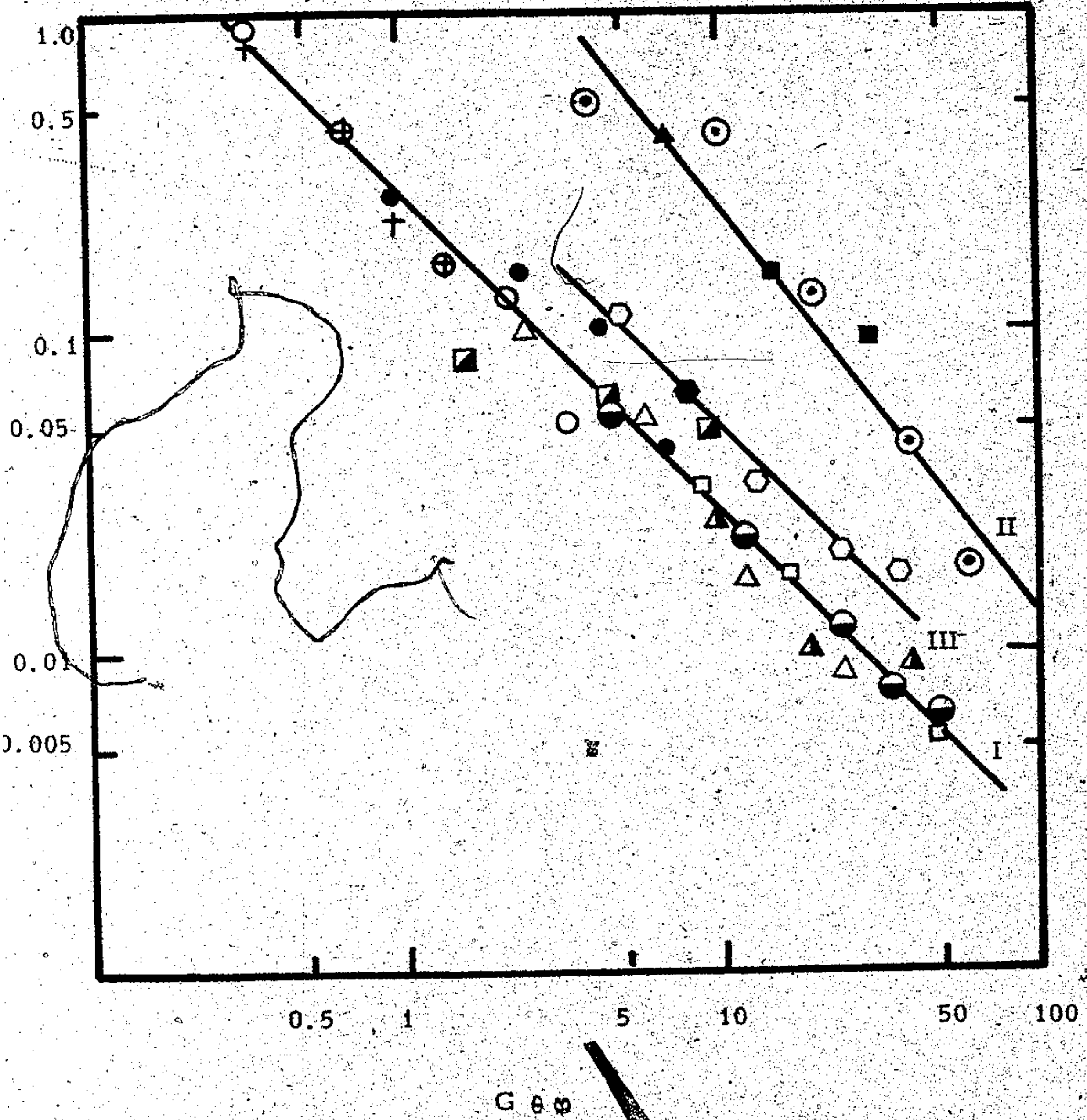


FIG-16 : A PLOT OF ξ VS G θ φ FOR SUPER FLOC-330
m AS THE PARAMETER.

CURVE	G, SEC^{-1}	θ, SEC	φ, 10^{-6}	m 10^{-3}
◪	VARIABLE	900	237	1.3
○	VARIABLE	900	50	1.3
◭	135	VARIABLE	237	1.3
+	7.2	VARIABLE	50	1.3
I ●	7.2	1800	VARIABLE	1.3
◒	170	VARIABLE	220	1.3
△	90	VARIABLE	220	1.3
□	135	VARIABLE	200	1.3
⊙	170	VARIABLE	190	1.05
II ■	135	VARIABLE	237	1.05
▲	135	900	50	1.05
III ⬡	170	VARIABLE	237	2.10
⬢	135	900	50	2.0

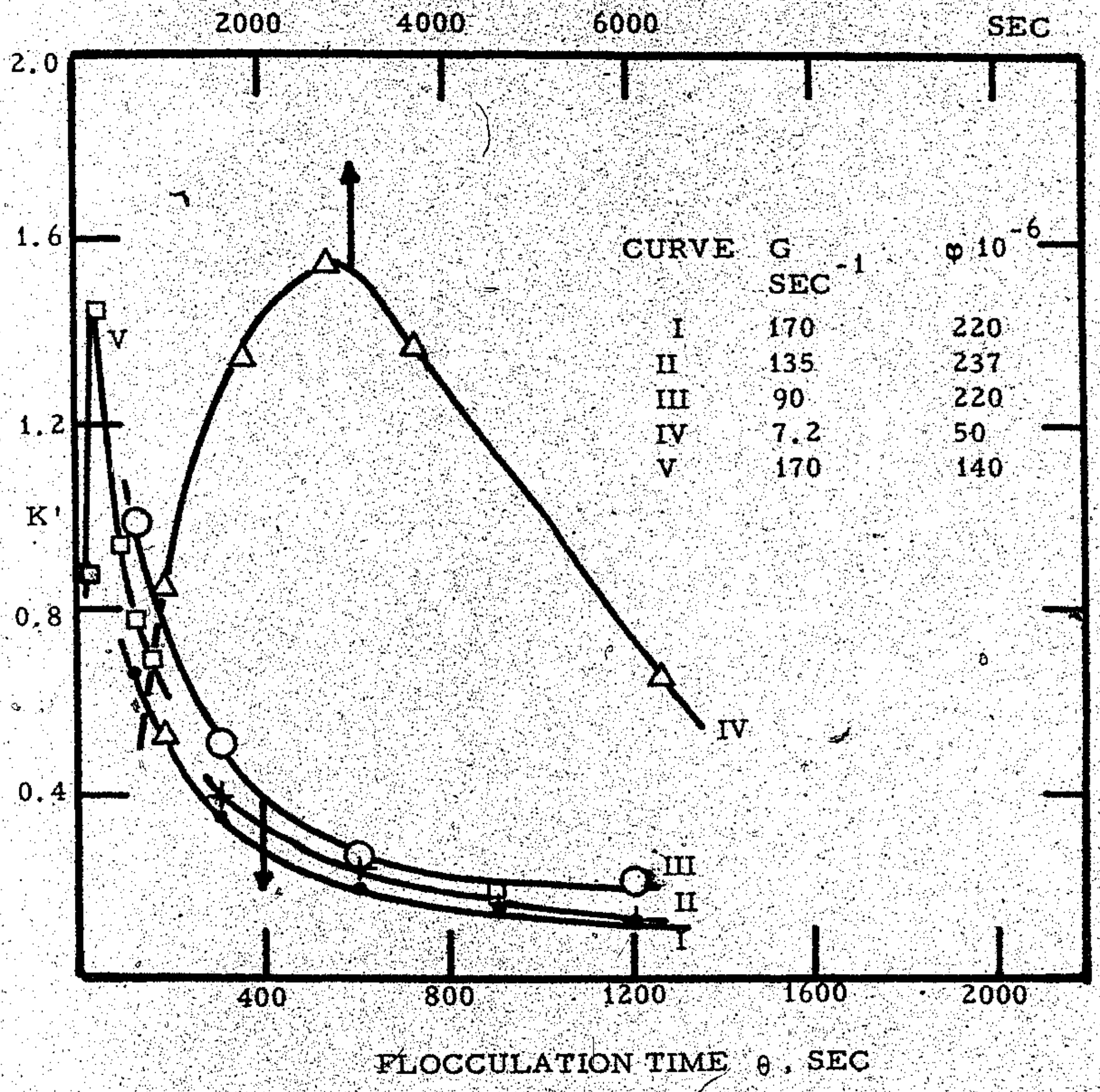


FIG-17 : A PLOT OF K' VS θ .

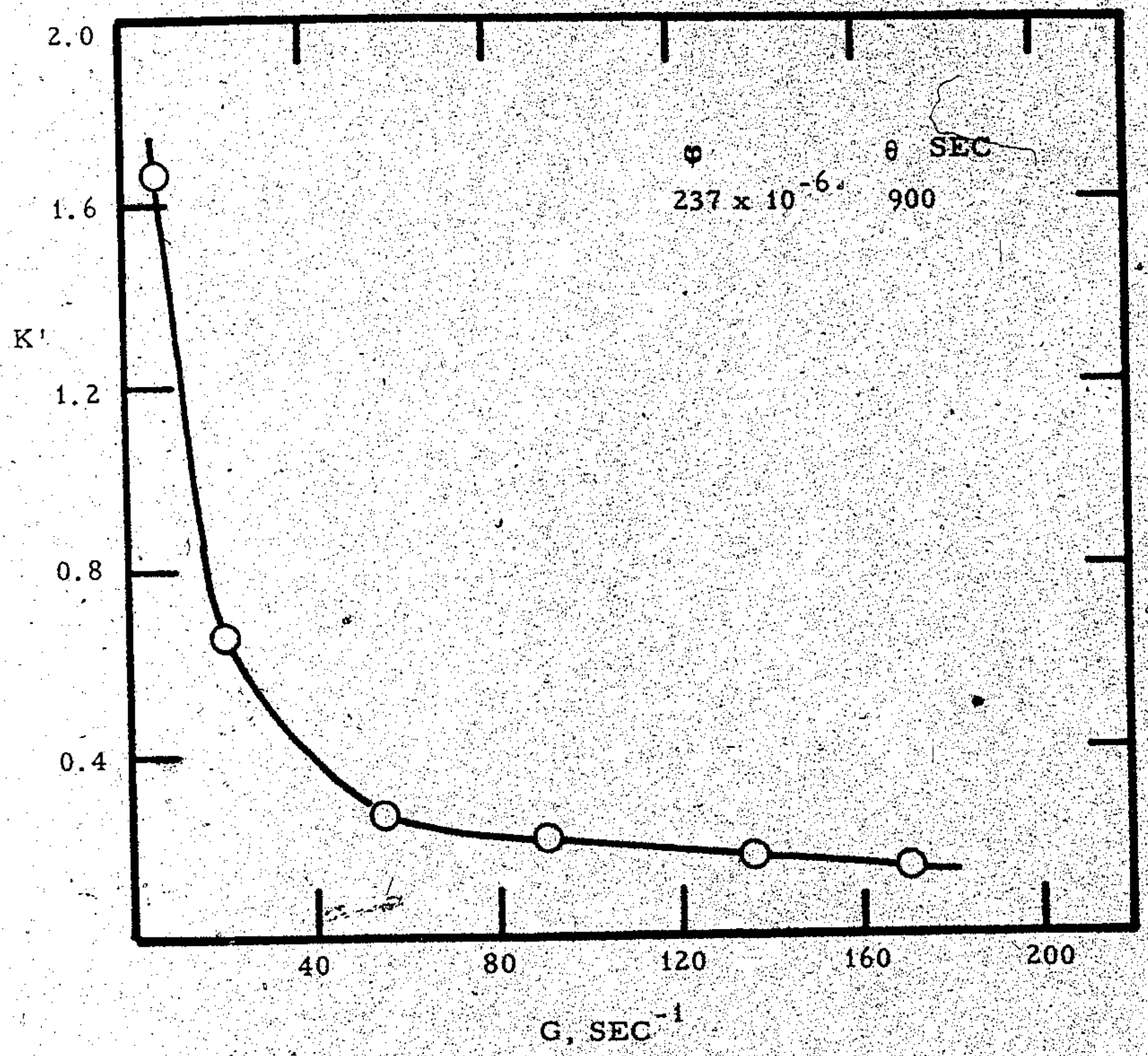


FIG-18 : A PLOT OF K' VS G.

FLOCCULANT - SUPER FLOC
FLOCCULANT DOSAGE - 1.3 mg/gm of TiO_2
CONCENTRATION OF TiO_2 - 900 ppm
STIRRING RATE - 80 rpm.

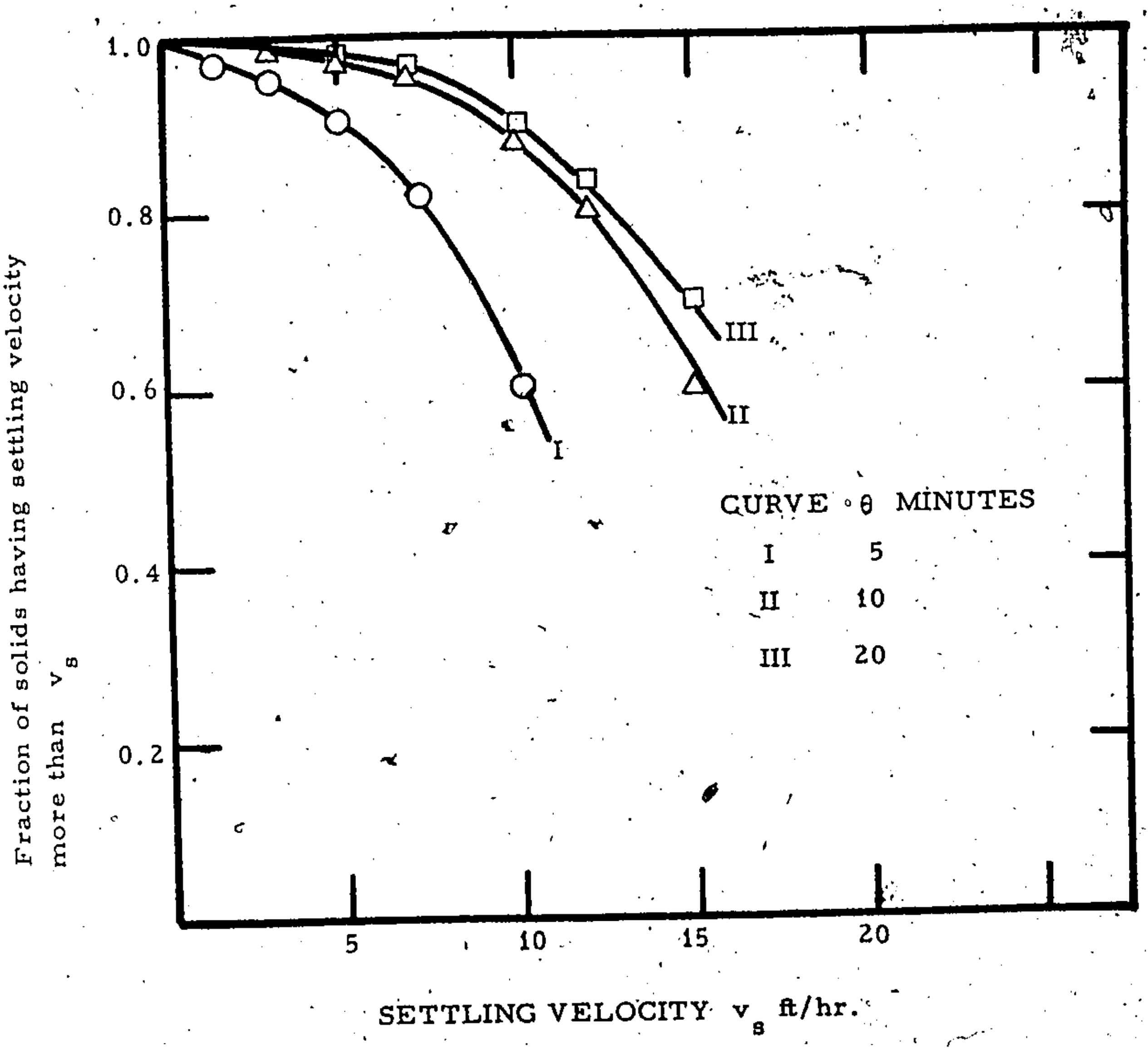


FIGURE-19: A RELATION BETWEEN THE FLOCCULATION TIME AND THE FRACTION OF SOLIDS HAVING SETTLING VELOCITY MORE THAN v_s.

3.4.2 A Study of the Flocculation and the Sedimentation Behaviour of TiO_2 Suspensions, Using Alum as the Flocculant:

The variables considered in this study were the following :

1) the dosage of alum (m) ,
2) the flocculation time (θ)
and, 3) the pH value of the medium.

The stirring rate n was maintained constant at 80 rpm, and the concentration (x) at 900 ppm of TiO_2. .

3.4.2.1. Effect of Varying the Dosage Without Adjusting the pH of the Medium:

Alum dosages were varied between 55 - 555 mg/gm of TiO_2, while the flocculation time θ was maintained constant at 30 minutes. The value of pH was initially 6.8. Due to the addition of alum solution pH of the medium was lowered and its value depended on the amount of alum added. The final values of the pH were 5 and 4, for the alum dosage m of 55 and 555 mg/gm of TiO_2, respectively. After flocculation, sedimentation characteristics was determined. Experimental results are presented in Table-11. The sedimentation characteristics of the flocculated suspensions for different values of alum dosage are shown in Fig-20. The curves I, II, III, IV and V represent the dosages of 55.5, 111, 166, 275 and 555 mg/gm of TiO_2, respectively.

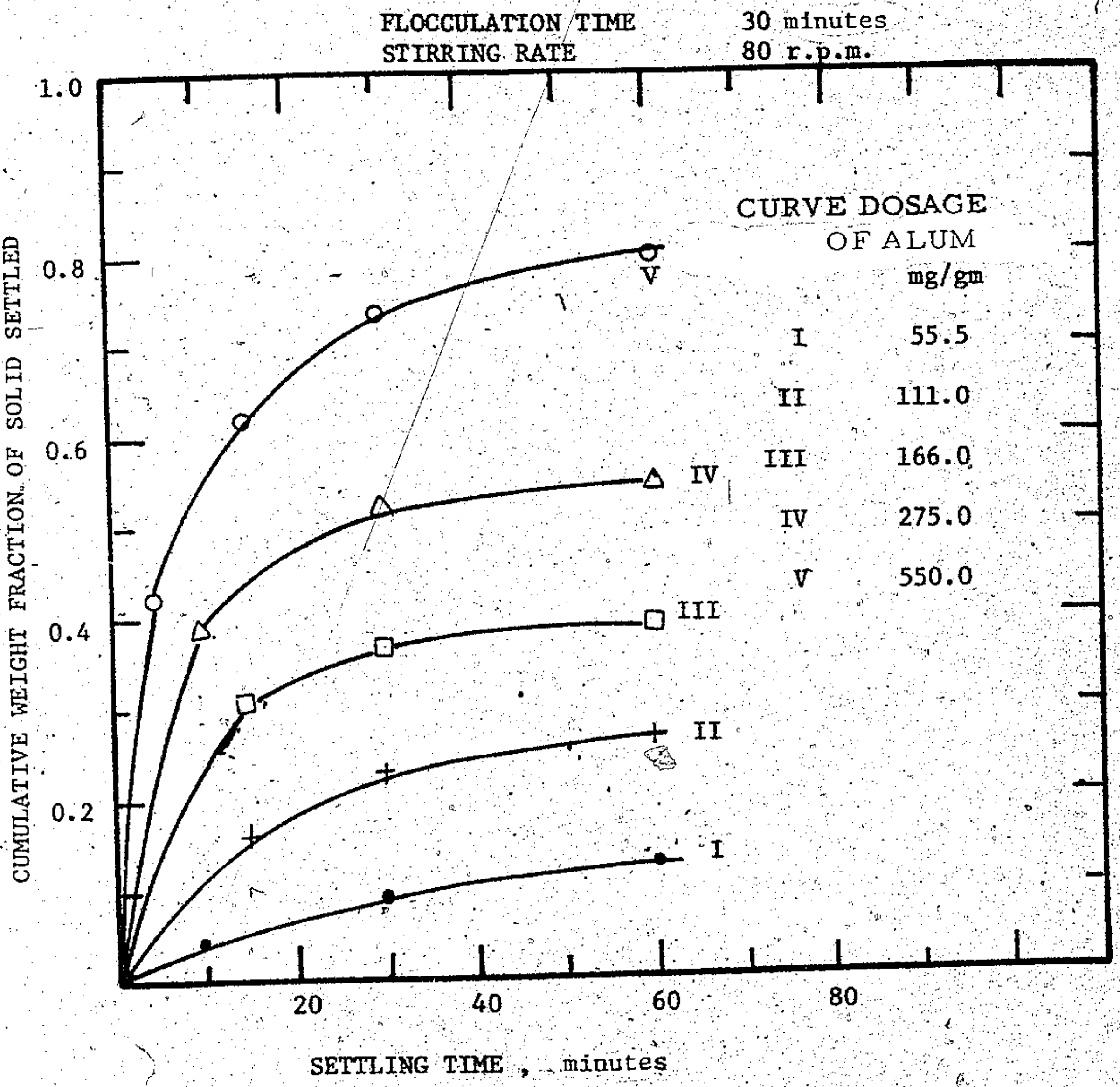


FIGURE- 20: SEDIMENTATION CHARACTERISTICS OF THE FLOCCULATED TiO_2 SUSPENSION OF 900 ppm CONCENTRATION AS A FUNCTION OF THE DOSAGE OF FLOCCULANT(ALUM) WITHOUT ADJUSTING THE pH OF THE MEDIUM.

3.4.2.2. Effect of Varying the Dosage with Adjusting the pH of the Medium:

After adding alum solution to the suspension, the pH value of the medium was adjusted to 6.5 by adding few drops of 1N NaOH solution. Alum dosage were varied between 28-111 mg/gm of TiO_2 while the flocculation time θ and the stirring rate n were maintained constant.

The experimental results are presented in Table-12 and Table-13 for a suspension concentration of 900 ppm and for the flocculation time θ of 5 and 15 minutes, respectively. The stirring rate was maintained at 80 rpm. The sedimentation characteristics of the flocculated suspensions for θ of 5 and 15 minutes are shown in Fig-21 and Fig-22 respectively. The curves I, II, III, IV and V of Fig-21 are for the alum dosage of 44.5, 55.5, 66.6, 83.5, 110.0 and 160.0, respectively and the curves I, II, III, IV and V of Fig-22 are for the alum dosage of 28.0, 44.0, 66.0, and 110 mg/gm of TiO_2, respectively.

3.4.2.3. Determination of the Flocculation Time θ as a Function of G, φ and m and the Evaluation of Flocculation Constant K':

Experimental results showing the relation of θ , G, φ and m with the flocculation constant K' are presented in Table-14.

The fraction of the solids remaining in the suspension as a function of alum dosage, the flocculation time θ as the parameter as shown in Fig-23. The curves I, II, III, and IV in Fig-23 represent the flocculation time θ of 2, 5 , 10, and 15 minutes, respectively. A log-log plot of the fraction of solids remaining

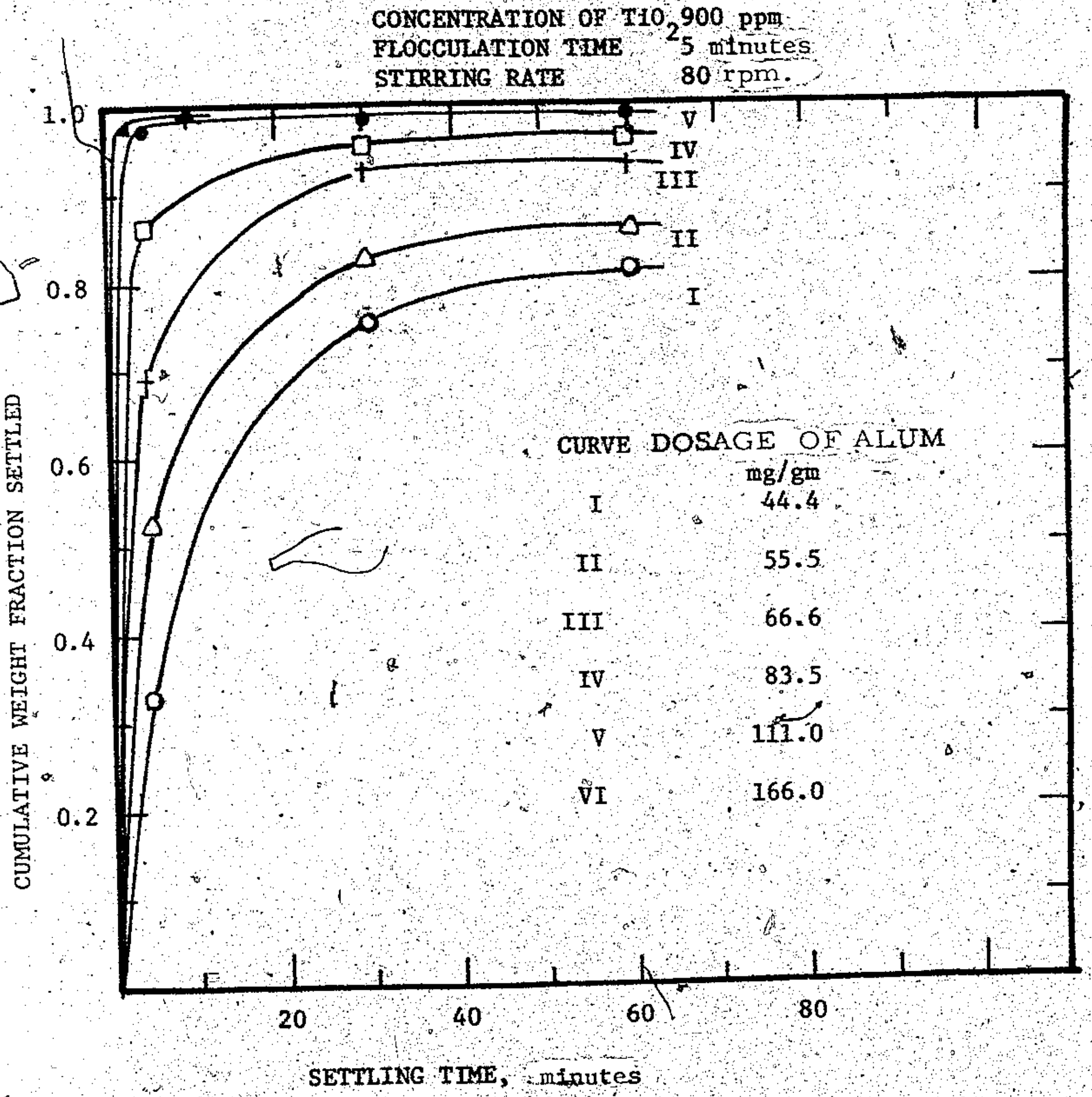


FIGURE- 21: SEDIMENTATION CHARACTERISTICS OF THE FLOCCULATED TiO_2 SUSPENSIONS OF 900 ppm CONCENTRATION AS A FUNCTION OF THE DOSAGE OF FLOCCULANT (ALUM), WITH ADJUSTING THE pH OF THE MEDIUM:

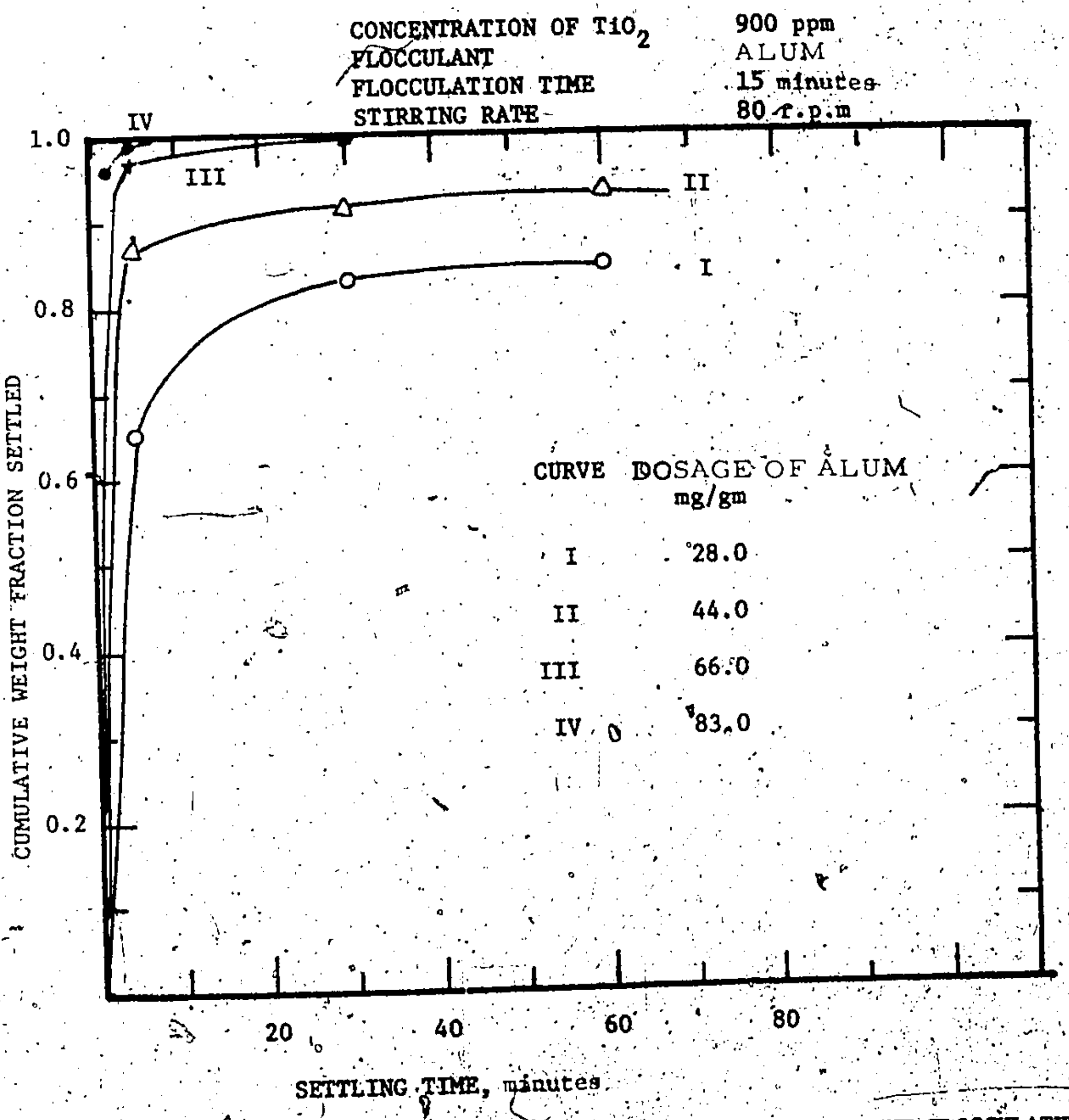


FIGURE- 22 : SEDIMENTATION CHARACTERISTICS OF THE FLOCCULATED TiO_2 SUSPENSION OF 900 ppm CONCENTRATION AS A FUNCTION OF THE DOSAGE OF FLOCCULANT(ALUM), WITH ADJUSTING THE pH OF THE MEDIUM

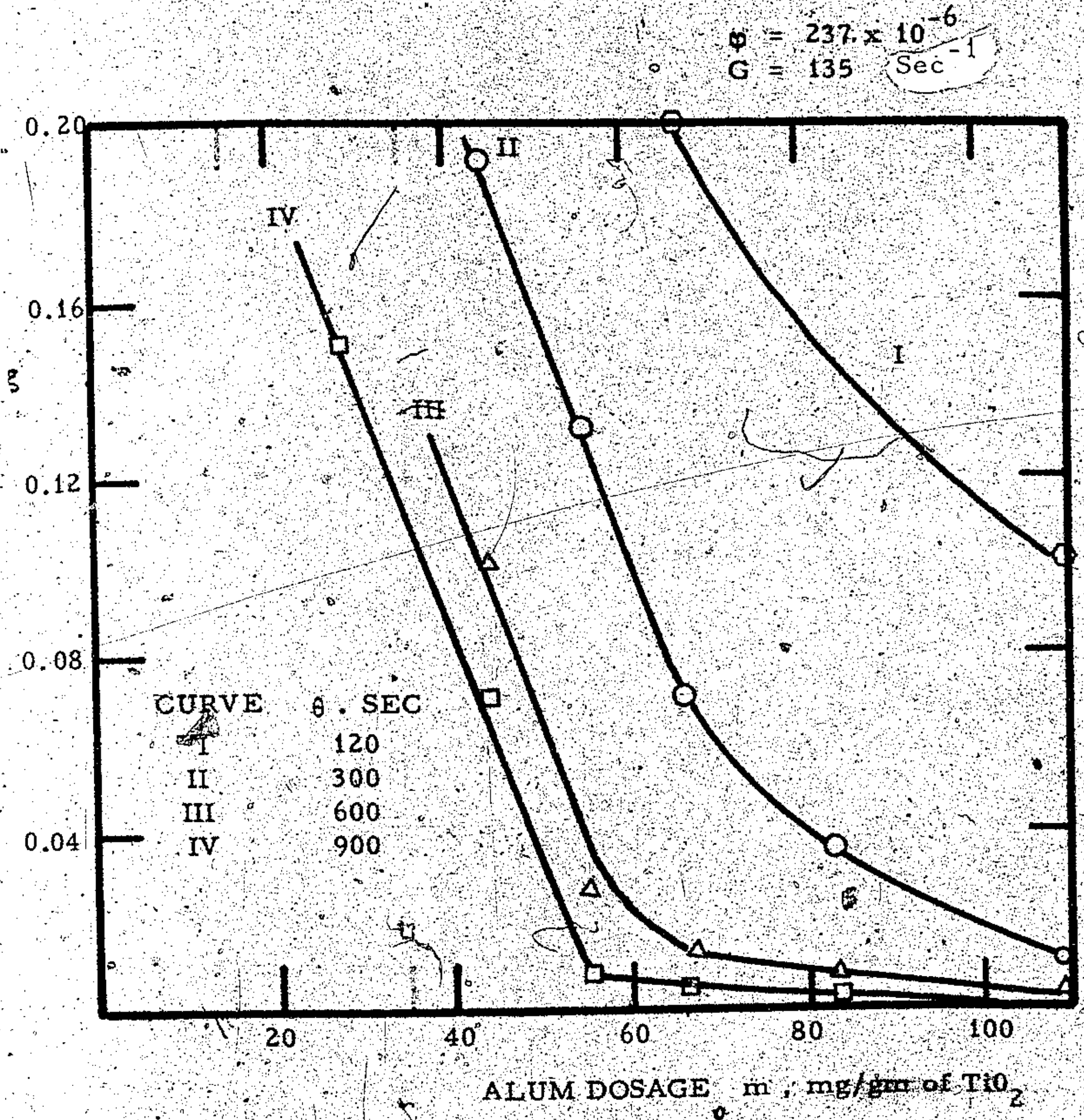


FIG-23: A PLOT OF ξ VS m FOR ALUM FLOCCULATION.

in the suspension against the dimensionless product $G\theta\varphi$ is shown in Fig-24. The curves I, II, III, IV, and V in Fig-24 represent the alum of dosages of 44, 55, 66, 83 and 111 mg/gm of TiO_2, respectively. A plot of the value of K' as a function of θ for different values of m is shown in Fig-25.

3.4.2.4. Expressing the Settling Velocity v_s as a Function of the Flocculation Time θ :

The experimental results showing the fraction of solids having settling velocity greater a certain value v_s as a function of the flocculant dosage m and the flocculation time θ are presented in Table 15. The results are also shown in Fig-26, where the ordinate is the settling velocity v_s and the abcessia is the fraction of solids having settling velocity more than v_s, the parameter being the flocculation time θ .

3. 4. 3. A Study of the Sedimentation Behaviour of the Flocculated TiO_2 Suspensions, Using a Mixture of Alum and Super Floc-330 as the Flocculant:

The variable in this study was the dosage of Super Floc while other parameters were maintained constant. The dosage of alum was maintained at 33 mg/gm of TiO_2, while the amount of Super Floc was varied. After adding a mixture of alum and Super Floc, the pH of the medium was adjusted to 6.5. Flocculation process was carried on for a period of 15 minutes, while the stirring rate was maintained constant at 80 rpm . The flocculated suspensions were then allowed to settle for a period of 5 minutes. The amount of solids collected in the sediment and that remaining in the suspensions were determined. Experimental results are presented in Table-16. The fraction of solid having settling velocity more than v_s shown as a function of the Super Floc dosage in Fig-27.

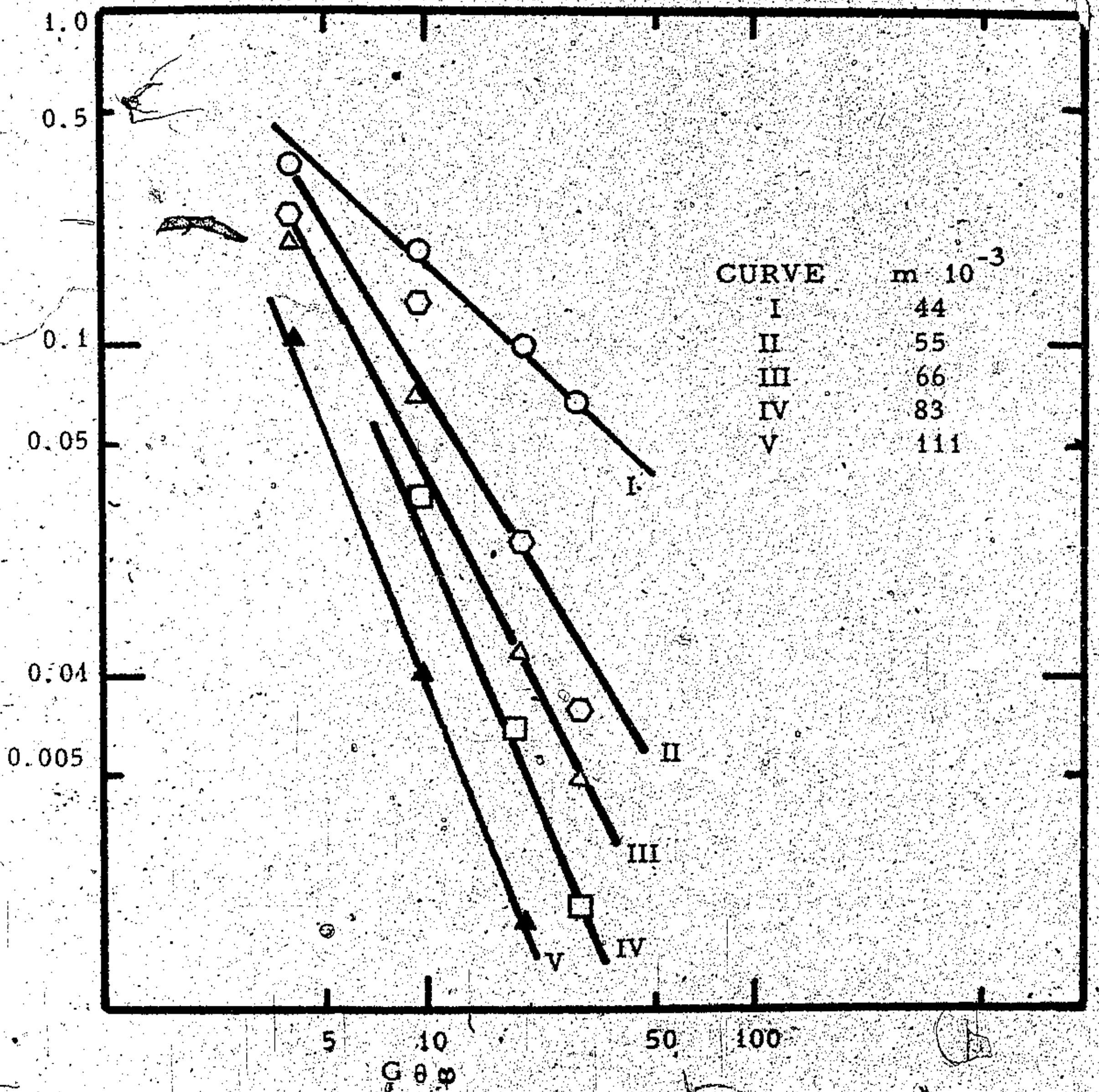


FIG-24. A PLOT OF ξ VS G θ φ FOR ALUM FLOCCULATION m AS THE PARAMETER.

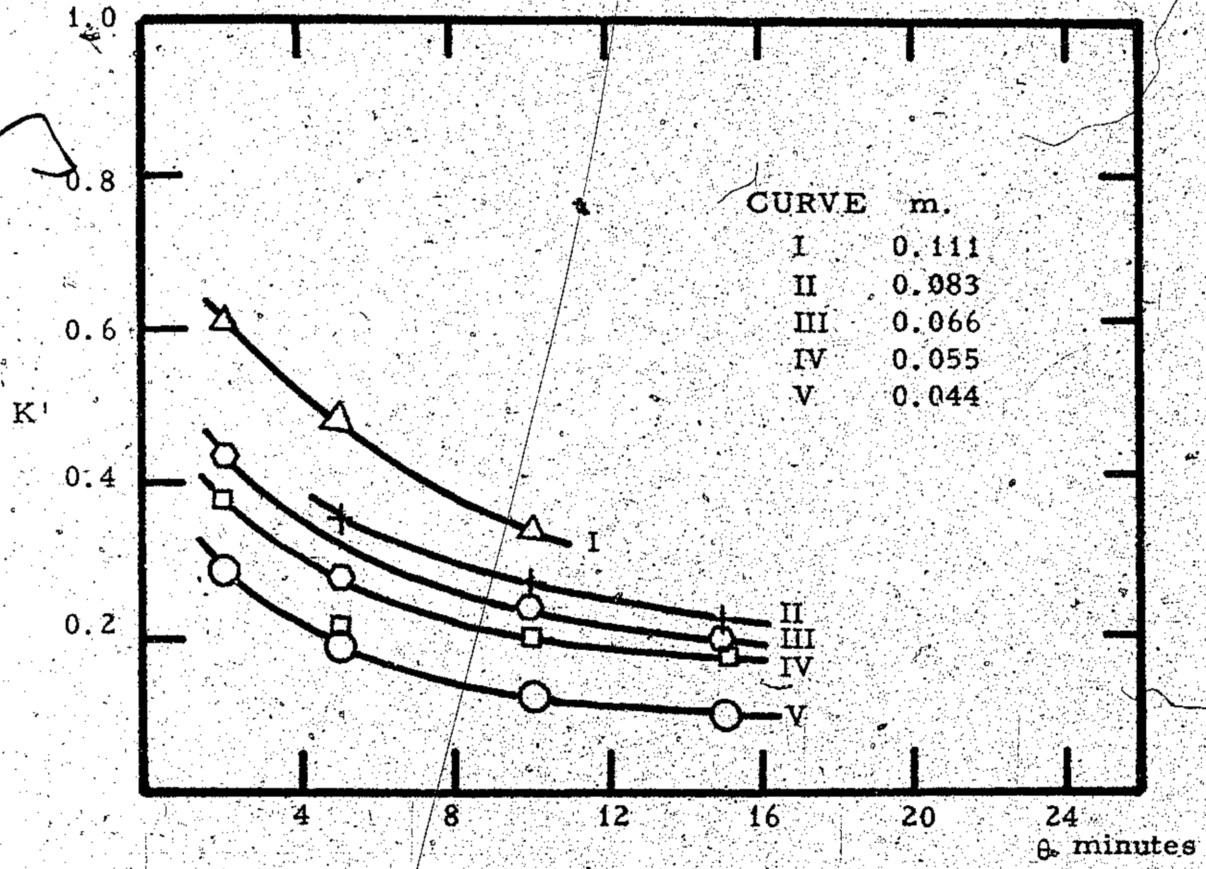


FIG. 25: A PLOT OF K' VS θ, m AS THE PARAMETER.

CONCENTRATION OF TiO_2 - 900 ppm
STIRRING RATE - 80 rpm.
pH - 6.5

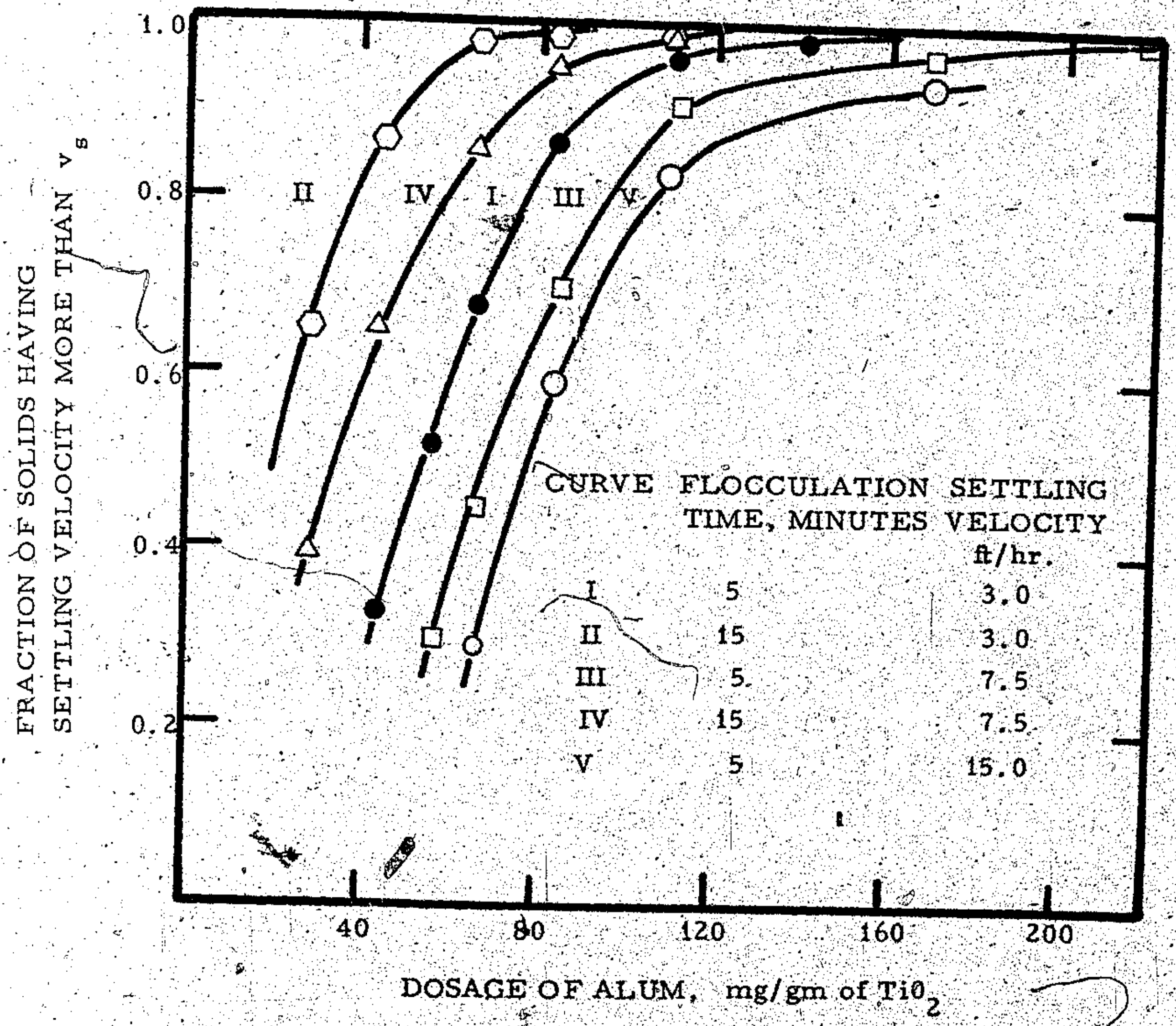


FIGURE-26: A RELATION BETWEEN THE FLOCCULATION TIME, ALUM DOSAGE, AND THE FRACTION OF SOLIDS HAVING SETTLING VELOCITY MORE THAN v_s.

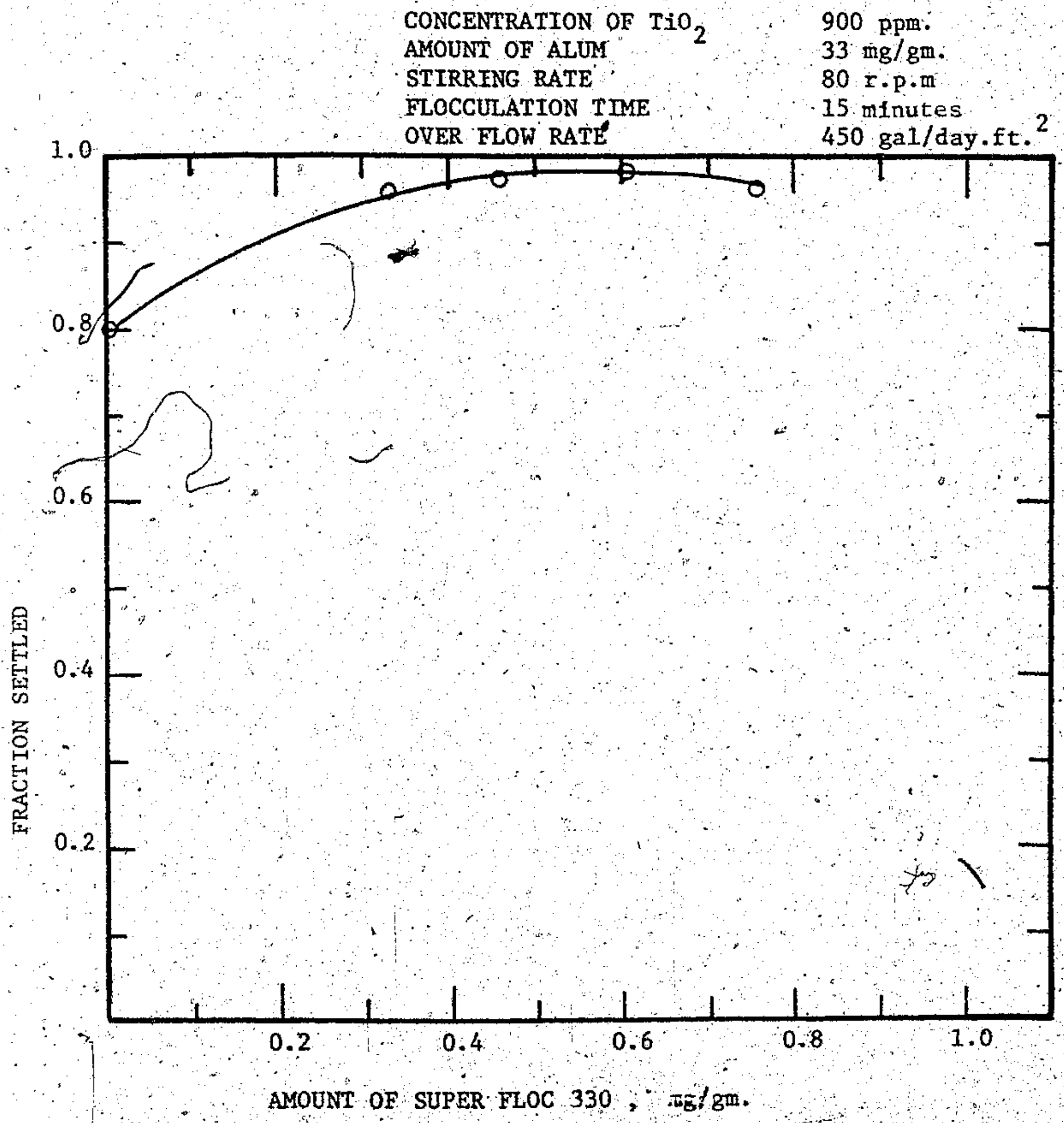


FIGURE 27 : FRACTION OF SOLID REMOVED AS A FUNCTION OF THE DOSE OF SUPER FLOC, FOR THE TREATMENT WITH THE MIXTURE OF ALUM AND SUPER FLOC.

3.4.4. A Study on the Flocculation of Clay Suspensions, Using Alum and Super Floc-330 as the Flocculants.

Clay suspensions were flocculated using various amounts of alum and Super Floc. Flocculation time (θ), the stirring rate (n) and the concentration of the suspension (φ) were maintained constant in this series of experiment. In the case of alum flocculation, the pH value of the medium was adjusted to 6.5 by adding few drops of 1N NaOH solution. Samples were flocculated for a period of 3 minutes and allowed to settle for a period of 2 minutes. Experimental results are presented in Table-17. In the case of polymer flocculation, the value of θ was maintained constant at 5 minutes and the settling time of 2 minutes. Experimental results are presented in Table-18. The fraction of solids removed from the flocculated suspensions are plotted as a function of the flocculant dosages in Figure 28. The curves I and II in Figure 28 are for alum and Super Floc respectively.

3.4.5. A Study on the Flocculation of Paper Fines Using Alum and Super Floc as the Flocculant:

Freshly dispersed suspensions containing 900 ppm of paper fines were flocculated using various amount of alum and Super Flock for a period of 3 minutes the stirring rate was maintained constant at 80 rpm. The flocculated suspensions were flocculated for a period of 2 minutes. The amount of solids settled and that remaining in the suspensions were determined. In the case of alum flocculation, the pH of the medium was adjusted pH to 6.5. Experimental results for the treatment with alum and Super Floc are presented in Table-19.

CONCENTRATION OF CLAY	900 ppm
STIRRING RATE	80 r.p.m.
FLOCCULATION TIME	5 minutes
OVER FLOW RATE	1073 gal/day.ft^2

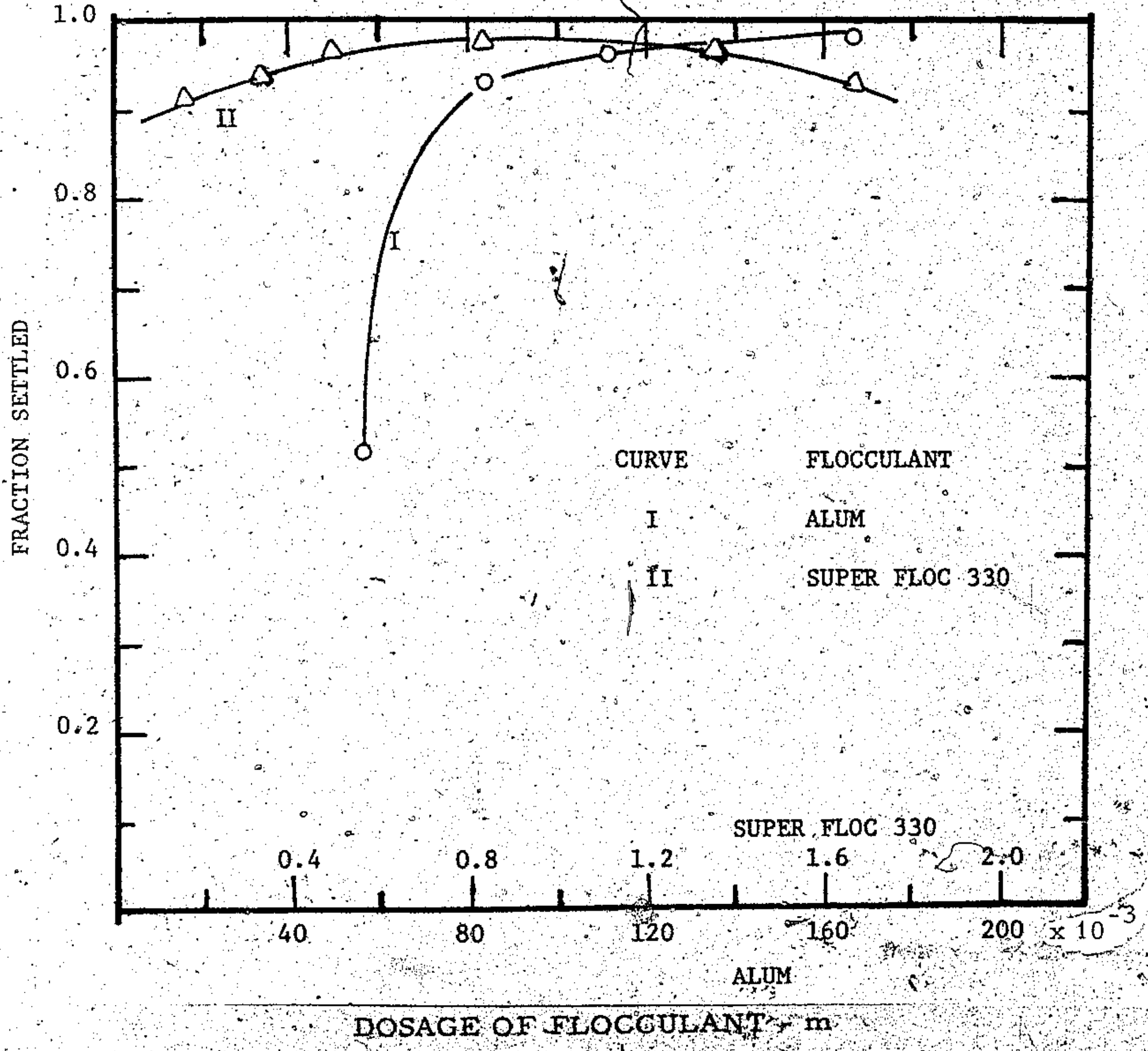


FIGURE 28 : FRACTION OF SOLID REMOVED FROM THE CLAY SUSPENSION AS A FUNCTION OF THE FLOCCULANT DOSAGE.

3.4.6. Experiments on the Treatment of the Effluent Stream of a Paper Mill :

Fresh samples of the mill waste were flocculated using:

i) alum (pH was adjusted to 6.5)
ii) Super Floc
and, iii) a mixture of alum and Super Floc.

The variable in this study was the dosages of the flocculants. The stirring rate (n) was maintained at 80 rpm and the flocculation time θ at 3 minutes. The flocculated suspensions were allowed to settle for a period of 2 minutes and the amount of sediment collected were determined. Experimental results for the treatment with alum, and Super Floc are presented in Table-20. The fraction of solid removed is plotted against the dosages of the flocculant in Fig-29. The curves I and II in Fig-29 represent the results for alum and Super Floc treatments, respectively. The Biological Oxygen Demand of the Effluent stream was determined before and after the alum treatment using a standard procedure. A reduction from its initial level of 80 ppm to 10 ppm was obtained .

3.4.7. A Study of the Sedimentation Behaviour of Untreated TiO_2 Suspensions:

This study was undertaken to obtain informations about the stability of the colloid suspension. Suspensions of TiO_2 were prepared using a procedure stated earlier. The media were : deionized, distilled and tap water. Tap water was used because

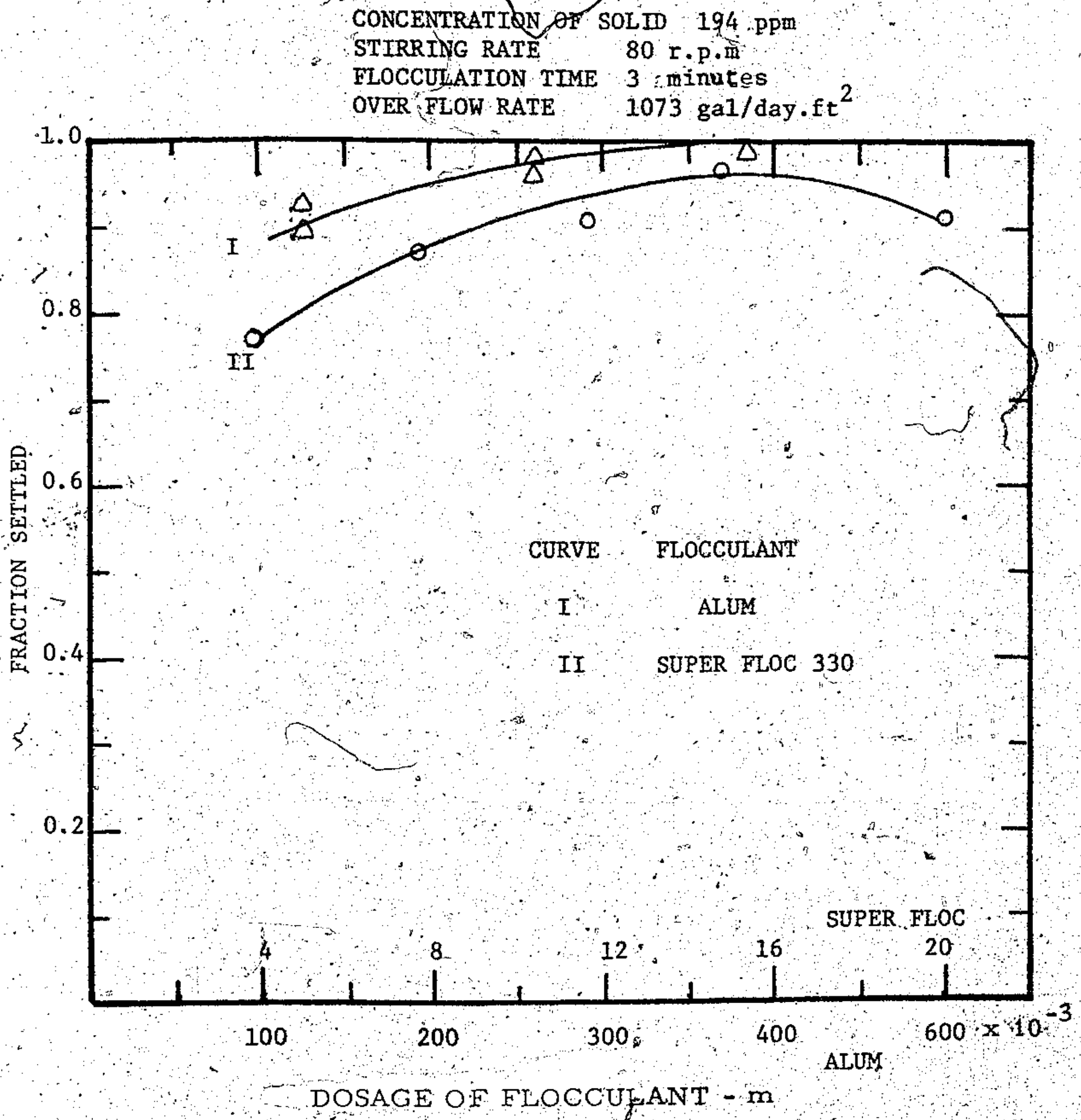


FIGURE 29: FRACTION OF SOLID REMOVED FROM THE PAPER MILL WASTE AS A FUNCTION OF THE FLOCCULANT DOSAGE

actual industrial waste will be closer to it. Sedimentation characteristics of each of these suspensions were determined, and compared with each other.

The effluent stream of a paper mill contains about 1 ppm anionic poly-electrolyte of the poly-acryloamide class. This is used as the retention agent in the paper making process. A study was conducted in order to determine whether the stability of TiO_2 suspension was affected by its addition.

1 millilitre of solution containing 400 mg/litre of poly-acryloamide was added to 400 ml of freshly dispersed suspension of TiO_2 in tap water, and was stirred vigorously for a period of 15 minutes. The sedimentation characteristics were then determined.

Experimental results are presented in Table-21. The sedimentation characteristics of TiO_2 suspensions in different media are presented in Figure-30. The curves I, II, and III in Figure-30 are for the dispersion medium of de-ionized, distilled and the tap water containing 1.5 ppm of poly-acryloamide in solution.

3.4.8. A Study on the Effect of Addition of Starch on the Coagulating Behaviour of TiO_2 Colloid :

One gram of starch was slowly added to a beaker of water while agitating continuously. The suspension was then boiled till the starch solution was made and was diluted to one litre. Starch solution so made was added to a suspension of TiO_2 such that the final suspension contains about 3% starch of the total amount of

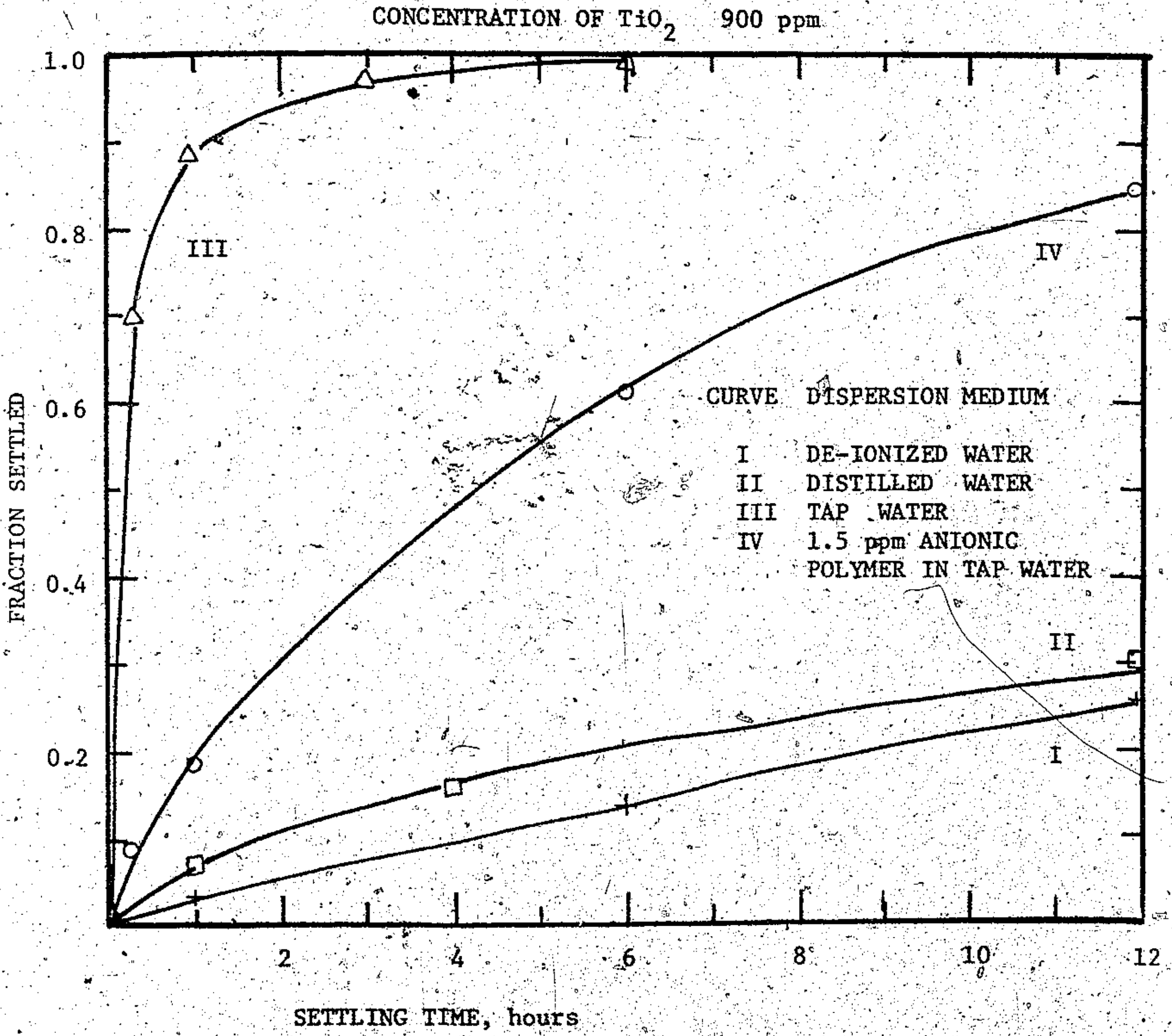


FIGURE-30: SEDIMENTATION CHARACTERISTICS OF FRESHLY DISPERSED TiO_2 SUSPENSION FOR DIFFERENT DISPERSION MEDIUM suspended TiO_2. A suspension containing 900 ppm of TiO_2 as suspended solids and 27 ppm of starch was blended several times using high speed blender. Well dispersed suspensions were flocculated for a period of 15 minutes at a stirring rate of 80 rpm using various amount of alum and Super Floc. The flocculated suspensions were allowed to settle for a period of one hour. The results are presented in Table-22.

3.4.9. Experiments on Electrolytic Process.

3.4.9.1. A Visual Study of the Effect of Passing an Electric Current (D.C) Through a Suspension of TiO_2 :

Cell A was completely filled up with a freshly dispersed suspension containing 900 ppm of TiO_2 and a D.C potential was applied across a pair of stainless steel electrodes immersed in the suspension. A visual observation was made by shining light across the transparent window of the cell. The electric potential was varied between 5 to 100 volts. The electric current was allowed to pass through the suspension for a period of 15 minutes. The current was measured with the help of an ammeter. In order to obtain a quantitative information about the particle growth, the clearer suspension was decanted carefully, leaving the settled solids behind. The amount of solids present in the decanted sample was determined. A mass balance was made by determining the amount of solids left behind in the cell. The walls of cell and the surface of electrodes were washed thoroughly to remove any adhered particle, and added to the solids left behind in the cell. These experiments represent electrolytic treatment without any mechanically induced velocity gradient.

On application of a d.c. potential between a pair of electrodes immersed in a suspension of TiO_2 the following developments were observed.

i) The particles moved towards the anode and a fraction of it adhered to it.

ii) Immediately following the cathode, a layer completely depleted of the solid formed. The thickness of the depleted layer increased till it reached a maximum size.

iii) In the space between the electrodes, particle agglomeration took place, which was followed by a gradual sedimentation of the agglomerates formed. The time required for the formation of the visible depleted layer varied from a few seconds to several minutes depending on the concentration of the suspension and the value of the applied potential. The time required to form the depleted layer increased as the concentration of the suspension was lowered. By lowering the applied potential similar results were obtained. A noticeable settling of the suspended particles occurred at an applied voltage gradient of 5 volts/cm, with a corresponding current density of 50 micro amperes/sq. cm. The rate of settling increased with the increase in applied field till 50 volts/cm, and then started decreasing.

Experimental results showing the fraction of solids settled as a function of the applied potential are presented in Table-23.

3.4.9.2. A Study on the Kinetics of Particle Growth Induced by the Passage of the Electric Current (D.C) Through the Colloidal Suspensions :

These experiments were conducted in order to obtain a quantitative information about the kinetics of particle growth induced by the passage of an electric current. These particles are subjected to a mechanically induced velocity gradient in addition to that due to the passage of an electric current. In order to maintain an uniform effect, the stirring rate was maintained at the same level throughout. This was done by maintaining the control knob of the magnetic stirrer, always at a fixed position.

The cell was placed in a 600 ml beaker and a magnetic stirrer was placed underneath. 400 ml. of a freshly dispersed suspension of TiO_2 having a concentration of 866 ppm was poured into the beaker. An electrical potential was applied across a pair of electrodes immersed in the suspension. The current was allowed to pass through the suspension for a definite period of time, after which the coagulated suspension was poured into a clean beaker. Particles adhering to the electrode surfaces and the cell walls were washed and added to the coagulated suspension. The sedimentation characteristics were determined using the method mentioned earlier.

Suspensions were treated electrolytically for different periods of time maintaining the applied potential constant. Experiments were conducted using the potential difference of 20, 100 and 150 volts.

A series of experiments was conducted using suspensions having a concentration of 173 ppm.

Experimental results are presented in Table-24 and 25. The sedimentation characteristics of the electrolytically treated suspensions are shown in Fig-31. The curves I and II are for the applied potential difference of 100 volts for the treatment time of 30 and 90 minutes, respectively. The curves III and IV represent similarly for 20 volts. The curves V and VI are for the potential difference of 150 volts, but the duration of treatment were 10 and 30 minutes, respectively, instead. The curve VII in the figure represent the suspension in which 50 ppm of alum was added prior to the electrolytic treatment. The concentration of suspension considered in this study was 866 ppm of TiO_2.

Experimental results showing the effect of allowing current to pass for a longer period of time, are presented in Table-25. The concentration of the suspension was 173 ppm of TiO_2. The weight fraction of the solids settled in an hour, is plotted as a function of the duration of electric treatment, in Figure 32.

3.4.9.3 The Effect of Adding an Electrolyte in the Suspension Before an Electrolytic Treatment :

One ml of a solution containing 20 mg of alum was added to 400 ml of a suspension containing 866 ppm of TiO_2. The suspension was treated at 100 volts for a period of 30 minutes, after which the sedimentation characteristic was obtained.

Similar experiments were conducted using other electrolytes such as HCl and NaOH. Before an electrolytic treatment, the pH of the solution was adjusted to a value of 3 and 12, respectively.

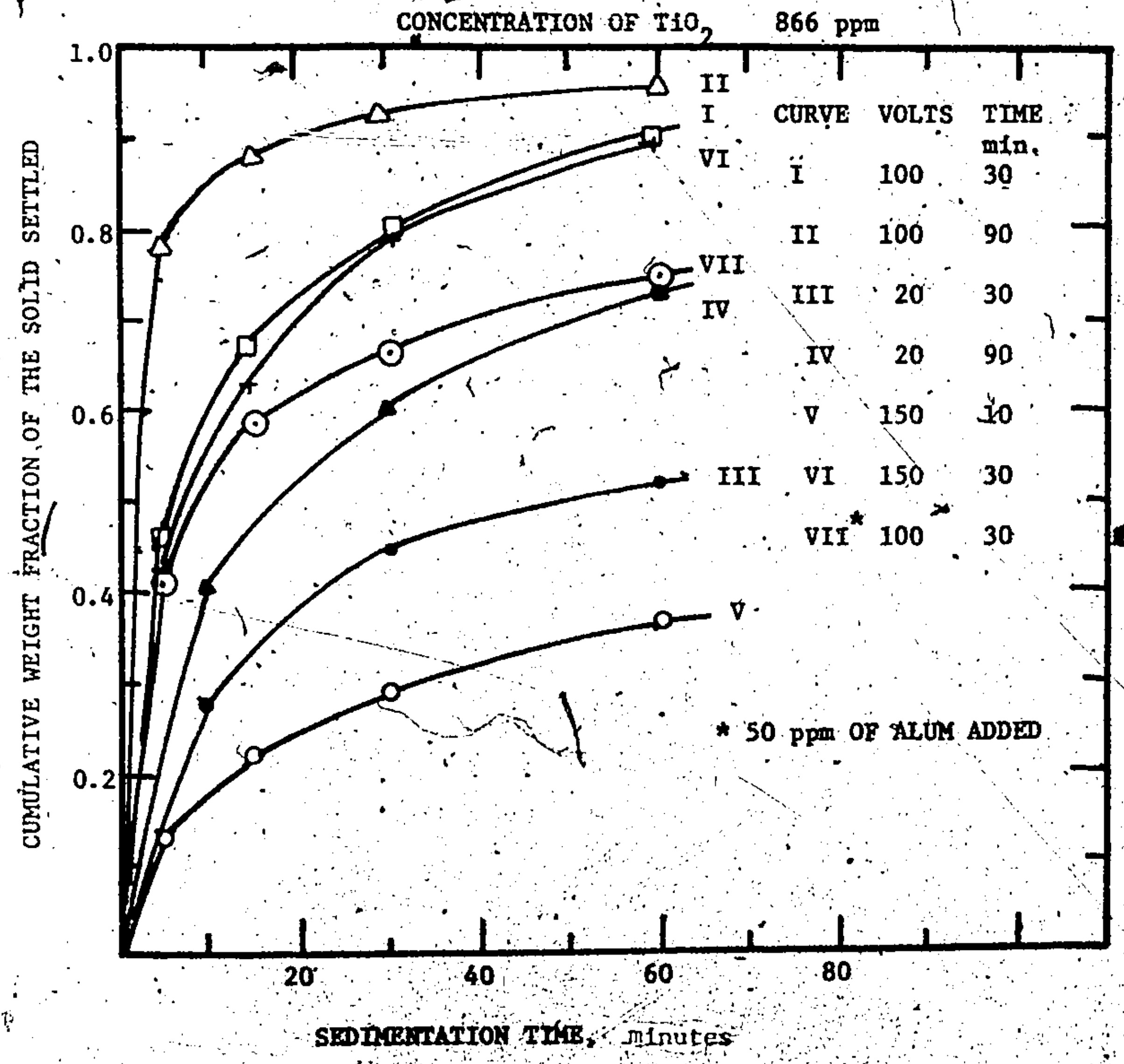


FIGURE- 31 : SEDIMENTATION CHARACTERISTICS OF THE ELECTROLYTICALLY TREATED TiO_2 SUSPENSIONS

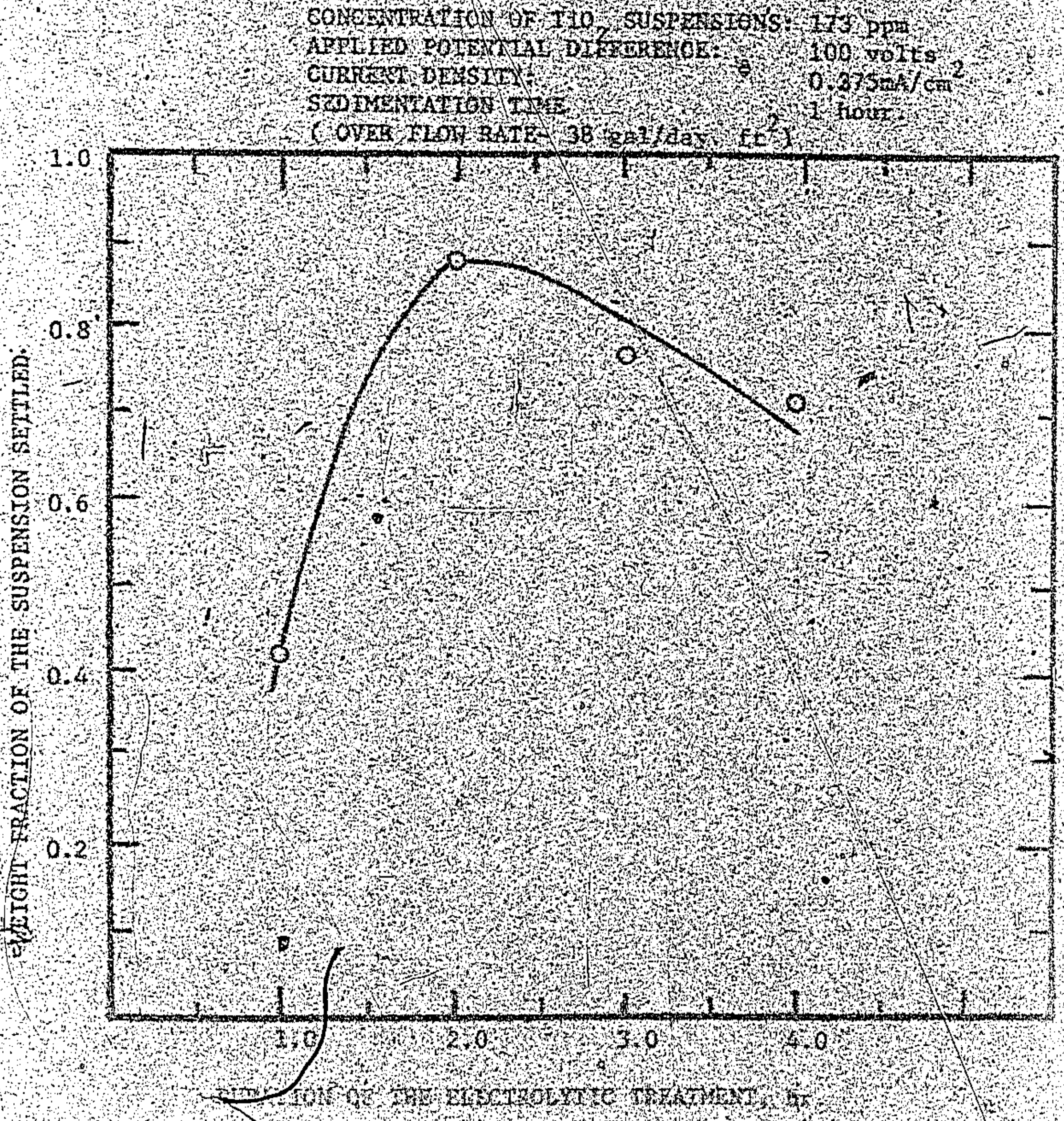


FIGURE 32 : FRACTION OF SOLID REMOVED AS A FUNCTION OF THE DURATION OF ELECTROLYTIC TREATMENT.

In both these cases, a faster rate of the particle agglomeration took place during the electrolytic treatment. The agglomerates were however of light yellow and brown colors, respectively. The reason was due to the dissolution of anodic material. A current density of 1-2 orders of magnitude higher was observed. This resulted also in the heating of the suspension.

4. DISCUSSION

4.1. Discussion on the Experimental Results:

4.1.1. Flocculation of Titanium dioxide suspension

The results of flocculation of titanium dioxide suspension show that the fraction of solids remaining in the suspension after flocculation could be expressed as a function of $G\,\theta\,\varphi$. A linear relationship between $\ln\,\xi$ and $\ln\,G\,\theta\,\varphi$ is obtained for both polymer (Figure 16) and alum flocculation (Figure 23). However, such a relationship is in contrary to that given by Smolochowsky's expression which predicts a linear relationship between $\ln\,\xi$ and $G\,\theta\,\varphi$. The measured value of the flocculation constant K' according to Equation 10 show that it is neither independent of θ nor G. The value of K' decreases with increasing θ. This is shown in Figure 17 for polymer flocculation and in Figure 24 for alum flocculation. An initial increase in the value of K' with θ as shown in Fig-17 might represent an improper mixing of the flocculant with the colloid.

The value of the flocculation constant K' is found to decrease with increasing G as in Figure 18. However, this is expected from the theory of flocculation. According to Lamer and Heally, the process of flocculation is associated with continuous formation and redispersion of the flocs formed. Redispersion is due to the breaking up of the floc aggregates by continuous shear. The flocculation state is a metastable equilibrium state which is determined by the mechanical strength of the flocs formed and the shear rate to which the flocs are subjected. It has been mentioned that at a particular shear rate, the flocs could disappear and the process of redispersion overwhelms the process of flocculation. A continuous decrease in the value of G is an indication of such process. A complete disappearance of the flocs will be indicated if K' approaches zero. In the experimental range of G this was, however, not realized.

The value of K' is a function of the attachment coefficient β. The values of β have been measured by Akhira[33] during the growth of the particles using coulter counter and it indicates that with time the value of attachment coefficient β increases attaining a maximum value and finally starts decreasing. The value of K' at the beginning of flocculation shows a similar trend. For any particular value of $G\theta\varphi$ the fraction of solids remaining in the suspension (ξ) depends on the dosage value m. In the case of polymer flocculation there is an optimum dosage requirement. In the case of alum flocculation, however, the value of $G\theta\varphi$ for any value of ξ decrease steadily with increasing value of m in the region investigated in this study. Comparing the value of $G\theta\varphi$ for alum flocculation (Figure-23) with that of polymer flocculation (Figure-16) one could say that with alum it is possible to flocculate titanium dioxide suspension much faster than with Super Floc.

In the case of alum flocculation it is necessary to adjust the pH of the medium close to neutral value of 7.0. This is necessary not only to reduce the amount of alum required, but also to make the flocculation process faster. A comparison of the result in Figure-19 for alum flocculation without adjusting the pH of the medium with that in Figure 20 and 21 for alum flocculation while the pH is adjusted, shows that the rate flocculation increases several times, if the pH is adjusted.

The mechanism of alum flocculation has been well discussed in the literature [47,48]. It has been revealed that the pH of the medium plays a vital role in the flocculation with alum. In the region of pH 5-8, $Al(OH)_3$ precipitates out from the solution. Depending on the pH value of the medium different polymerization product of aluminium hydroxide forms thus behaving themselves like an inorganic polyelectrolyte. The concentration of alum the concentration of colloid, and the pH value, all play important roles. Both in the case of polymer and alum flocculation cross-linking results in the formation of three dimension floc structure which settles very easily. It is possible to reduce the amount of flocculant by using a mixture of alum and polymer. This is revealed in Figure-25.

The fraction of solids to be removed from the suspension determines the value of $G \theta \varphi$ which is also a function of m. The floc size distribution in a flocculated suspension which determines the size of the sedimentation unit depend on the value of θ. Hence, θ, m and τ_s are inter-dependent term and should be evaluated from the cost considerations only. This has been discussed in section 4.2.

4.1.2. Treatment of Paper Mill Effluent Stream.

In order to evaluate the problem of separation of suspended solids from a much complicated system like that of effluent stream of a paper mill, experiments with individual components such as titanium dioxide, clay paper fines, were conducted. A comparison of the dosage-requirement for different systems are presented in Table 26. The dosage requirements vary a great deal. It is to be noted that the ratio of alum to Super Floc needed are almost the same in all cases. The reason for the difference in the dosage requirements for different constituents could be due to different particle size involved. The dosage requirement is proportional to the surface area concentration instead of volume concentrations. $Ti0_2$ particles are the finest, while clay is finer than the paper fines.. The value of m are in the same decreasing order from $Ti0_2$ to paper fines.

It is to be noted from Table-26, that the amount of flocculant required for the treatment of mill waste is considerably higher than that required on the basis of individual constituents. The amount of alum required for the treatment of mill waste is at least 4 times and in the case of polymer, it is 20 times greater than that required on the basis of individual ingredients. A comparison of the value of $G \theta \varphi$ show that the rate of flocculation of the paper mill waste is considerably higher than that of individual ingredients. The effluent stream could be flocculated very easily, using alum as the flocculant. The amount of alum required depends on the degree of separation desired.

In the case of mill waste, because of the presence of large amount of hydrophyllic colloids such as starch, resin, color complexes, the dosage requirements are expected to be large. Those hydrophyllic colloids normally coat the surface of other inorganic materials present, which are hydrophobic in nature, thus providing them with the property of the mixed colloid. Besides, there are anionic polyelectrolyte present in the mill waste, which are added in the paper making process as the retention aid. It is shown in Figure-29, how the stability of the $Ti0_2$ colloid could be increased by using this type of polyelectrolyte.

In Table-22, the effect of starch on the flocculating behaviour of TiO_2 colloid using alum and Super-Floc as the flocculants, is shown. In the case of alum flocculation it is revealed that an addition of 3% starch of the total amount of solids present, increases the amount of alum requirement by an order of magnitude. For similar case, no appreciable flocculation was observed using even a flocculant of dosage of 50 times than that required if only titania is present. It shows that the amount of excess flocculant needed for the flocculation of mill waste is due to the presence of starch. It is also possible that the presence of anionic polyelectrolyte affects the flocculant requirement.

4.1.3. Electrolytic Process :

The results on electrolytic process as presented in Table-23 indicate that the rate of particle growth increases initially with an increase in the applied potential and finally starts decreasing. Similar results are also revealed in Table-25, where the suspensions are kept well stirred during the treatment and the distance of separation between the electrodes are twice than in the former case. It appears that the controlling parameter is the applied field.

Sedimentation characteristics of the agglomerated suspension as shown in Figure-31 reveal a gradual charge of slope indicating a relatively even distribution of particle sizes over the entire range. The characteristics differ distinctly from the chemically flocculated suspension, where due to the floc aggregation flocs of completely different character forms which settle much faster than in this case. Addition of an electrolyte such as alum increases the energy consumption by an order of magnitude while not improving the settlability.

4.2. Cost Estimates:

The experimental results established the relation between the individual process parameters of the separation process. However, the selection of these parameters should be made only on the basis of economics. So, in this section, an attempt has been made to evaluate the cost items of the process. The estimates of cost presented here are made on the basis of Equation 20. In order to estimate the cost it is necessary to obtain the unit cost factors and establish an engineering design basis of the separation plant. The estimates are made for the treatment of one million gallons per day on the basis of the values of unit cost factors given below:

Unit cost factors

i) unit cost of chemicals (a) = 2.25 ¢ /lb of alum
and, $1.5/lb of Super Floc-330

(based on the supplier's catalogue price) of 1972.

The cost factors c_2 and c_3 are calculated on the basis of cost data presented in the 'cost of Water Treatment' by DiGregorio[48]. The values of c_2 and c_3 depend on the size of the units, and they decrease with the increase in size. The value of c_3 for a capacity of 100,000 gallons is approximately $0.8/gallon. This cost includes the cost of equipment, cost of concrete and the cost of mechanical device needed for the removal of sludge. As the cost is based on 1968 price, a realistic value of $1.0/gallon has been considered.

ii) unit cost factors of flocculator c_2 = $ 1.50 / gallon

iii) unit cost factors of sedimentation tank c_3 = $ 1.0 gallon.

The value of c_2 is usually 50% more than that of c_3 mainly because of the different size element involved.

iv) capital depreciation factor y :

The amortization rate has been considered at the rate of 10% per year. In the cost estimates of water treatment presented by Koenig, Louise a capital amortization rate of 7.8% has been assumed for a similar process. However, this value was based on a comparatively lower rate of interest 5% existing in 1966. The value of 10% may be more realistic. The retention time of the flocculator could be estimated from the relation between ξ and $G\theta\varphi$ as established earlier.

In calculating the retention time of the sedimentation unit, it is necessary to assume a value for its height. The height of the sedimentation tank is determined mainly from the mechanical considerations. It varies between 7 to 15 feet. In this study a minimum value of 7 feet has been considered. Besides, in calculating the actual retention time of settler, it is necessary to evaluate the efficiency factor. The data obtained from jar test experiment is that of quiscent settling condition and the performance of actual settler never approaches that of an ideal settler. The efficiency factor is a function of the solid removal desired. The first limit is set by the design parameters of the flocculater and the second limit is set by the diviation from the performance of an ideal settler. In actual settler there are movements of the particles due to horizontal flow and also due to the scouring of the bed. A relation between the efficiency factor and the fractional solid removal desired has been presented by Camp[52]. For a solid removal of 75%, it is necessary to assume a multiplication factor of 1.8, while for 95% solid removal the value is five.

4.2.1. Cost Estimates for the Separation of TiO_2

The cost estimates for the treatment of titanium dioxide suspension having a concentration of 900 ppm using the values of cost factors mentioned earlier, are presented below.

The estimates are prepared for alum and Super Floc treatments using the experimental data on τ_F, τ_S and m for the separating efficiency of 0.75 and 0.95. The results are presented in Table-28, 29, respectively. The results of the cost estimates for alum treatment as a function of the overflow rate for a separating efficiency of 0.95 and a solid removal of 90% are shown in Figure-33. The curves I, III, V of Figure-33 represent the cost of chemicals, the capital depreciation and the total cost, respectively, assuming a flocculation time of 5 minutes. The curves II, IV and VI represent similarly for τ_F of 15 minutes. Similar results for the treatment with Super Floc are shown in Figure-34.

It is indicated in Figure-33 and in Table-28 that by increasing the amount spent on chemical, the total cost of separation could be decreased because of a faster decrease in the cost of capital. By increasing the flocculation time from 5 minutes to 15 minutes, a substantial reduction in the cost of chemicals could be achieved without resulting in an increase in the capital cost appreciably, thereby decreasing the total cost of treatment. In the case of Super Floc treatment, the optimum design conditions are very critical because of a critical dosage requirement.

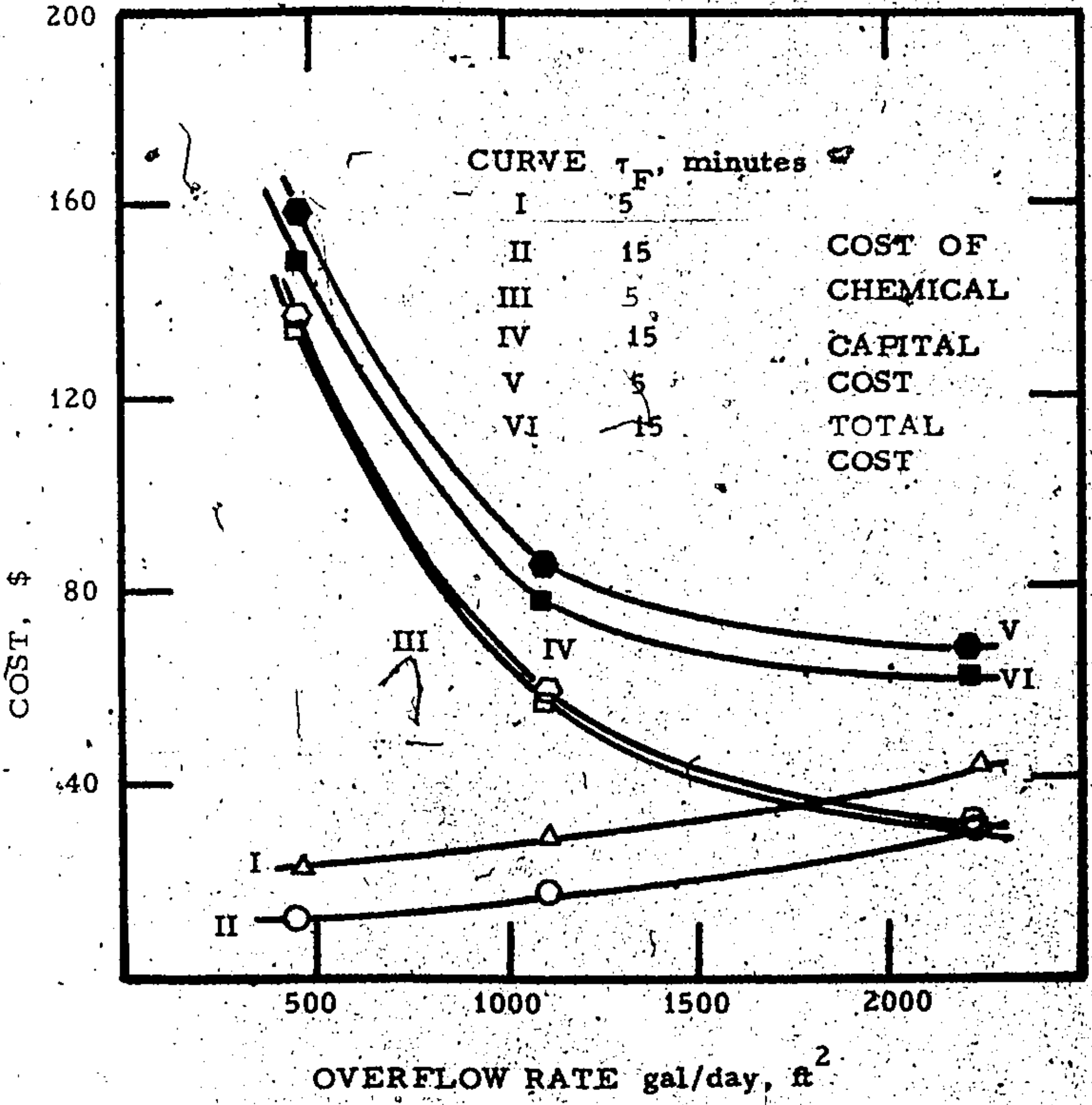


FIGURE-33: COST ESTIMATES FOR ALUM TREATMENT OF TiO_2 SUSPENSION AS A FUNCTION OF THE OVERFLOW RATE FOR 90% SOLID REMOVAL.

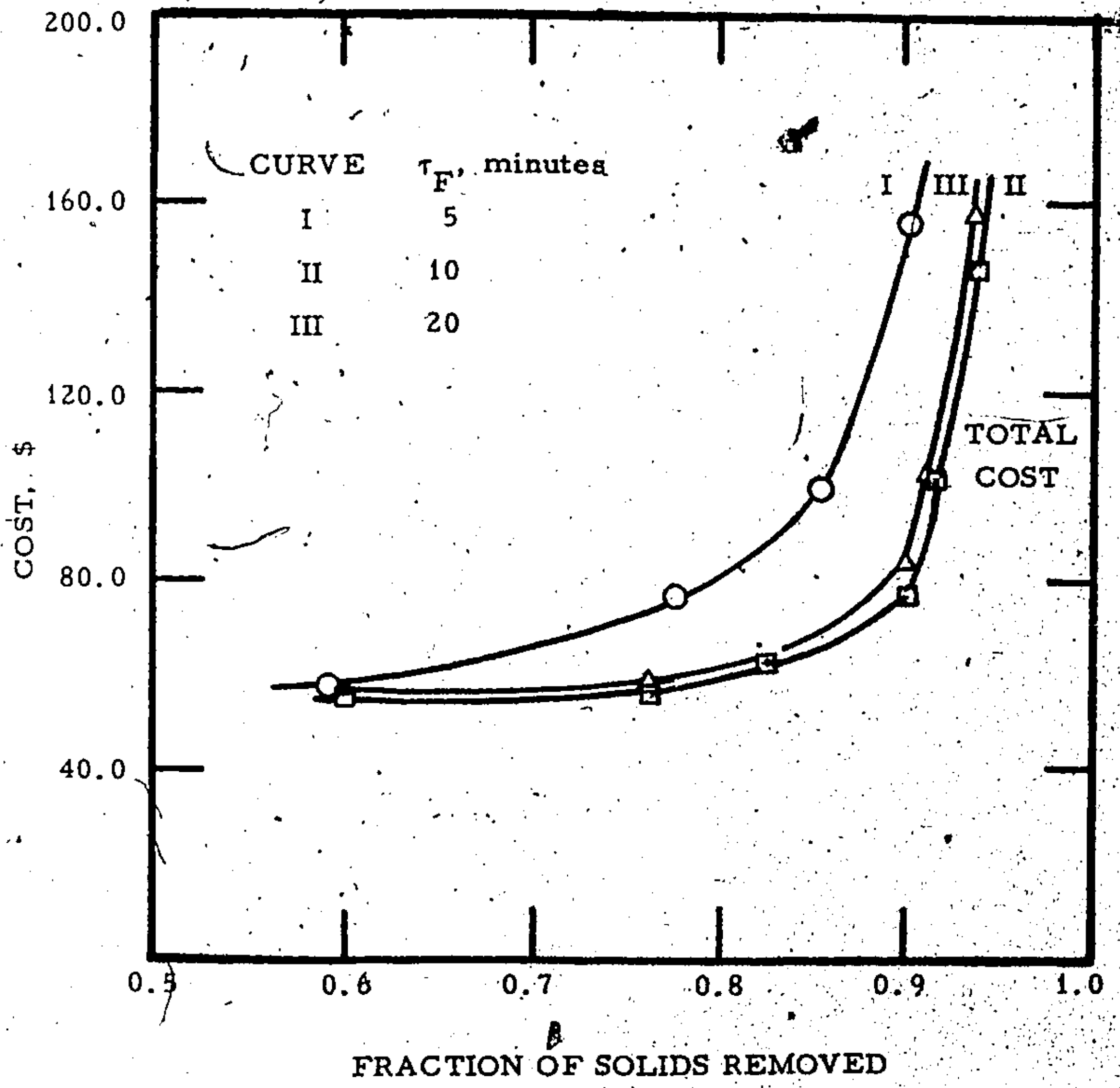


FIG-34: COST ESTIMATES FOR THE TREATMENT WITH SUPER FLOC AS A FUNCTION OF THE FRACTION OF SOLIDS REMOVED.

Cost estimates presented in this study show that the cost of chemicals and the cost of sedimentation units are two major cost items of the separation processes. The cost of flocculation unit is relatively of less importance because of the smaller ratio of τ_F / τ_S (the ratio of sedimentation to flocculation rate), for the two flocculants considered in this study. The chemical cost and the cost of sedimentation unit contribute almost equally to the total cost. However, these break-down percentages will depend on the nature of the chemicals used, and the concentration of the suspension to be treated, and the fraction of solids to be removed.

The chemical cost is proportional to the surface area concentration of the suspended solid and depends on the charge neutralization ability of the chemicals. The cost of sedimentation unit, on the other hand, is inversely proportional to the square of the final agglomerate size attained after the flocculation. It has been suggested in the literature [28], that the mechanical strength of the agglomerates formed plays a major role in determining the maximum floc size attained. By increasing the flocculation time indefinitely it is not possible to increase the floc size as redispersion limits the floc growth. A high value of G is necessary to decrease the flocculation time, but it sets a limit to the maximum floc size attained, because of the breaking down of the aggregates. The mechanical strength of the floc aggregates is determined by the nature of bonding between the flocculant and the particle.

The chemical cost decreases with the decrease in the concentration of the suspension, while the cost of sedimentation unit remains unaffected within relatively wider range of concentration. It might be necessary to increase the retention time of the flocculation unit, but it would have very little influence on the total cost. The cost of flocculator becomes appreciable only when the concentration of the suspended solid is below 100 ppm to start with.

A Mixture of Alum and Super Floc Reduces the Cost of Treatment.

The comparative figures on chemical cost for the treatments with alum, Super Floc and a mixture of both, are presented in Table-30. It is indicated in the table, that by using a mixture of alum and Super Floc, the cost of chemical could be reduced by 16.5% over that of alum treatment. The capital cost requirements are not affected appreciably.

4.2.2. Cost Estimates For The Tre[illegible]ment of Paper Mill Effluent Stream :

Cost estimates for the treatment of paper mill effluent stream using alum and Super Floc as the flocculants are presented in Table-31. The estimated cost is on the basis of one million gallons of waste water having a suspended solid concentration of 200 ppm. The cost of treatment (the sum of the chemical and capital depreciation cost) is plotted in Figure-35, as a function of the fraction of solid removed. The curves I and II represent the cost of treatment with alum and Super Floc, respectively.

The cost of alum treatment, as indicated in Figure-35, is considerably lower than that of alum treatment. It is possible to remove 75% of the suspended solid by alum treatment at a cost of $44/mgd., as compared to $78 in the case of Super Floc for a similar performance. Considering an initial concentration of 200 ppm, a 75% solid removal would reduce the concentration

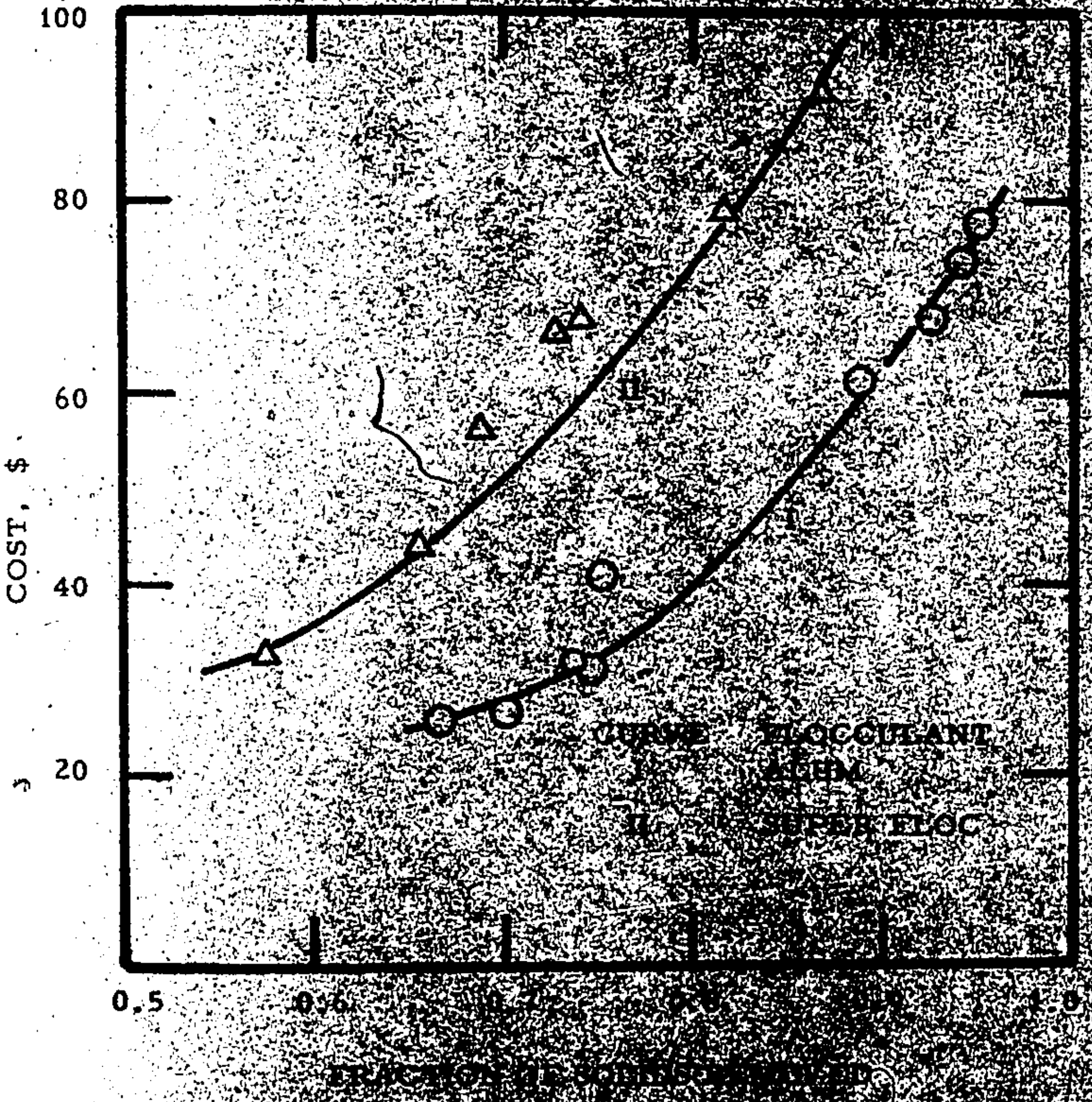

100
80
60
40
20
COST, $
0.5
0.6
0.7
0.8
1.0
FRACTION OF SOLIDS REMOVED
I
II
CURVE FLOCCULANT
I ALUM
II SUPER FLOC

FIGURE 35 [illegible]

of final solution to a permissible value of 50 ppm. Considering other expenses such as plant maintenance, over-heads, land sites and building cost as 40% of the total cost, the cost of alum treatment could be $70, approximately. It is possible to remove 95% of the total solids at a cost around $ 100/mgd.

It may be noted that the estimates are strictly true for the particular mill effluent, considered in this investigation. With an increase in the hydrophyllic character of the effluent stream, depending on the amount of different hydrophyllic type colloids present, the amount of chemicals needed might differ widely.

Above estimates are based on the result obtained in the jar test. The jar test results have been successfully used in scale-up to industrial size. This is particularly true when the value of G is low. Failure of the use of jar test result for scale-up has been discussed by Agraman,[47] in the case of high value of G. As the scaling-up is beyond the scope of this work, it is not considered. The primary objective of this cost estimate is to present the relative magnitude of the cost items and to obtain an idea as to the future approach in reducing the cost of pollution abatement.

4.2.3. Cost Estimates for the Electrolytic Process:

The operational cost items of the electrolytic process are the cost of electricity, the cost of electrode replacement and other maintenance cost, while the capital cost items are, the cost of electrolytic cell including electrode materials, and the cost of rectifier. The cost estimates presented by Knipe and Muller[43] show that the capital cost requirement for the treatment of one mgd may run into several millions of dollars. More over, on the basis of results obtained in this investigation, the cost of electricity alone, considering an unit cost of 1¢ / k.w.hr, would run between \$600 - \$1000 per mgd for a separating efficiency of 75 % .

4. 3. The Abatement of Pollution could be made a Profitable Proposition :

The cost of pollution abatement is the sum of the cost of treatment and the cost of sludge disposal. The sludge contains all the suspended solids present in the paper mill waste together with the flocculants used for the treatment. It amounts to one ton of dry solid per million gallons per day, on the basis of 200 ppm of suspended solids. The sludge contains more than 90% water. The disposal process normally consists of dewatering, incineration and the final disposal of incinerated materials, the cost of which should be taken into consideration. The paper fines constitute more than 50% of dry solid waste and provide an useful energy source, thus recovering a part of the cost. However, a considerable cost saving could be achieved, if the sludge and the process water are reclaimed.

A break-down of the cost of raw materials present in the waste is given below :

i)	cost of paper fines-	0.65	x	\$160	=	\$104
ii)	cost of TiO_2	0.15	x	\$450	=	\$ 68
iii)	cost of clay	0.2	x	\$ 40	=	\$ 8
	Total	1.0			=	\$180

and the cost of industrial water vary between \$50-100/million gallons, depending on the place. On the basis of these figures, the value of the waste stream is estimated to be more than \$200/million gallons. As the treatment cost works out to be less than \$100/million gallons, considerably lower than the value of the waste materials, there is a possibility of reducing the cost to such an extent that the entire process becomes profitable. Therefore, an investigation along this direction is worth considering.

4. 3. 1. Sludge Reclaim :

The sludge of the treatment process could either be recycled in the process itself, or be used elsewhere, as building material and land filler. These possibilities have been suggested in the literature. It is apparent that a maximum cost saving could be realized, if the sludge is recycled directly.

In case of the alum treatment, the sludge would not contain any chemicals that are foreign to a paper mill. The amount of alum needed for the treatment is 0.4 tons/million gallons. This value is obtained from the experimental results and calculated on the basis of 200 ppm concentration of the suspended solids in the effluent stream. In the paper making process, alum is used as a sizing agent up to 3% of the dry solid. It amounts to 1.5 tons for a 50 tons/day paper mill, with the assumption that water consumption is 20,000 gals. /ton of paper. The amount of extra alum needed for the treatment represent about 26.5% more. The sludge of the treatment plant would contain 28.5% alum of the dry solids, with the assumption that the entire amount of alum is precipitated out. In fact, an addition of the same amount of alum, i.e 1.5 tons in two stages, and recycling of the sludge formed (along with its alum content) might reduce the cost of chemicals even further, thus reducing the cost of treatment.

Experiments were conducted to evaluate this possibility of sludge recycling. Paper samples were prepared using the sludge obtained from the treatment process. The paper samples so produced, did not possess the desired mechanical property, such as the tensile strength and toughness. This was attributed to the excess amount of alum used for the treatment. By adjusting the paper pulp concentration to a right proportion, in order to compensate for the extra alum, it was possible to improve the quality. However, it is felt that a detailed evaluation of the mechanical property is necessary.

4.3.2. Problems of Sludge Recycling :

To many paper mills, the sludge of the treatment process would appear as an useless material to be disposed off at an extra cost. This is primarily because of the following reasons :

i) Many paper mills produce varieties of paper instead of a single item, requiring separate treatment plants for each of the mills.

ii) Chemicals present in the waste are used at different stages of the process instead of a mixture. This is necessary to provide a particular property to the paper. For example TiO_2 is used as the coating material to improve the whiteness of paper. And, it may be undesirable to use it as filler, as it reduces the mechanical strength of the paper.

But, considering the insignificance of the amount of sludge added to the total material used in the process, such addition might not affect the quality of the paper produced. If the sludge is not recyclable, it can be used to make cheaper grades of paper. Whatever it may be, the sludge definitely represents some value and could be used in reducing the cost of pollution abatement.

4.3.3. Water Reclaiming.:

The process water could be reused after the treatment, if it is brought back to the initial condition.

The experimental results show that it is possible to remove 100% of the suspended solid and most of the B.O.D. Besides these, water contains dissolved solids to an amount twice than that of the suspended matter. Unless they are removed there will be an increase in their value up to an equilibrium concentration. But, how far this will affect the operation, requires a further investigation.

In the case of alum treatment, it is necessary to adjust the pH of the suspension to a value around 7.0, in order to reduce the consumption of alum. The solubility of alum at that pH is negligible. The entire amount of alum added is precipitated out as hydroxides of aluminium and there will be a negligible amount of alum remaining dissolved in the treated waste stream. It is necessary to investigate, whether the treatment removes a part of the dissolved solids. Otherwise, a further treatment may be necessary, before the water is reusable.

It should be noted that, although the solubility of alum at a pH of 6.5 is negligible, it is possible for the effluent stream to contain the suspended non settlable aluminium hydroxide nuclei. Depending on the value of the over flow rate and the amount of alum used, the aluminium content will differ. Hence, it is possible that the effluent stream will contain some aluminium in the form of hydroxide .

4.4. Summary and Conclusions :

Alum flocculation appears to be more effective in the removal of suspended solids than Super Floc-330. Alum flocculates faster than Super Floc and produces flocs of higher settling rate, thus requiring less retention time of the sedimentation tank for the same value of ξ, the fraction of solids remaining in the suspension.

The logarithm of the fraction of solids remaining in the suspension (ξ) bears a linear relationship with the logarithm of the dimensionless product $G\ \theta\ \varphi$. The value of $G\ \theta\ \varphi$ required for any value of ξ is also a function of the dosage (m) of flocculant.

In the case of Super Floc there is an optimum dosage requirement giving a maximum rate of flocculation. The effect of under-dosage is more prominent than that of over dosage.

In the case of alum flocculation, no such optimum dosage requirement is observed in the range considered in this investigation. The rate of flocculation was found to increase with the dosage m.

The value of $G\ \theta\ \varphi$ required for 99% solid removal is 30 times in the case of Super Floc with the dosage of 0.0013 and varies between 10-40 for alum dosage of 0.111 - 0.055.

Although the value of m for alum is 50 times more than that of the Super Floc, because of a lower unit cost, the cost of chemical is slightly less. By using a mixture of alum and Super Floc it is possible to reduce the cost of chemicals by 16.5%.

The major cost factors of the separation process are m and τ_S. τ_F is relatively of less importance because of a low ratio of the sedimentation to the flocculation rates. The cost of chemicals and the cost of sedimentation units for the treatment of 900 ppm suspension considering 75% solids removal, represent almost equally to the total cost. Whereas, for the removal of 95% solids the capital cost requirements are twice that of the cost due to chemicals. Because of a slightly lower cost of chemical and lower capital cost requirements the cost of alum treatment works out to be less than that of Super Floc.

The value of m required for the treatment of paper mill waste is considerably higher than that required, if only the individual main ingredients are present. The value of m is 4 times higher in the case of alum treatment, whereas, in the case of Super Floc it is 20 times. The cost of alum treatment on the basis of 75% solid removal is $40.0 per million gallon per day on the basis of 200 ppm of suspended solids. The treatment also reduces the B.O.D. content to 10 ppm from its initial value around 100 ppm.

By the reutilization of the sludge either by recycling the sludge back into the paper making process or by using elsewhere the cost of pollution abatement could be substantially reduced. If alum is used as the flocculant, there is a greater recycling possibility of the sludge, as alum is one of the ingredient in the paper making process.

Electrolytic process appears to be extremely costly. Cost of electricity is almost one order of magnitude higher than the cost of chemicals. The settlability of the electrically treated suspension is poorer than that chemically flocculated suspension. Besides, it is less efficient in removing the suspended solids.

4.5. Recommendation for Future Work :

As the acceptability of any method of pollution abatement depends on its cost, any future programme should be directed towards a reduction of this cost. By reusing the sludge of the treatment process in the paper making process and by reclaiming the water, it is possible to recover a substantial portion of this cost. However, it is necessary to investigate further on its real possibilities. A further cost reduction could be attempted by reducing the amount of chemicals needed.

The experiment results reveal that the presence of starch increases the amount of flocculant needed by several times over that of a system free of any hydrophyllic type of colloid. It may be possible to reduce the amount of chemical needed by reducing the amount of starch to a level absolutely necessary. It is also necessary to understand the flocculating behavior of the mixed colloid system having starch as the hydrophyllic component. Such understanding will help us in selecting a particular type of flocculant which will be best for such a system.

The cost of sedimentation unit is one of the major cost element in the separation process, and there is a considerable scope in reducing this item. It is necessary to increase the strength of the flocs in order that they grow to bigger sizes having higher settling rates. It is necessary to investigate along these directions.

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APPENDIX-I

A LIST OF CHEMICALS USED IN THE PAPER MAKING PROCESS:

	Ingredients.	Composition %
1.	Paper pulp	65
2.	Clay	15
3.	Titanium dioxide	12
4.	Talc	3
5.	Calcium Carbonate	
6.	Starch	2
7.	Alum	3
8.	Rosin	Small amount.
9.	Na- Aluminate	Small amount.
10.	Na- Triphosphate	0.2
11.	Anionic poly-electrolyte	0.075
12.	Dyes	Small amount.

APPENDIX -II

CALCULATION OF THE SETTLING VELOCITY :-

The settling characteristics of the flocculated suspension are presented as cumulative weight fraction settled vs time. Knowing the height of the settling column it is possible to express the result in terms of the settling velocity. However, the true settling velocity will differ from it because, all the particles do not settle from the top. As they are evenly distributed throughout the suspension, the fraction of the solids collected have two parts. A fraction has a settling velocity more than v_s calculated on the basis of total height of the column and the other fraction represents the particles having settling velocity less than v_s, but settled because of their intermediate position. A detailed method of evaluation of the amount having settling velocity more than v_s from the cumulative weight fraction vs time curve has been presented in Cahn's Technical Bulletin No - 103[34]. The true fraction having settling velocity more than v_s is calculated by determining the slope of the cumulative weight fraction curve at any time t. The amount that would have settled in a specified period of time t is calculated on the basis of this slope and is subtracted from the actual amount settled. The result so obtained represent the fraction of the particle having settling velocity more than v_s calculated on the basis of the total height.

Retention time of the sedimentation unit : -

τ_S ideal is calculated assuming ideal performance of the sedimentation unit.

In order to calculate τ_S actual, the method presented by Camp[52] has been used. The value of $\frac{\tau_S \text{ actual}}{\tau_S \text{ ideal}}$ varies with the separating efficiency desired. It also depends on the characteristics of the system considered. Hence, the value is approximate only. The values taken for calculation are for settler whose performance can be classified as good.

APPENDIX-III

Power Requirement in a Flocculator :

It is necessary to bring the particles in contact with each other after distabilization by means of a mechanically induced velocity gradient., such that the particle aggregation could take place at an appreciable rate. The power dissipation, P per unit volume of the liquid is given by ηG^2

where, η = viscosity of the liquid

G = root mean square velocity gradient or the shear rate.

The value of P depends on the geometry of the rotor, stator and the container and upon the speed of rotor. It could be measured by measuring the torque only. The power dissipation could be expressed as:

$$P = \frac{2 \pi n T_x}{v}$$

where,

n = speed of rotation of the stirrer

T_x = torque

v = volume of the liquid.

The value of P could be stated in terms of the drag on the rotor, stator, and walls as follows :

$$P = (2 \pi n)^3 \rho A C_{t/2}$$

where,

ρ = density of the medium

A = area of the rotor

C_t = turbulant drag coefficient determined by the geometry of the system.

The value of G for a standard jar test apparatus with 3" x 1" blade has been determined by Camp[50] and is presented as a function of the rpm of the stirrer in Table-9. The considered temperature is 25°C. The power requirement could be calculated knowing the value of G. The power requirement for the treatment of one million gallons per day in a flocculator has been expressed as a function of $G\theta$ by Hudson and Wolfner[51]. For the flocculation time θ of 300 sec the power requirement as a function of G is presented below in Table-A.

TABLE-A

Power requirement in a flocculator for the treatment of 1 million gal/day as a function of G. Temperature of water- 4°C. Retention time- 300 sec.

No	G, sec^{-1}	P, h.p / million gal/day.
1.	20	0.012
2.	40	0.045
3.	60	0.1
4.	80	0.18
5.	100	0.3
6.	150	0.5
7.	200	1.1

The power requirement for $G\theta$ of 4.5×10^4 at a temperature of 4°C works and to be 0.5 h.p/ mgd.

The cost of electrical power on the basis of unit cost b of 1 ¢ / Kw.hr. is

$$\left(\frac{0.5}{1.34}\ \text{K.w.}\right)(24\ \text{hrs.})\ (\$\ 0.01\ /\ \text{Kw hr})$$

$$= \$\ 0.09/\text{mgd.}$$

It should be pointed out that in any industrial plant, flash mixing is an essential requirement for a proper distabilization of the colloid. This is done prior to flocculation, using a comparatively high value of G for a short period of time. A value of G around 300 sec^{-1} for a period of 30 sec. is quite common. The power requirement for flash mixing is in the same range of magnitude as that of a flocculator. Considering both these factors, the total power cost is negligible.

APPENDIX-IV

Numerical values of the experimental results.

TABLE-1

Results: Preliminary Experiments :

System- TiO_2 suspensions; Flocculant- Super Floc-330.

Concentration of suspension-	900 ppm
Flocculation time-	15 minutes.
Stirring rate-	Const. (Magnetic stirring).

Sedimentation Data of the Flocculated Suspensions:

n no	Dosage of flocculant. ml.	m mg./gm.	Settling time θ min.	Amount of solids settled. w, mg.	Total solids collected. W, mg.	Cumulative wt.fraction settled. $\frac{\Sigma w}{W}$	Fraction remaining in suspn. $1-\frac{\Sigma w}{W}$ (ppm)	% Lost. $\frac{360-W}{360} \times 100\%$
			5	184.1		0.525		
I	4.0	0.66	30	26.29	350.6	0.6	0.36	2.6
			60	14.06		0.64	(315)	
			5	230.47		0.66		
II	5.0	0.83	30	38.41	349.2	0.77	0.21	3.0
			60	6.98		0.79	(183)	
			5	263.62		0.75		
III	6.0	1.0	30	52.72	351.5	0.90	0.09 (80)	2.0
			60	3.52		0.91		

Cont'd . . .

TABLE-1 (Con'd.)

Run no	Dosage of flocculant ml.	m mg/gm	Settling time θ min.	Amount of solids-settled w,mg.	Total solids collected W, mg.	Cumulative wt. fraction settled. $\frac{\Sigma w}{W}$	Fraction remaining in suspn. $1 - \frac{\Sigma w}{W}$	% Lost $\frac{360-W}{360}$ x 100%
			5	309.89		0.89		
IV	7.0	1.16	30	10.44	348.2	0.92	0.07	2.0
			60	3.55		0.93	(60.9)	
			5	322.18		0.92		
V	8.0	1.33	30	14.00	350.2	0.96	0.03	2.7
			60.	3.52		0.97	(26.4)	
			5	324.6		0.93		
VI	10.0	1.66	30	12.26	349.6	0.965	0.965	2.9
			60	3.52		0.975	(22.0)	
			5	253.44		0.72		
VII	12.0	2.0	30	49.28	352.0	0.86	0.11	2.2
			60	9.86		0.89		

TABLE-2

Experimental Results: Stirring Rate as the Variable Parameter.

System- TiO_2 suspensions; Flocculant- Super Floc-330.

Concentration-	900 ppm
Flocculant dosage	1.3 mg./gm. of TiO_2.
Flocculation time-	15 minutes.

Sedimentation Data of the Flocculated Suspensions:

Run no	Stirring rate r.p.m.	Settling time min.	Amount of solids settled, w, mg.	Total solids collected W, mg.	Cumulative wt. fraction settled $\frac{\Sigma w}{W}$	Fraction remaining in suspn. $1 - \frac{\Sigma w}{W}$ (p.p.m)	%Lost $\frac{360-W}{360} \times 100\%$
I	10	5	293.32	353.4	0.83	0.08 (71)	1.5
		30	24.73		0.9		
		60	7.06		0.92		
II	20	5	321.34	351.2	0.915	0.06 (53)	2.4
		30	7.02		0.935		
		60	1.75		0.96		
III	40	5	327.82	350.6	0.935	0.04 (35)	2.6
		30	5.25		0.95		
		60	3.25		0.96		
IV	80	5	339.59	348.3	0.975	0.01 (9)	3.2
		30	3.49		0.985		
		60	1.72		0.99		

TABLE-3

Experimental Results: Stirring rate as the Variable Parameter.

System- TiO_2 suspensions; Flocculant- Super Floc-330

Concentration-	190 p.p.m
Flocculant dosage	1.3 mg./gm. of TiO_2.
Flocculation time-	15 minutes.

Sedimentation Data of the Flocculated Suspensions:

Run no	Stirring rate	Settling time θ min.	Amount of solids settled w, mg.	Total solids collected W, mg.	Cumulative wt. fraction settled. $\frac{\Sigma w}{W}$	Fraction remaining in suspn. $1 - \frac{\Sigma w}{W}$ (ppm)	%Lost $\frac{360-W}{W}$ x100%
I	10	10	4.77	73.42	0.065	0.825 (147.5)	3.4
		30	5.50		0.14		
		60	2.56		0.175		
II	20	7	48.04	72.85	0.66	0.26 (46)	4.15
		30	4.36		0.72		
		60	1.45		0.74		
III	40	5	60.05	74.63	0.805	0.15 (27.3)	1.94
		30	1.86		0.83		
		60	1.49		0.85		
IV	60	5	60.51	73.8	0.82	0.1 (18.0)	2.9
		30	5.16		0.89		
		60	1.02		0.90		
V	80	5	66.61	72.41	0.92	0.04 (7.0)	4.7
		30	1.45		0.94		
		60	1.43		0.96		

TABLE-4

Experimental Results: Flocculation Time as the Variable Parameter.

System- TiO_2 suspensions; Flocculant- Super Floc-330

Concentration- 900 p.p.m.
Flocculant dosage 1.3 mg./gm. of TiO_2.
Stirring rate- 80 r.p.m.

Sedimentation Data of the Flocculated Suspensions:

Run no	Flocculation time, minutes.	Sedimentation time, minutes.	Amount of solids settled. w, mg.	Total solids collected W, mg.	Cumulative wt. fraction settled. $\frac{\Sigma w}{W}$	Fraction remaining in suspn. $1 - \frac{\Sigma w}{W}$
		2	278.56		0.8	
I	5	5	52.27	348.27	0.95	0.025
		30	7.68		0.972	(23.5)
		60	1.05		0.975	
		2	330.87		0.945	
II	10	5	12.94	350.12	0.982	0.01
		30	2.80		0.990	(9.0)
		60	0.12		0.991	
		2	333.96		0.955	
III	20	5	12.23	349.69	0.99	0.099
		30	0.25		0.991	(8.1)
		60	0.16		0.991	

TABLE-5

Experimental Results: Flocculation time as the Variable Parameter.

System- TiO_2 suspensions ; Flocculant- Super Floc-330

Concentration-	190 ppm.
Stirring rate-	10 rpm.
Flocculant dosage	1.3 mg./gm. of TiO_2.

Sedimentation Data of the Flocculated Suspensions,

Run no	Flocculation time, minutes	Settling time, minutes	Amount of solids settled. w, mg.	Total solids collected W, mg.	Cumulative wt. fraction settled $\frac{\Sigma w}{W}$	Fraction remaining in suspension. $1 - \frac{\Sigma w}{W}$
I	15	15	6.58	73.2	0.09	0.76 (137)
		30	4.40		0.15	
		60	6.62		0.24	
II	30	5	31.64	73.6	0.43	0.42 (75.3)
		30	9.56		0.56	
		60	1.48		0.58	
III	45	5	53.21	72.8	0.73	0.22 (39.0)
		30	2.93		0.77	
		60	1.02		0.78	
IV	60	5	56.84	73.8	0.77	0.17 (30)
		30	3.68		0.82	
		60	0.84		0.83	
V	105	5	48.24	72.0	0.67	0.23 (37.0)
		30	5.76		0.75	
		60	1.44		0.77	

TABLE-6

Experimental Results: Concentration of the Suspension as the Variable Parameter.

System- TiO_2 suspensions; Flocculant- Super Floc-330.

Flocculant dosage	1.3 mg./gm. of TiO_2.
Flocculation time-	30 minutes.
Stirring rate-	10 r.p.m.

Sedimentation Data of the Flocculated Suspensions:

Run no	Concentration of suspension p.p.m.	Settling time min.	Amount of solids settled w, mg.	Total solids collected W, mg.	Cumulative wt. fraction settled. $\frac{\Sigma w}{W}$	Fraction remaining in suspension. $1 - \frac{\Sigma w}{W}$ (ppm.)
I	200	5	35.62	75.8	0.47	0.42 (80)
		30	6.84		0.56	
		60	1.52		0.58	
II	400	5	100.98	153.0	0.66	0.16 (61)
		30	24.48		0.82	
		60	3.06		0.84	
III	600	5	187.52	231.5	0.81	0.13 (75.6)
		30	9.24		0.85	
		60	4.64		0.87	
IV	900	5	317.84	349.2	0.9	0.05 (44)
		30	10.46		0.94	
		60	3.52		0.95	

TABLE-7

Experimental Results: Dosage of Flocculant as the Variable Parameter.

System- TiO_2 suspension ; Flocculant- Super Floc-330

Flocculation time-	15 minutes
Stirring rate-	80 rpm.

Run no	Dose of flocculant mg./gm. of TiO_2	Amount of solids settled mg.	Amount of solid remaining in suspension, mg.	Total amount of solids mg.	Fraction settled	Fraction remaining in suspension. (ppm)
Concentration of TiO_2 in suspension - 190 ppm						
I	0.769	31.14	41.28	72.42	0.43	0.57 (100)
II	0.961	42.14	28.72	70.86	0.595	0.405 (70)
III	1.438	67.46	2.46	69.92	0.965	0.035 (6)
IV	1.92	67.93	3.28	71.21	0.954	0.046 (8)
V	2.32	68.28	3.30	71.58	0.951	0.049 (8)
VI	3.07	67.87	5.36	73.23	0.927	0.073 (13)
VII	3.46	67.49	5.33	72.82	0.927	0.073 (13)
VIII	5.38	54.33	17.23	71.56	0.76	0.24 (42)
IX	7.69	30.77	40.15	70.92	0.434	0.566 (98)
X *	0.66	221.42	131.23	352.65	0.628	0.372 (336)
XI *	1.0	318.05	33.37	351.42	0.905	0.095 (85)
XII *	1.18	326.89	22.73	349.62	0.935	0.065 (58)
XIII *	1.33	347.98	5.30	353.28	0.985	0.015 (13.5)
XIV *	1.66	348.90	3.56	352.46	0.99	0.01 (9)
XV *	2.0	331.15	19.12	350.27	0.945	0.055 (49.5)

* Concentration of TiO_2 in suspension - 900 ppm.

TABLE-8

Experimental results relating ξ, G, θ, φ and m

m = 0.0013

	Concentration of the suspension φ', 10^{-6}	Stirring rate rpm.	Shear rate G. Sec^{-1}	Flocculation time, θ, Sec	Dimensionless Group $G\theta\varphi$	ξ	$K' = -\frac{\ln \xi}{G\theta\varphi}$
	237	10	7.2	900	1.55	0.08	+1.629
	237	20	20.0	900	4.30	0.06	+0.654
	237	40	55.0	900	11.84	0.04	+0.237
	237	80	135.0	900	29.07	0.01	+0.1584
	50	10	7.2	900	0.326	0.825	+0.520
	50	20	20.0	900	0.908	0.26	+1.483
7	50	40	55.0	900	2.480	0.15	+0.7597
8	50	60	90.0	900	4.08	0.1	+0.563
9	50	80	135.0	900	6.13	0.04	+0.122
10	237	80	135.0	300	9.6	0.025	+0.384
11	237	80	135.0	600	19.2	0.01	+0.239
12	237	80	135.0	1200	38.4	0.009	+0.122
13	50	10	7.2	900	0.327	0.76	+0.841
14	50	10	7.2	1800	0.654	0.42	+1.326
15	50	10	7.2	2700	0.981	0.22	+1.543
16	50	10	7.2	3600	1.3	0.17	+1.352
17	50	10	7.2	6300	2.28	0.23	+0.644
18	52	10	7.2	1800	0.688	0.42	+1.26
19	104	10	7.2	1800	1.36	0.16	+1.34
20	156	10	7.2	1800	2.06	0.13	+0.990
21	236	10	7.2	1800	3.09	0.05	+0.969

TABLE-8 (CONT'D)

Experimental Data Flocculant- Super Floc-330

$m = 0.0013$

	Concentration of the suspension $\varphi \cdot 10^{-6}$ 10^{-6}	Stirring rate, rpm.	Shear rate, n G. Sec^{-1}	Flocculation time θ, Sec	Dimensionless Group $G\theta\varphi$	ξ	$K \doteqdot -\frac{\ln \xi}{G\theta\varphi}$
23	220	100	170	120	4.48	0.056	0.643
24	220	100	170	300	11.2	0.022	0.34
25	220	100	170	600	22.4	0.012	0.197
26	220	100	170	900	33.6	0.0075	0.145
27	220	100	170	1200	44.8	0.0064	0.112
28	220	60	90	120	2.36	0.098	0.984
29	220	60	90	300	5.94	0.052	0.497
30	220	60	90	600	11.88	0.0165	0.226
31	220	60	90	1200	23.76	0.0885	0.200
32	200	80	135	300	8.1	0.031	0.424
33	200	80	135	600	16.2	0.017	0.251
34	200	80	135	1800	48.6	0.0054	0.107
	$m = 0.00210$						
35	237	100	170	120	4.83	0.11	0.456
36	237	100	170	300	12.1	0.034	0.279
37	237	100	170	600	24.2	0.020	0.161
38	237	100	170	900	36.3	0.018	0.110
	$m = 0.00105$						
39	190	100	170	120	3.87	0.52	0.168
40	190	100	170	300	9.69	0.39	0.0971
41	190	100	170	660	19.38	0.13	0.105
42	190	100	170	1200	38.8	0.042	0.081
43	190	100	170	1800	58.1	0.018	0.069
44	237	100	170	300	12.5	0.140	0.154
45	237	80	135	900	28.7	0.095	0.082
46	50	700	72	1800	6.5	0.405	0.140

TABLE-9

A relation between n and G for a standard jar test apparatus: dimension of the blades- 3" x 1" : temperature of water - 25°C

No	Revolution of the stirrer n, r.p.m.	G $sec.^{-1}$
1.	20	20
2.	40	55
3.	60	90
4.	80	135
5.	100	170

TABLE-10

Experimental results relating θ, v_s and ξ

System - TiO_2, Flocculant - Super Floc-330.

Concentration - 900 ppm of TiO_2
Dosage - 1.3 mg/gm of TiO_2
Stirring rate - 80 rpm.

No.	θ minutes	Settling velocity v_s ft / hr.	Overflow rate L gallons/day,sq.ft.	Fraction having settling velocity more than v_s	Fraction in the effluent stream at an overflow rate L
1	5	1.5	225	0.97	0.03
2	5	3.0	450	0.95	0.050
3	5	5.0	750	0.9	0.10
4	5	7.0	1050	0.82	0.18
5	5	10	1500	0.6	0.4
6	10	3.0	450	0.985	0.015
7	10	5.0	750	0.965	0.035
8	10	7.0	1050	0.95	0.05
9	10	10.0	1500	0.87	0.13
10	10	12.0	1800	0.80	0.20
11	10	15	2250	0.60	0.40
12	20	3.0	450	0.99	0.01
13	20	5.0	750	0.972	0.028
14	20	7.0	1050	0.960	0.04
15	20	10.0	1500	0.90	0.1
16	20	12.0	1800	0.83	0.17
17	20	15.0	2250	0.65	0.35

TABLE-11

Experimental Results: Dosage of Flocculant as the Variable Parameter.

System- TiO_2 suspension; Flocculant- Alum

(The pH of the suspension is not adjusted.)

Concentration-	900 p.p.m.
Flocculation time-	15 minutes.
Stirring rate-	80 r.p.m.

Sedimentation Data of the Flocculated Suspensions:

Run no	Dosage of Alum (ppm)mg./gm. of TiO_2	Settling time, min.	Amount of solids settled w, mg.	Total solids collected. W,mg.	Cumulative wt. fraction collected. $\frac{\Sigma w}{W}$	Fraction remaining in supension. $1 - \frac{\Sigma w}{W}$
I	(50) 55.5	10	14.62	358.2	0.04	0.88
		30	17.90		0.09	
		60	10.74		0.12	
II	(100) 111.0	15	59.24	369.2	0.16	0.73
		30	25.92		0.23	
		60	14.75		0.27	
III	(150) 166.0	15	111.32	371.12	0.3	0.605
		30	26.12		0.37	
		60	9.36		0.395	

TABLE-11 (cont'd.)

Run no	Dosage of Alum (ppm)mg./gm. of TiO_2	Settling time, min.	Amount of solids settled w, mg.	Total solids collected. W, mg.	Cumulative wt. fraction collected. $\frac{\Sigma w}{W}$	Fraction remaining in suspension $1 - \frac{\Sigma w}{W}$
IV	(275) 250	10	164.46		0.4	
		30	49.36	411.0	0.52	0.46
	pH- 4.1	60	8.24		0.54	
V	(555) 500	.5	181.72		0.42	
		15	86.58	432.8	0.62	0.2
	pH-4.0	30	51.96		0.74	
		60	25.99		0.80	

TABLE-12

Experimental Results: Dose of Flocculant as the Variable Parameter.

System- TiO_2 suspension ; Flocculant- Alum

(The pH of the suspension is adjusted to 6.5)

Concentration-	900 p.p.m.
Flocculation time-	5 minutes.
Stirring rate-	80 r.p.m.

Sedimentation Data of the Flocculated Suspensions.

Run no	Dosage of Alum (ppm)mg./gm. of TiO_2	Settling time, min.	Amount of solids settled w, mg.	Total solids collected. W, mg.	Cumulative wt.fraction collected. $\frac{\Sigma w}{W}$	Fraction Remaining in suspension $1 - \frac{\Sigma w}{W}$
I	(40) 44	5	119.19	361.2	0.33	
		30	153.51		0.755	0.19
		60	19.86		0.81	(171)
II	(50) 55	5	187.42		0.525	
		30	103.71	356.6	0.825	0.13
		60	16.44		0.87	(117)
III	(60) 66	5	249.78		0.68	
		30	87.41	367.3	0.918	0.07
		60	4.52		0.93	(63)

....cont'd.

TABLE-12 (Cont'd.)

Run no	Dosage of Alum (ppm) mg,/gm. of TiO_2	Settling time, min.	Amount of solids settled w, mg.	Total solids collected. W, mg.	Cumulative wt. fraction collected. $\frac{\Sigma w}{W}$	Fraction remaining in suspension $1 - \frac{\Sigma w}{W}$
IV	(75) 83	5	318.70	368.4	0.865	0.035
		30	33.16		0.955	(32.0)
		60	37.18		0.965	
V	(100) 111	5	365.94	374.2	0.978	0.01
		30	2.96		0.986	(9)
		60	1.52		0.990	
VI	(150) 166	5	370.65	372.56	0.995	0.0
		30	1.91		1.0	(0.0)
		60	0.0		1.0	
VII	(200) 222	5	371.65		0.996	0.0
		30	1.63		1.0	(0.0)
		60	0.0		1.0	

TABLE-13

Experimental Results: Dosage of Flocculant as the Variable Parameter.
System- TiO_2 suspension; Flocculant- Alum.

(The pH of the suspension is adjusted to 6.5)

Concentration-	900 p.p.m.
Flocculation time-	15 minutes.
Stirring rate-	80 r.p.m.

Sedimentation Data of the Flocculated Suspensions.

Run no	Dosage of Alum (p.p.m)mg./gm. of TiO_2	Settling time, min.	Amount of solids settled w, mg.	Total solids collected. W, mg.	Cumulative wt.fraction collected. $\frac{\Sigma w}{W}$	Fraction remaining in suspension. $1 - \frac{\Sigma w}{W}$
I	(25) 28	5	234.49	360.8	0.65	0.15
		30	64.96		0.83	(135)
		60	7.32		0.85	
II	(40) 44	5	313.41	362.3	0.865	0.065
		30	18.12		0.915	(58)
		60	7.28		0.935	
III	(60) 66	5	355.42	365.6	0.972	0.005
		30	6.54		0.990	(0,0)
		60	1.83		0.995	

...cont'd.

TABLE-13 (cont'd.)

Run no	Dosage of Alum (ppm)mg./gm. of TiO_2	Settling time, min.	Amount of solids settled w, mg.	Total solids collected.W,mg.	Cumulative wt. fraction collected. $\frac{\Sigma w}{W}$	Fraction remaining in suspension $1 - \frac{\Sigma w}{W}$
		5	362.91		0.985	
IV	(75) 83	30	3.72	368.4	0.995	0.0
		60	1.77		1.0	(0,0)
		5	369.36	372.3	0.992	
V	(100) 111	30	2.94		1.0	0.0
		60	0.0		1.0	(0.0)
		5	187.11		0.977	
VI*	(25) 55	30	2.51	191.5	0.99	0.008
		60	0.42		0.992	(36)

* Concentration of TiO_2 - 450 p.p.m.

TABLE-14

Experimental results relating ξ, G, θ, φ and m for Alum: pH = 6.5

	Concentration of the suspension. φ 10^{-6}	Shear rate G sec^{-1}	Flocculation time. θ sec	Dimensionless group $G\theta\varphi$	m 10^{-3}	ξ	$K' = \frac{-\ln\xi}{G\theta\varphi}$
1	237	135	120	3.83	44	0.34	0.2816
2	237	135	300	9.59	44	0.19	0.1730
3	237	135	600	19.2	44	0.1	0.1199
4	237	135	900	28.8	44	0.065	0.0959
5	237	135	120	3.83	55	0.24	0.372
6	237	135	300	9.59	55	0.13	0.212
7	237	135	600	19.2	55	0.025	0.192
8	237	135	900	28.8	55	0.008	0.167
9	237	135	120	3.83	66	0.20	0.42
10	237	135	300	9.59	66	0.07	0.277
11	237	135	600	19.2	66	0.012	0.23
12	237	135	900	28.8	66	0.005	0.183
13	237	135	300	9.59	83	0.035	0.349
14	237	135	600	19.2	83	0.007	0.258
15	237	135	900	28.8	83	0.002	0.215
16	237	135	120	3.83	111	0.1	0.601
17	237	135	300	9.59	111	0.01	0.480
18	237	135	600	19.2	111	0.001	0.329
19	237	135	900	28.8	280	0.15	0.0658

TABLE-15

Experimental results relating θ, v_s, m and ξ for Alum.

System- TiO_2 Flocculant- Alum
pH is adjusted to 6.5
Concentration of the suspension- 900 ppm
Stirring rate 80 rpm

No.	θ minutes	Settling velocity v_s, ft/hr.	Overflow rate L, gallons/day sq.ft.	m mg/gm of TiO_2	Fraction having settling velocity v_s	Fraction in the effluent stream of an overflow rate L.
1	5	3	450	54	0.5	0.5
2	5	3	450	76	0.8	0.3
3	5	3	450	90	0.9	0.1
4	5	3	450	106	0.95	0.05
5	5	3	450	150.0	0.99	0.01
6	5	7.3	1100	68.0	0.5	0.50
7	5	7.3	1100	94.0	0.8	0.30
8	5	7.3	1100	110.0	0.9	0.10
9	5	7.3	1100	140.0	0.95	0.05
10	5	15.0	2200	76.0	0.5	0.5
11	5	15.0	2200	200.0	0.95	0.05
12	15	3	450	20.0	0.5	0.5
13	15	3	450	36.0	0.8	0.3
14	15	3	450	48.0	0.9	0.1
15	15	3	450	56.0	0.95	0.05
16	15	3	450	100.0	0.99	0.01
17	15	7.3	1100	33.0	0.5	0.5
18	15	7.3	1100	60.0	0.8	0.2
19	15	7.3	1100	72.0	0.90	0.1
20	15	7.3	1100	140.0	0.99	0.01
21	15	7.3	1100			

TABLE-16

Experimental Results:

System- TiO_2 ; Flocculant- Super Floc 330 and Alum Mixture.

Concentration-	900 p. p. m.
Flocculation time-	15 minutes
Stirring rate-	80 r. p. m.
Dosage of Alum-	33 mg/gm. of TiO_2
Sedimentation time-	5 minutes
Estimated overflow rate-	450 gal. /day. ft^2.

Run no	Dosage of Super Floc mg. /gm. of TiO_2	Amount of solids settled mg.	Amount of solid remaining in suspension mg.	Total solids mg.	Fraction settled
I	0. 334	356. 75	13. 87	370. 62	0. 956
II	0. 5[illegible]	365. 35	10. 50	375. 85	0. 973
III	0. 688	369. 50	8. 06	377. 56	0. 979
IV	0. 833	357. 95	14. 60	372. 45	0. 961

TABLE-17

Experimental Results:

System-Clay; Flocculant-Alum

Concentration-	900 p.p.m.
Flocculation time-	3 minutes.
Stirring rate-	80 r.p.m.
Sedimentation time-	2 minutes
Estimated Overflow rate-	1073 gal./day.ft.^{2}

Run no	Dosage of alum ml. (p.p.m)	Dosage of alum mg./gm of clay	Amount of solids settled mg.	Amount of solid remaining in suspension mg.	Total amount of solids mg.	Fraction settled
I	1.0 (50)	55.5	180.74	187.52	368.26	0.512
II	1.5 (75)	83.3	349.82	22.76	372.58	0.938
III	2.0 (100)	111.0	369.86	15.40	385.32	0.96
IV	3.0 (150)	166.0	390.23	6.40	396.47	0.984

TABLE-18

Experimental Results :

Suspension- Clay ; Flocculant- Super Floc-330

Concentration- 900 p.p.m.
Flocculation time- 5 minutes.
Stirring rate- 80 r.p.m.
Overflow rate- 1073 gals/day.ft.^{2}

Run no	Dosage mg./gm	Amount of solid remaining in suspension mg.	Amount of solids sediment mg.	Total solids mg.	Fraction settled
I	0.166	29.9	313.6	343.5	0.913
II	0.332	21.5	324.2	345.7	0.938
III	0.498	10.8	330.8	341.6	0.9683
IV	0.83	10.1	330.1	340.2	0.971
V	1.32	10.2	336.4	346.6	0.97
VI	1.66	22.2	326.0	348.2	0.937

TABLE-19

Experimental Results:

Suspension - Paper Fines

Concentration- 900 p.p.m.
Flocculation time- 3 minutes.
Overflow rate- 1073 gal./day.ft^2.

Run	Chemicals	Dosage mg./gm.	Amount of solids settled mg.	Amount in suspension remaining mg.	Total amount of solids mg.	Fraction settled
I	Alum	27.7	344.3	0.9	345.2	0.998
II	Alum	55.5	350.0	0.5	350.5	0.999
III	Super Floc	0.166	329.96	9.30	339.26	0.975
IV	Super Floc	0.332	341.0	2.80	343.8	0.992
V	Super Floc	0.5	341.0	0.5	341.5	0.999

TABLE-20

Experimental Results of the Treatment of Paper Mill Waste

Concentration of the effluent stream-	194 p.p.m.
Flocculation time-	3-minutes.
Stirring rate-	80 r.p.m.
Sedimentation time	2 minutes.
(Equivalent overflow rate-	1073 gallons/day.ft^2.)

Run no	Flocculant	Dosage ml. (p.p.m)	Dosage mg/gm	Sediment collected	Amount of solids remaining in suspension. mg.	Total amount of solids collected mg.	Fraction settled
I	Alum (pH is adjusted to 6.5)	0.5 (25)	128.5	81.87	5.37	87.24	0.933
II		0.5 (25)	128.5	79.40	8.94	88.34	0.898
III		1.0 (50)	257.0	105.21	1.81	107.02	0.986
IV		1.0 (50)	257.0	101.21	4.26	105.47	0.965
V		1.5 (75)	385.0	107.62	1.16	108.78	0.99
VI		2.0 (100)	514.0	107.52	0	107.52	1.0
VII	Super Floc-330	5.0 (0.75)	3.87	51.48	15.23	66.71	0.77
VIII		10.0 (1.5)	7.74	63.68	9.58	73.26	0.87
IX		15.0 (2.25)	11.61	65.68	6.41	72.09	0.91
X		20. (3.0)	14.48	74.84	2.33	77.17	0.97
XI		25.0 (3.75)	19.35	68.62	6.64	75.26	0.905
XII	Alum + Super Floc.	0.5 2.0)	128.5 1.45	83.90	1.16	85.06	0.983
XIII		0.5 2.0)	128.5 1.45	78.42	4.36	82.78	0.95

TABLE-21

Experimental Results:

Sedimentation Data; System- Untreated TiO_2 Suspensions.

Concentration - 900 p. p. m.

Run no	Medium	Settling time hr.	Amount of solids settled w, mg.	Total amount of solids collected. W, mg.	Cumulative wt. fraction settled. $\frac{\Sigma w}{W}$	% Lost
I	Distilled water	1.0	25.92	345.6	0.075	4.0
		4.0	25.86		0.15	
		6.0	17.28		0.20	
		12.0	34.56		0.30	
II	De-ionized water	1.0	11.14	348.2	0.032	3.38
		4.0	23.67		0.10	
		6.0	13.92		0.14	
		12.0	38.35		0.25	
III	Tap water	0.25	246.75	352.5	0.7	2.08
		1.0	66.97		0.89	
		3.0	28.2		0.97	
		6.0	8.12		0.995	
IV	Tap water Anionic poly-electr.	0.25	31.60	357.2	0.09	2.50
		1.0	31.42		0.18	
		6.0	154.52		0.62	
		12.0	80.77		0.85	

TABLE-22

Experimental results showing the effect of addition of starch on the coagulating behaviour of TiO_2 suspensions:

Concentration of TiO_2 -	900 ppm.
Concentration of starch -	27 ppm.
Flocculation time -	15 minutes
Stirring rate -	100 rpm.
Settling time -	1 hr.

No.	Flocculant	Flocculant dosage mg/gm of TiO_2	Amount of solids remaining in the suspension mg	Amount of solids settled mg	Total solids collected mg	Fraction remaining in suspension
1	Super Floc-330	1.0	345.3	18.2	363.5	0.95
2	"	1.3	341.3	19.9	361.2	0.945
3	"	1.5	337.2	25.2	362.4	0.93
4	"	5.0	337.6	25.2	262.8	0.93
5	"	50.0	333.7	27.1	360.8	0.925
6	Alum pH = 6.5	55.0	341.9	19.9	361.8	0.945
7	"	83.0	340.8	21.7	362.5	0.94
8	"	111.0	337.9	25.3	363.2	0.93
9	"	222.0	285.8	95.2	381.0	0.75
10	"	555.0	4.3	42.3	425.6	0.01

TABLE-23

Experimental Results - Electrolytic Process (Cell -A)

Concentration of TiO_2 - 900 p.p.m
Duration of experiment - 15 minutes

Run no	Applied potential Volt	Field Volt/cm.	Current m. Amp.	Current density mA/cm^2	Fraction collected	Energy consumption, m.Watt.hr.
1	10	10	1.3	0.065	0.25	3.25
2	50	50	7.0	0.35	0.85	87.5
3	100	150	15.0	0.75	0.65	375

Calculated overflow rate - 100 gal. /day. ft^2.

TABLE-24

Experimental Results- Electrolytic Process (Cell-B) :

Concentration of TiO_2 - 866 p. p. m.

Run no	Applied potential Volt (Field: Volt/cm.)	Current m. Amp. (density: m.Amp./cm^2)	Duration of experiment minutes.	Energy consumption Watt. hr
I	20, (10)	3.5,(0.175)	30	0.035
II	20, (10)	3.5,(0.175)	90	0.105
III	100, (50)	21.0,(1.05)	30	1.05
IV	100, (50)	21.0,(1.05)	90	3.15
V	150, (75)	40.0,(2.0)	10	1.0
VI	150, (75)	40.0,(2.0)	30	3.0
VII*	100, (50)	100.0,(5.5)	30	5.5

* 50 p. p. m. of Alum was added.

TABLE-25

Experimental Results- Electrolytic Process (Cell-B)

Sedimentation Data

Run no	No	Sedimentation time, minutes	Amount settled w, mg	Total solids collected W, mg.	Cumulative wt.fraction $\frac{\Sigma w}{W}$	Fraction remaining in suspension. $1-\frac{\Sigma w}{W}$	%Lost
I	1	10	93.86		0.275		
	2	30	59.74	341.2	0.45	0.48	1.5
	3	60	23.92		0.52		
II	1	5	71.13		0.24		
	2	10	67.76	338.63	0.41	0.27	2.24
	3	30	67.58		0.61		
	4	60	40.61		0.91		
III	1	5	154.46		0.46		
	2	10	74.16		0.68	0.09	2.76
	3	30	40.39		0.8		
	4	60	37.12		0.91		
IV	1	5	259.46		0.78		
	2	15	33.31	332.62	0.88	0.045	3.97
	3	30	16.68		0.93		
	4	60	8.49		0.955		

...cont'd..

TABLE-25 (cont'd.)

Run no	No	Sedimentation time, minutes.	Amount settled w, mg.	Total solids collected W, mg.	Cumulative wt. fraction settled. $\frac{\Sigma w}{W}$	Fraction remaining in suspension, $1-\frac{\Sigma w}{W}$	%Lost
V	1	5	43.46	339.29	0.128	0.635	2.05
	2	15	32.93		0.225		
	3	30	20.36		0.285		
	4	60	27.15		0.365		
VI	1	5	143.96	338.60	0.425	0.2	2.25
	2	15	69.42		0.63		
	3	30	52.49		0.785		
	4	60	5.08		0.8		
VII	1	5	138.42	337.57	0.41	0.25	2.5
	2	15	60.78		0.59		
	3	30	23.68		0.66		
	4	60	30.38		0.75		

TABLE-26

Experimental Results- Electrolytic Process (Cell-B)

Concentration of TiO_2- 173 p. p. m.
Potential difference- 180 Volts.
Field - 50 Volts/cm.
Current - 7.5 m. Amp.
Current density- 0.375 m. A/cm^2.
Sedimentation time- 60 minutes.
Corresponding overflow rate- 37.5 gal. /day. ft^2.

Run no	Duration of experiment minutes.	Energy consumption Watt. hr.	Amount of solids settled mg.	Amount of solids remaining in suspension, mg.	Fraction settled	% Lost.
1	60	0.75	21.72	31.0	0.41	19.5
2	120	1.5	43.6	5.84	0.88	28.5
3	180	2.25	40.3	12.2	0.766	24.1
4	240	3.0	40.0	15.9	0.715	19.2

TABLE - 27

The Dosage of Flocculant Required for Different Systems :

No	System studied	Flocculant	m	θ sec.	Overflow rate gal/day ft^2.	$G\theta\varphi$	Fraction of solids removed in an ideal settler.
1.	TiO_2	Alum	0.22	300	1100	9.6	0.98
2.	TiO_2	Super Floc-330	0.0013	300	1100	9.6	0.87
3.	Clay	Alum	0.166	180	1100	5.85	0.984
4.	Clay	Super Floc-330	0.00083	300	1100	9.6	0.97
5.	Paper fines	Alum	0.028	180	1100	5.85	0.998
6.	Paper fines	Super Floc-330	0.00016	300	1100	9.6	0.992
7.	Mill effluent	Alum	0.25	180	1100	1.22	0.98
8.	Mill effluent	Super Floc-330	0.0077	300	1100	2.02	0.87

TABLE-28

Cost Estimates of TiO_2 Separation, Using Alum as the Flocculant.

Basis :

Q = one million gallons/day

x = 900 ppm of TiO_2

a = \$0.0225 /lb of alum

c_2 = \$1.5 / gallon

c_3 = \$1.0 / gallon

y = \$0.19/minute gallon.

Separation efficiency = 0.75

$\frac{\tau_s \text{(actual)}}{\tau_s \text{(ideal)}} = 1.8$

No.	$\theta = \tau_F$ minutes	v_s Ft/hr	Overflow rate, gal/day ft^2	τ_S (ideal) minutes.	m lb/lb	Fraction of solids having settling velocity more than v_s	τ_S (actual) minutes	Cost \$ Chemical	Cost \$ Capital	Cost \$ Total	Fraction of solids removed.
1	5	3	450	140	0.054	0.5	252	10.9	49.3	60.2	0.375
2	5	3	450	140	0.076	0.8	252	15.4	49.3	64.7	0.6
3	5	3	450	140	0.090	0.9	252	18.3	49.3	67.6	0.675
4	5	3	450	140	0.106	0.95	252	21.5	49.3	70.8	0.71
5	5	3	450	140	0.150	0.99	252	31.2	49.3	80.5	0.74
6	5	7.3	1100	58	0.068	0.5	104	13.8	21.2	35.0	0.375
7	5	7.3	1100	58	0.094	0.8	104	19.2	21.2	40.9	0.6
8	5	7.3	1100	58	0.110	0.9	104	22.4	21.2	43.6	0.675
9	5	7.3	1100	58	0.140	0.95	104	28.4	21.2	49.6	0.71

Cont'd.....

TABLE-28 (CONT'D)

No.	$\theta = \tau_F$ minutes	v_s Ft/hr	Overflow rate, gal/day ft^2	τ_S(ideal) minutes	m lb/lb	Fraction of solids having settling velocity more than v_s	τ_S(actual) minutes	Cost $ Chemical	Cost $ Capital	Cost $ Total	Fraction of solids removed.
10	5	15.0	2200	29	0.076	0.5	52	15.4	11.3	26.7	0.375
11	5	15.0	2200	29	0.20	0.95	52	40.6	11.3	51.9	0.71
12	15	3.0	450	140	0.02	0.5	252	4.06	52.2	56.26	0.375
13	15	3.0	450	140	0.036	0.8	252	7.3	52.2	59.5	0.6
14	15	3.0	450	140	0.048	0.9	252	9.72	52.2	61.9	0.675
15	15	3.0	450	140	0.056	0.95	252	11.4	52.2	63.6	0.71
16	15	3.0	450	140	0.10	0.99	252	20.2	52.2	72.4	0.74
17	15	7.3	1100	58	0.033	0.5	104	6.7	24.1	31.5	0.375
18	15	7.3	1100	58	0.060	0.8	104	12.2	24.1	36.3	0.6
19	15	7.3	1100	58	0.072	0.9	104	14.6	24.1	38.7	0.675
20	15	7.3	1100	58	0.084	0.95	104	17.0	24.1	41.1	0.71
21	15	7.3	1100	58	0.140	0.99	104	28.4	24.1	52.5	0.74
22	15	15	2200	29	0.140	0.95	52	28.4	14.2	42.6	0.71

Cont'd....

TABLE-28 (CONT'D)

No.	$\theta = \tau_F$ minutes	v_s Ft/hr	Overflow rate, gal/day ft^2	τ_S(ideal) minutes	$\tilde{m}$ lb/lb	Fraction of solids having settling velocity more than v_s	τ_S(actual) minutes	Cost $			Fraction of solids removed.
								Chemical	Capital	Total	
	Separation efficiency = 0.95										
	$\frac{\tau_S\text{(actual)}}{\tau_S\text{(ideal)}} = 5.0$										
1	5	3	450	140	0.054	0.5	700	10.9	134.4	145.3	0.475
2	5	3	450	140	0.076	0.8	700	15.4	134.4	149.8	0.758
3	5	3	450	140	0.090	0.9	700	18.3	134.4	152.7	0.853
4	5	3	450	140	0.106	0.95	700	21.5	134.4	155.9	0.9
5	5	3	450	140	0.150	0.99	700	31.2	134.4	165.6	0.94
6	5	7.3	1100	58	0.068	0.5	290	13.8	56.6	70.4	0.475
7	5	7.3	1100	58	0.094	0.8	290	19.2	56.6	74.8	0.758
8	5	7.3	1100	58	0.110	0.9	290	22.4	56.6	79.0	0.853
9	5	7.3	1100	58	0.140	0.95	290	28.4	56.6	85.0	0.9
10	5	15.0	2200	29	0.076	0.5	145	15.4	29.0	44.4	0.475
11	5	15.0	2200	29	0.20	0.95	145	40.6	29.0	69.6	0.9
12	15	3.0	450	140	0.02	0.5	700	4.06	137.3	141.36	0.475

Cont'd.......

TABLE-28 (CONT'D)

No.	$\theta = \tau_F$ minutes	v_s Ft/hr	Overflow rate, gal/day ft^2	τ_S(ideal) minutes	m lb/lb	Fraction of solids having settling velocity more than v_s	τ_S(actual) minutes	Cost $ Chemical	Cost $ Capital	Cost $ Total	Fraction of solids removed.
13	15	3.0	450	140	0.036	0.8	700	7.3	137.3	144.6	0.758
14	15	3.0	450	140	0.048	0.9	700	9.72	137.3	147.0	0.853
15	15	3.0	450	140	0.056	0.95	700	11.4	137.3	148.7	0.9
16	15	3.0	450	140	0.10	0.99	700	20.2	137.3	157.5	0.94
17	15	7.3	1100	58	0.033	0.5	290	6.7	59.5	66.2	0.475
18	15	7.3	1100	58	0.066	0.8	290	12.2	59.5	71.7	0.758
19	15	7.3	1100	58	0.072	0.9	290	14.6	59.5	74.1	0.853
20	15	7.3	1100	58	0.084	0.95	290	17.0	59.5	76.5	0.9
21	15	7.3	1600	58	0.140	0.99	290	28.4	59.5	87.9	0.94
22	15	15	2200	29	0.140	0.95	145	28.4	32.1	60.5	0.9

TABLE-29

Cost estimates of TiO_2 separation, using Super Floc-330 as the flocculant

Basis: Q = 1 million gallons/day
x = 900 ppm of TiO_2
a = \$1.50/lb of Super Floc
c_2 = \$1.50/gallon
c_3 = \$1.0/gallon
y = \$ 0.19/minute .

No	Overflow rate, gal/day ft^2	$\theta = \tau_F$ minutes	τ_S ideal minutes	Fraction of solids removed in an ideal settler	τ_S actual		\$ Cost					Fraction of solids in the effluent stream.	
					effy = 0.75 1.8 τ_S ideal	effy = 0.95 5.0 τ_S ideal	Chemicals	Capital		Total			
								effy = 0.75	effy = 0.95	effy = 0.75	effy = 0.95	effy = 0.75	effy = 0.95
1	225	5	284	0.97	512	1420	17.5	98.72	269.4	116.2	287.9	0.73	0.91
2	450	5	142	0.95	256	710	17.5	50.0	136.4	67.5	153.9	0.713	0.902
3	750	5	85	0.90	153	425	17.5	30.62	82.0	48.12	99.5	0.675	0.855
4	1050	5	61	0.82	110	305	17.5	22.22	59.3	39.72	76.8	0.615	0.778
5	1500	5	43	0.60	73.5	215	17.5	15.37	42.2	32.57	59.7	0.45	0.57
6	450	10	142	0.985	256	710	17.5	51.44	137.6	68.94	145.3	0.732	0.935
7	750	10	85	0.985	153	425	17.5	31.90	83.4	49.4	100.9	0.722	0.916
8	1050	10	61	0.95	110	305	17.5	23.74	60.3	41.24	77.8	0.712	0.902
9	1500	10	43	0.87	73.5	215	17.5	16.79	43.6	34.49	61.1	0.652	0.826
10	1800	10	35.5	0.80	64.0	178	17.5	14.99	36.6	32.49	54.1	0.6	0.76
11	2250	10	28.4	0.60	51.2	142	17.5	12.6	29.8	30.1	47.3	0.45	0.57
12	450	20	142	0.990	256	710	17.5	54.3	140.7	71.8	158.2	0.742	0.94
13	750	20	85	0.972	153	425	17.5	34.8	86.3	52.3	103.8	0.73	0.923
14	1050	20	61	0.960	110	305	17.5	26.6	63.6	44.1	81.1	0.72	0.912
15	1500	20	43	0.90	73.5	215	17.5	19.6	46.5	37.1	64.0	0.676	0.855
16	1800	20	35.5	0.83	64	178	17.5	17.85	39.5	35.35	57.0	0.622	0.788
17	2250	20	28.4	0.65	51.2	142	17.5	15.40	32.7	32.9	50.2	0.487	0.618

TABLE-30

Cost Estimates for the Separation of TiO_2, Using a Mixture of alum and Super Floc-330 as the Flocculant.

Cost of Chemicals:

The dosage of flocculant, mg/gm of TiO_2		Cost of chemicals, \$/mgd.
alum	Super Floc	
66	0	13.5
0	1.3	17.8
33	0.45	11.25

The cost of chemicals for a treatment with a mixture of alum and Super Floc is $\frac{13.5 - 11.25}{13.5}$ 100% = 16.5% less than that of alum treatment.

TABLE-31

Cost estimates for the treatment of effluent stream of a paper mill.

Basis: Q = 1 million gallons/day
x = 200 ppm of suspended solids

a = \$0.0225 / lb of alum
a = \$1.50/lb of Super Floc
c_2 = \$1.50/gallon
c_3 = \$1.0 / gallon
y = \$0.19 / minute

No	Overflow rate, gal/day ft^2	$\theta = \tau_F$ minutes	τ_S ideal minutes	Fraction of solids removed in an ideal settler	τ_S(actual)		m lb/lb	\$ Cost					Fraction of solids in the effluent steam	
					effy =0.75 1.8 τ_S ideal	effy =0.95 5.0 τ_S ideal		Chemicals	Capital effy =0.75	Capital effy =0.95	Total effy =0.75	Total effy 0.95	effy =0.75	effy =0.95
	Alum Treatment													
1	1100	3	58	0.93	104	290	0.128	5.8	20.65	56.0	26.45	61.8	0.70	0.885
2	1100	3	58	0.89	104	290	0.128	5.8	20.65	56.0	26.45	61.8	0.668	0.845
3	1100	3	58	0.986	104	290	0.257	11.6	20.65	56.0	32.25	67.6	0.73	0.926
4	1100	3	58	0.965	104	290	0.257	11.6	20.65	56.0	32.25	67.6	0.724	0.915
5	1100	3	58	0.99	104	290	0.385	16.4	20.65	56.0	37.05	72.4	0.742	0.94
6	1100	3	58	1.0	104	290	0.514	23.2	20.65	56.0	43.85	79.2	0.75	0.95
	Super Floc Treatment													
1	1100	3	58	0.77	104	290	0.00387	11.6	20.65	56.0	32.25	67.6	0.578	0.731
2	1100	3	58	0.87	104	290	0.00774	23.2	20.65	56.0	43.85	79.2	0.652	0.826
3	1100	3	58	0.91	104	290	0.0116	34.8	20.65	56.0	55.45	90.8	0.682	0.864
4	1100	3	58	0.97	104	290	0.0144	46.4	20.65	56.0	67.05	102.4	0.728	0.92
5	1100	3	58	0.95	104	290	0.0193	58.0	20.65	56.0	78.65	114.0	0.715	0.9

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