THE FLOCCULATION OF KAOLIN WITH POLYACRYLAMIDES

by

ADRIAN PATERSON

A thesis submitted to the Faculty of Engineering,
University of Cape Town
in fulfilment of the requirements of the degree of
Doctor of Philosophy in Engineering.

November 1982

This thesis is dedicated to my wife,

Cathy,

without whom it would not have been possible.

ACKNOWLEDGEMENTS

I wish to thank the following people who have been involved in this project:-

Firstly my supervisor Professor Oelof Heckroodt, who suggested the field of research and has been a source of guidance and encouragement as the work progressed.
Secondly Dr. Peter Harris of the Council for Mineral Technology (MINTEK) who was my liason officer at that organisation. His assistance in procuring equipment and in discussion was invaluable.
Mr. Bernard Greeves prepared the photographs for this thesis and contributed in the technical aspects of developing a method of floc photography.
Professor G. Marais of the Department of Civil Engineering and Dr. P. Mitchell of Organic Chemistry generously loaned equipment for the duration of the project.
Mr. E. Alston of Allied Colloids provided a range of flocculants and technical information about them.
Mrs. A. Squires digitized a number of floc photographs, prepared the initial typed draft of the thesis and performed countless tasks that helped in the final stages of the project.
The staff of Word Designs, Cape Town prepared the subsequent drafts of the thesis.

I wish to acknowledge the financial support of the Council for Mineral Technology and the University of Cape Town.

Ian Clark, Ken Salo and Grahame Fogel provided many hours of comradeship and support.

ABSTRACT

Flocculation occurs when high molecular mass organic molecules form bridges between particles, causing them to aggregate. This modifies the sedimentation properties of the mineral slurry. Thus classical measures of flocculation, among them the settled bed height and the supernatant turbidity, have tended to focus on the properties of the suspension rather than the flocculant.

The kaolin - polyacrylamide system is investigated in this study. In the literature review the development of surface charge, the electrical double layer and classical DLVO theory are discussed. The description of the properties of the kaolin is balanced by discussion of the behaviour of polyelectrolytes in solution, the adsorption of polyelectrolytes and attempts to extend the DLVO theory to include interactions with polymers. The importance of agitation in flocculation, the nature of turbulence in stirred tanks and the empirical description of stirred tanks is discussed.

The findings of the literature review suggested the development of a stirring system based on empirical stirrer criteria. Two systems were analysed and tested. An impeller stirrer was chosen as the most appropriate apparatus for the bulk of the experimental work. This consisted of the investigation of the flocculation of three homoionic forms of kaolin (Na^+, Ca^{2+}, H^+) with six flocculants. Experimental measurements include settled bed height, supernatant turbidity, floc photography and a method of determining the floc size/density relationship from the analysis of single floc settling data. The effect of pH variation and changes in the ionic strength is also considered using a nonionic flocculant and a highly anionic flocculant.

Floc photography used in conjunction with classical measures of flocculation and flocculant adsorption allows the description of the observed phenomena from the point of view of the interaction of the flocculant with the mineral surface. The findings and models of flocculation of other researchers are dicussed in the light of this description. The particular contribution of agitation is discussed.

Specific findings of this study include the following:-

1) The level of flocculant adsorption on H^+ kaolin decreases with increasing anionic character of the flocculant.
2) For singly valent homoionic kaolins a highly anionic flocculant shows a minimum in flocculant adsorption at pH 6 - 7 that is associated with the most stable flocs (under agitation) generated across the pH range.
3) Anionic flocculants do not flocculate singly valent homoionic kaolins at high pH even though substantial amounts of flocculant are adsorbed.

A model of flocculation based on the hydrodynamic volume of the flocculant molecule, its rigidity and the strength of bonding to the kaolin surface under conditions of shear is suggested.

Appendices give details of experimental methods. About fifty photographs and micrographs of flocs are included in the text. The bibliography has 125 references.

CONTENTS

CHAPTER 2. DEVELOPMENT OF EXPERIMENTAL METHOD

CHAPTER 3. THE FLOCCULATION OF KAOLIN

NOMENCLATURE

In a study of this nature inevitably mathematical derivations arise from a number of different disciplines. In order to develop a completely unambiguous nomenclature the familiar form of many common equations would have to be substantially changed.
To avoid this the nomenclature in this study has been divided into two categories:-

(a) Symbols arising from clay and colloid chemistry excluding hydrodynamic symbols

(b) Symbols arising from aggregation (collision) theory and hydrodynamics.

(a) Symbols arising from clay and colloid chemistry.

A = i. Hamaker constant
ii. a constant - refiltration theory
B = a constant - refiltration theory
C = capacity of the double layer
c_c = critical coagulation concentration
e = electronic charge
k = Boltzmann constant
n_i = bulk concentration of the counterion
Q = rate of refiltration through the flocculated bed
Q_o = rate of refiltration through the unflocculated bed
P_o = flocculant dosage
P_m = optimum flocculant dosage (theoretical)
P_e = dosage for the maximum refiltration rate
r = particle separation
s = thickness of the extended loop layer
T = absolute temperature
t = time
V = net energy of interaction
V_A = net energy of attraction
V_{aa} = adsorption attraction
V_e = energy due to the electrical double layer
V_R = net repulsive energy

V_{st} = steric contribution

V_b = bridging contribution

X = the amount of adsorbed polyelectrolyte

x = distance from the interface

Greek symbols

α = degree of dissociation

δ = the nominal loop length

ε = i. bulk dielectric constant

ii. nonionic energy of adsorption

κ = the diffuse layer thickness

θ = surface coverage

ρ = fraction of surface adsorbed polymer segments

σ_o = surface charge

σ_b = charge at the IHP

σ_d = charge at the OHP

ψ_o = surface potential; wall potential

ψ_b = potential at the IHP

ψ_d = potential at the OHP

ζ = zeta potential

(b) Symbols arising from hydrodynamics.

A = numerical constant

a_t = tank radius

b_{ij} = collision rate of particles i,j

C = numerical constant

d = floc diameter

D = diffusion coefficient

G = shear rate

G' = instantaneous velocity gradient

H = height of the liquid/air interface

k = wave number (turbulence)

k_d = wave number of the dissipation microscale

k_e = wave number of the macroscale

ℓ = breakup mode parameter

L = impeller diameter
l_e = Kolmogoroff macroscale
N = impeller speed (r.p.m.)
N_o = original particle concentration
N_t = number of free particles at time t
P = power input
Po = Power number
P_m = power input per unit mass
$p(d)$ = force required for floc rupture
r_{ij} = particle radii of particles i,j
Re = Reynolds number
Re_l = Reynolds number for the macroscale
Re_t = Reynolds number for a stirred tank
Re_λ = Reynolds number for the microscale
U = instantaneous fluid velocity
U = mean bulk velocity
u = instantaneous fluid velocity fluctuation
u' = root mean squared velocity fluctuation; turbulent intensity
V = floc volume
V_f = volumetric flow rate
v_{ij} = number concentration of aggregates i,j

Greek symbols

ε = average power input per unit mass; total energy dissipation
λ_g = dissipation microscale
μ = absolute viscosity
ν = kinematic viscosity
ρ = fluid density
η = Kolmogoroff microscale
τ = shearing force
τ_{crit} = critical shearing force

CHAPTER ONE

INTRODUCTION - LITERATURE SURVEY

CHAPTER ONE

1. INTRODUCTION

1.1 Definition of Terms

The term flocculation has many different and sometimes conflicting meanings. In different disciplines it may, for instance, be a synonym for coagulation or a distinctive term having an exclusive or inclusive meaning. Frequently, then, in defining what is meant by flocculation a researcher is establishing the academic territory that he will occupy. The complexity of the processes involved in the stabilization, dispersion and aggregation of mineral particles makes any definition immediately assailable from a number of different points of view. However some form of definition is necessary otherwise it is not possible without a new terminology to describe some of the observed phenomena.

Flocculation can be said to have occurred when a particulate suspension is aggregated by the formation of molecular bridges between the particles. By contrast to coagula, which are formed by modification of the interfacial electrical properties of the particles only, flocs are, in general, observably more stable under agitation as a result of the interparticle bridges. Thus in flocculation an important property of the flocculated suspension is the level of adsorption of the flocculant; while in coagulation it is rather the critical concentration of electrolyte that gives rise to the observable phenomena. Another property of flocculation is that its effectiveness or efficiency is dependant on the tenacity of the interparticle bridges and thus to properly investigate flocculating systems some assessment has to be made of the variables that affect the floc stability.

Thus when used in this study flocculation is a term that implies a contrasting behaviour to that of coagulation in a sense that requires a differentiation of mechanisms rather than a differentiation of the methods by which the resultant phenomena are measured. Those measurements of the properties of flocculated suspensions are referred to as 'flocculation parameters'. In this study they are the settled bed height and the turbidity of the supernatant liquor at a given time. They do not however allow a particular system to be distinguished as 'flocculating' or 'coagulating' as these parameters can equally well be measured in coagulating systems. Rather the sense in which 'flocculation parameter' is used is, given that flocculant is added, it allows an assessment of the extent to which flocculation has taken place. Of course, under certain conditions, flocculation does not occur. In this situation it is difficult to determine whether the suspension has maintained a degree of dispersion which was already present, in which case it could still be considered to be dispersed; or whether the flocculant has in fact contributed to the stabilization of the suspension by being adsorbed on the mineral surface. This is a complex problem which is necessarily involved in the dynamic interaction of the flocculated suspension with the flocculant under different conditions of agitation. It is not possible to give an exclusive definition that separates the phenomenon of dispersion from that of stabilization but in general 'dispersion' as a term will refer to a suspension not treated with flocculant. A stabilized suspension will be one that has, after treatment with flocculant, become less likely to aggregate than a suspension identical except for the addition of flocculant. If this is not the case and flocculant has been added the two terms are used interchangably.

It is also necessary to distinguish the term 'stability' from the phrase 'floc stability'. The former refers to the condition of a suspension that will not aggregate because it is stable in terms of a qualitative or quantitative analysis based on the classical DLVO theory.

'Floc stability' refers to the resistance of a flocculated suspension to degradation by agitation. As such it is a comparative term that has been developed to meet the demand of assessing the results presented in this study. The term 'stability' by contrast arises from the empirical testing of DLVO theory, in particular, in systems which are coagulated by the addition of a critical concentration of electrolyte.

1.2 Structure of the Literature Survey

The literature survey has been organised in such a way as to relate the different disciplines and topics covered to the behaviour of the kaolin polyacrylamide system in particular. However, it has been necessary in the case of the discussion of approaches to colloid stability and hydrodynamics to begin with a fairly full treatment of the concepts involved in order to locate this present study within the wider scope of the two disciplines. The treatment of the hydrodynamic aspects was also demanded by the comparatively recent renewal of interest in this topic.

It was also important to review the role of inorganic polyions (particularly aluminium) to some extent in order to establish the uncertainties associated with kaolin as a material in particular with respect to the irreversability of some surface reactions and the uncertainty about the nature of the surface itself. This was necessary to balance the modelistic descriptions of behaviour that accompany a thesis that is concerned not so much with the nature of kaolin but the phenomenon of flocculation. In this study particular attention is paid to the ionic character of the flocculant placing, it is hoped, an emphasis on the role of the flocculant. This is evidenced by the discussion of its conformation in suspension, its adsorption and discussion of recent developments of stability theory. The emphasis of the latter part of the literature survey (1.3.10 and 3.1) is on the establishment of techniques of measurement of flocculation and their meaning. It suggests approaches that are then described in the experimental section of the thesis and thereby reinforces the interplay of the results of the present study and the research of earlier and contemporary researchers that has been examined.

1.3 Concepts in the study of colloids and flocculation with particular emphasis on kaolin suspensions.

1.3.1 Surface charge on kaolin

Kaolinite is a hydrous aluminium silicate of composition $Al_2O_3.2SiO_2.2H_2O$ (Grim).

It is composed of a single sheet of tetrahedral silica and a single sheet of octahedral alumina, sharing a common layer of oxygen atoms which hold the two sheets together. The crystal morphology, idealized as an hexagonal platelet, is built up of successive layers of silica/alumina sheets bonded together by hydrogen bonding between layers.

The considerable body of work on the bulk structure of kaolinite has been reviewed by Grim.

Of particular interest in this study are the minerological parameters that give rise to surface charge on oxide surfaces in suspensions.

1) Lattice substitution of Al^{3+} for Si^{4+} leaves the surface with a net negative charge, due to unsatisfied oxide linkages. Very small replacement frequences (1 in 400) would give rise to levels of surface charge that could account for the bulk of the cation exchange phenomenon.

2) Broken and unsatisfied bonds at the edges of silica alumina sheets give rise to charge. Two different types of charge can arise.

   a) Hydroxyls in broken silica tetrahedra would be ionized to form $Si-O^-$ causing a net negative charge on the lattice above about pH 2.5.

b) Exposed aluminium octahedral groups, accepting protons, would acquire a net positive charge at low pH and a negative charge above pH 9.

3) The third mechanism would be the ionization of surface groups. These reactions can result in positive or negative charge generation. In the case of silicates the isoelectric point is at a very low pH and therefore the Si-O$^-$ group tends to predominate. In the case of surface Al-OH groups the behaviour results in either positive or negative surface charge depending on the pH.

A further mechanism of charge modification is the specific adsorption of ions or polyions onto the surface.

The first mechanism of charge generation is not pH dependant.

At low pH the ionization of edge silica tetrahedra is unlikely, while the acceptance of a proton by the octahedral alumina is quite likely. Thus the edges achieve a net positive charge at low pH. At high pH this situation is reversed and the edge can have a net negative charge. These mechanisms of charge generation imply that H$^+$ and OH$^-$ are behaving as potential determining ions (PDI) (Hughes; van Olphen).

The simple mechanisms described above are complicated to a large degree by the solubility of aluminium and silicon species from the crystallite edges. Aluminium may also play the role of a "potential determining" ion in kaolin suspensions (van Olphen). The role of aluminium and its hydrolysis products has been the source of considerable discussion in the literature (Buchanan and Oppenhein, 1968, 1972; van Olphen; Hall 1965, 1966; Jepson, Jeffs and Ferris; Bolland, Posner and Quirk 1980, 1976; Smith and Emerson; Packham 1965).

Buchanan and Oppenheim were able to show that preferential solution of aluminium species takes place at low pH and since Al^{3+} is the most stable form of the ion to about pH 4.5, it can be argued that below this pH, Al^{3+} will act as a PDI for clay edges and may also act as a counterion on the clay faces. Thus clays at low pH that have long times in suspension may acquire an increasing Al^{3+} cationic character and in addition may have increasing positive charges associated with their edges due to specific adsorption of Al^{3+} species on negatively charged unsatisfied silica-oxygen bonds on platelet edges (van Olphen). It has been shown that increase in ionic strength will reduce the rate of alumina solution from platelet edges (Hall 1966) and that coagulation across the pH range can be achieved by addition of aluminium complexions. The importance of these findings, in this study, relate to the preparation of homoionic forms of the clay (see Appendix 1) and the experimental system chosen for measuring and interpreting flocculant adsorption and flocculation parameters. The role of aluminium will be discussed, where appropriate, in the section dealing with the electrical double layer around a kaolinite particle.

To summarize:

1) There are 4 mechanisms giving rise to surface charge on kaolinite surfaces. One is not pH dependant (substitution).

2) Oxide surfaces have H^+ and OH^- as "potential determining" ions and kaolin can under some circumstances have Al^{3+} as a "potential determining" ion.

1.3.2 Surface Charge in Coagulation

Of importance in the understanding of coagulation of kaolinite is the relative contribution of pH dependent and pH independent surface charge. Bolland, Posner and Quirk in a recent paper (1980) conclude that most of the negative surface charge is due to lattice substitution. In their experimental technique they specifically correct for Al^{3+} dissolution from platelet edges. However since they compute surface charge from their cation exchange data, and do not regard Al^{3+} as a PDI at pH 3, it is possible that they may have overestimated the role of Al^{3+} in balancing substitutional charge. However their net surface charge (corrected for Al^{3+}) is still strongly negative at pH 3 (Fig. 4d in Bolland Posner and Quirk, 1980). Mobility curves that show an i.e.p. (which is at least qualitatively related to net surface charge) place it in the region of pH 3 - 4.5 (Hall 1965; Buchanan and Oppenheim, 1968; Mori et al). It is clear that the contribution of lattice substitution is significant and probably the predominant mechanism of charge generation on kaolin surface. The fact that edge charge is positive at low pH has a profound effect on the nature of kaolin coagulation.

Noting, then, that the mechanism of charge generation is predominantly due to pH independent lattice substitution only modified to any degree by the development of positive charge below pH 7 (although positive charge may persist to pH 8.5 or 9 (Quirk; Bolland, Posner and Quirk 1977, 1980)) the surface charge, in the absence of specific adsorption is probably fairly constant above pH 7. The net surface charge is probably substantially balanced by adsorption in the Stern layer of Al^{3+} and protonation of exposed gibbsitic oxygens at a pH of 3 - 4.5, resulting in a zero mobility.

Williams and Williams have endeavoured to isolate the edge charge to compute the face potential. They estimate the p.z.c. of the edge to be at pH 7.2 using a linearized model of an aluminosilicate. These findings however could not be used to construct an effective model of the charge distribution on real kaolinite surfaces. They do however qualitatively compare with the work of Flegmann et al.

The consequences of the nature of charge development in kaolins will be discussed following an examination of the theory of the electrical double layer and a discussion of colloid stability in the presence of simple electrolytes.

The above analysis of the source of surface charge and its implications for understanding the cation exchange phenomena will be used in this study. It must however be held in tension with the study of Ferris and Jepson who critically examined the concepts involved experimentally under varied conditions. They concluded that the classical view of the origin of cation exchange (that is, isomorphous substitution and a contribution from edge broken bonds) should be re-examined. They found no permanent value of cation exchange at low pH. This result suggested that the contribution of substitutional charge in the system does not occur. This is in sharp contradistinction to the results of Bolland et al (1977, 1980).

They also note in their paper the strong binding of the hydrogen ion in the lattice in silanol groups, thus supporting the view of its role as a potential determining ion. However, their view of the kaolinite surface represents such a complex interaction of different interface phenomena that it is difficult to apply in a study of this nature. It is necessary however to be cautious in the application of the classical view at low pH.

This particular point of dissent also shows the importance, in careful studies, of being aware as far as is possible of the condition of the kaolin surface or at least reporting the type of treatment that it has undergone prior to its use as a testing material so that some assessment of its behaviour may be made.

1.3.3 The Electrical Double-Layer

The charge-potential phenomena which are associated with the interface between two phases have been explained to some extent by the electrical double-layer theory. In its classical form the theory was due to M.Gouy and Chapman independantly (Habib and J O'M Bockris). The applications and extensions of the theory have been extensively reviewed elsewhere (eg. Bockris, Conway and Yaeger; Napper and Hunter; Overbeek and Lyklema) and a short summary will be presented here of the elements specifically important to the present study.

The essential elements of the double layer (Lyklema, 1978) arise from:

1) Surface charge (σ)
2) Solution counter charge
3) The double-layer potentials (ψ)
4) Capacity of the double-layer (C)
5) Point of zero charge (p.z.c.)

The origin and nature of surface charge, σ , was discussed earlier. In solution the surface charge gives rise to a counter-charge which is provided by ionized species in the suspension. In clay systems there are two sources of counter charge, the major contributor being cationic counterions balancing surface negative charges and a smaller anion counterionic charge balancing surface positive charge, if present.

The theory of Gouy and Chapman considered the surface charge to be smeared out, and evaluated the potential at the surface as seen by a point charge approaching from infinity, as a function of ionic strength, electrolyte valence, and temperature.

Charge and potential are related by the capacitance of the system (Lyklema). In general only the differential capacitance is accessible and is defined $C = d\sigma/d\psi$.

The mathematical formulation is based on the Poisson-Boltzmann equation. The model can be summarized in terms of the variation of the potential, ψ , with distance from the interface, x, (Hughes, in Solid-Liquid Separation) such that:

$$\frac{d\psi}{dx} = -\left(\frac{8\pi n_i kT}{\varepsilon}\right)^{\frac{1}{2}}\left[\exp\left(\frac{ze\psi}{kT}\right) - \exp\left(-\frac{ze\psi}{kT}\right)\right]$$

Equation 1.1

Where k is the Boltzman constant

z is the valency of the counterion

n_i is the bulk concentration of the counterion

ε is the bulk dielectric constant of the liquid

e is the electronic charge.

The fall off in potential with distance can be shown diagramatically. (Figure 1.1 below.)

A simpler form of equation 1.1 can be transformed, Given that

$$ze\psi/kT < 1 \text{ or } \psi = 25 / 2 \text{ millivolts,}$$

we can write

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi$$

(Overbeek and Lyklema) Equation 1.2

if $\Sigma\, zen_i(\infty) = 0$

and $$\kappa^2 = \frac{4\pi e^2 \Sigma n_i(\infty)z^2}{\varepsilon kT}$$

Equation 1.3

Equation 1.2 can be solved

$$\psi = \psi_0 \exp(-\kappa x)$$ Equation 1.4

showing $1/\kappa$ has dimensions of length and is the value of x for which

$$\psi = \psi_0 / e$$ Equation 1.5

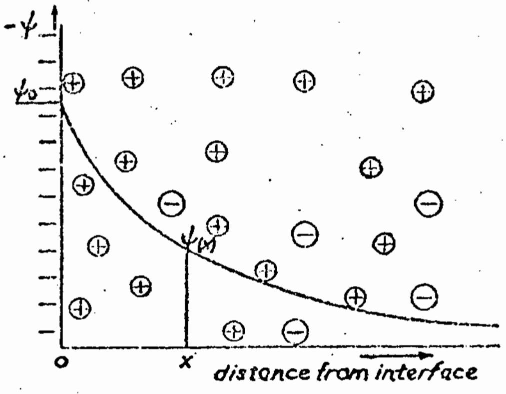
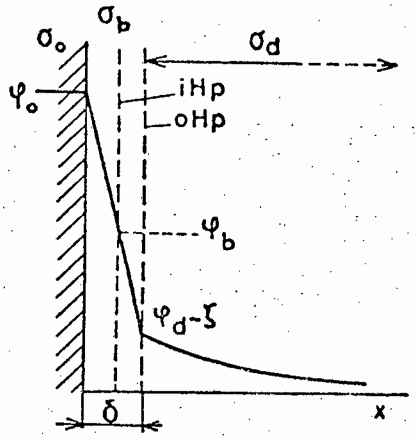
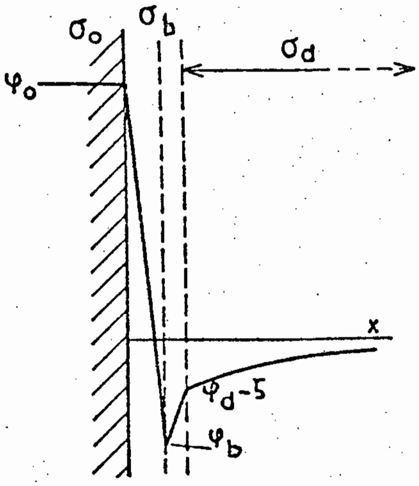


Figure 1.1: Potential drop and ion distribution as a function of distance from the interface according to GC theory. (after Overbeek and Lyklema)



A

Potential distribution in a double layer in the presence of specific adsorption of counterions. The inner- and outer Helmholtz plane are distinguished.



B

Potential distribution in a double layer with superequivalent adsorption of counterions in the Stern-layer.

Figure 1.2 A and B: Two situations that can arise at the interface in the presence of specifically adsorbed ions. Note the low potential at the OHP in both cases. (after Lyklema 1978, slightly modified)

For this reason $1/\kappa$ has become known as the "thickness of the double layer", or more accurately the diffuse layer thickness.

High ionic strengths (and high electrolyte valences) result in small values of the thickness that reflect the inappropriate assumptions of the Gouy-Chapman (GC) model. Similarly by using the Boltzmann equation an estimate of the ionic concentration close to the interface can be made. Those results, become meaninglessly high at high surface potentials (Overbeek and Lyklema).

The reason for this discrepancy is the GC assumption of point ionic charges.

Stern and later Grahame modified the GC theory close to the interface, by making provision for the finite size of ions, specific adsorption (chemical effects) and coulombic interactions (electrical effects).

In the CGS theory the diffuse layer develops because of the potential at the ionic centres of the counterions, rather than the potential at the interface.

Two types of interaction are identified:

1) Specifically adsorbed ions
2) Non specifically adsorbed ions.

In the case of the specific adsorption, the potential at the ionic centres, ψ_b, is due to specific chemical interaction with the surface and may raise or lower the wall potential, ψ_o, depending on the nature of the chemical interaction. The plane of the ionic centres is known as the Inner Helmholtz Plane (IHP). In the case of non-specifically adsorbed ions (those that maintain their hydration sheaths and therefore do not undergo specific chemical interactions) the absolute potential ψ_d is always lower than ψ_b and generally lower than ψ_o. The plane of the potential is called the Outer Helmholtz Plane (OHP). The whole region has been called the Stern layer.

The diffuse part of the double layer is then considered to develop as a result of the potential at the OHP, ψ_d, rather than as a result of the wall potential, ψ_o. The potential decay then tends to reflect more realistically the nature of the double layer since ion size has been accounted for to some extent in the adsorbed layer. Increases in ionic strength and valence tend to increase the population of the counterions in the Stern layer, resulting in lower values of ψ_d. This has the effect of compressing the diffuse part of the double layer; with increasing electrolyte valence compounding the effect.

In addition specific chemical interactions (as opposed to coulombic interactions) can be responsible for charge reversal on some surfaces. This has been shown to be the case for the Al^{3+} ion in kaolinitic suspensions in a number of studies (Hall 1966, Roberts et al)

It must be noted that non-specific adsorption cannot result in charge reversal.

The capacitance of the IHP and the OHP can be defined similarly to the capacitance, C, of the surface. The usefulness of capacitance is in giving an indication of the extent to which surface charge in screened. C tends to be increased by specific adsorption and reduced by organic additives (Lyklema). The stability of dispersions has also been assessed from the point of view of capacitance.

Below is a diagramatic representation of two situations that can arise at an interface in the case of specific adsorption. (Figure 1.2 above)

1.3.3.1 Specific Adsorption and Potential Determining Ions

An unresolved issue is the problem of analysing the potential determining role in oxide minerals as opposed to classical colloids like AgI (Healy 1971, in discussion; Levine and Smith 1971, in discussion) and whether they obey the Nernst equation as asserted by Healy or not as asserted by Levine and Smith.

However as Lyklema (1978) points out the description of H^+ and OH^- ions as potential determining in oxide systems is a qualitative statement. It is not possible to use the Nernst equation (a change in surface potential of 59mV per decade change in ionic activity) to find the surface charge since the shape of the σ_0 / ψ_0 curves for oxides are distinctively different from those for the model colloid AgI. This arises from the nature of the oxide surface which can be described by the site binding model and porous double layer model. However both these treatments in their quantitative aspects go beyond the scope of the present study. The potential determining role of ions therefore as referred to in this study is the qualitative action of surface charge generation and does not refer to the potential determining role of ions in the Nernst sense.

Studies of kaolin have indicated that hydrogen ions, hydroxylions and aluminium ions play a potential determining role. It is also clear that hydrogen, aluminium ions and hydroxylated aluminium complexes can behave as counterions for surface excess negative charge due to lattice substitution of aluminium for silicon. This is not a potential determining role.

Hydrogen, hydroxyl and aluminium ions can be considered to be potential determining when they occupy their normal lattice sites in an idealized kaolin crystallite, when in any other role they may be

i) specifically adsorbed, or
ii) behaving as counterions, or
iii) in the case of aluminium present as polyionic complexes in the non stoichiometric gel like layer (see 1.3.4)

In general specific adsorption (Habib and Bockris) depends on

1) Charge density

The amount of a specifically adsorbed ion increases with increase of wall charge of the opposite sign. Negative charges may adsorb specifically on negative interfaces.

2) Ion size

The greater the size of the ion the more specific adsorption it undergoes.

3) Ion type

Anions have a greater tendency to adsorb specifically.

4) Hydration

Ions with strong primary hydration sheaths undergo little specific adsorption. Thus large ions will adsorb specifically.

5) Specific adsorption increases with concentration of indifferent electrolytes.

6) It has been shown that specific adsorption increases with valency though this runs contrary to point 4. There does not seem to be a simple explanation for this phenomenon.

The CGS theory treats the interface as a smeared out charge or uniform potential. Recent developments have attempted to treat the surface as a net of discrete charges (Overbeek and Wiersma) but it is not considered appropriate to discuss these developments here.

1.3.4 Colloid Stability

Understanding of colloid stability has had two schools of interpretation approaching the subject from different directions.

The first is called the chemical school and the second is known as the physical school (Stumm and Morgan). Frequently the two schools have been at odds with each other, as, for example, in the Discussion of the Faraday Society on Colloid Stability (1966).

1.3.4.1 The DLVO Theory - The Physical School

When kaolin is suspended in water its bulk physical behaviour will be determined by the nature of the forces acting between the particles.

The theory of Derjaguin, Landau, Verwey and Overbeek (DLVO) considered this interaction as the sum of the Van der Waals forces, V_A, which are attractive and forces due to the electrical double layer (e.d.l.) which in general result in repulsion (V_R).

At any separation of the particles r_{ij} the sum

$V(r_{ij}) = V_A(r_{ij}) + V_R(r_{ij})$ (Equation 1.6) can be determined for particle pairs that are not perturbed by other particles.

The van der Waals interaction was calculated from the Hamaker constant, which is now known not to be a constant (eg. Ninham), and has the dimensions of energy. This constant was calculated on the basis of additive energies between pairs of atoms or molecules; assuming the energies to be proportional to the inverse sixth power of distance. (Lyklema 1978).

The forces resulting from the interaction of the repulsive forces between the electrical double layers were calculated from the Gouy-Chapman theory.

The sum of all the particle interactions at over the separation range can be computed

$$V = \sum_{i<j} V(r_{ij})$$

(Equation 1.7)
(von Mengen and Snook)

The e.d.l. repulsion decays exponentially and the van der Waals forces decay according to A^{-2} leading to a characteristic potential of force interaction curve.

Interaction curves, in general, have a maximum and a primary and secondary minimum (energy vs distance). A number of possible curves are presented diagramatically below: Figure 1.3 .

The maximum constitutes a repulsion at intermediate distances and can be considered to be the stability controlling element of the system. It has been likened to a potential energy barrier. In general an increase in electrolyte concentration reduces the height of the maximum, decreasing stability, since interaction can then take place at the primary minimum. The valence of the counterions can also be shown, from the theory, to be of great importance. An empirical measure of the electrolyte concentration, c_c, required to induce coagulation has been shown to decrease, according to a z^6 power law. This can be seen from the DLVO equation for the critical concentration of electrolyte required to destabilize the suspension (Lyklema 1978):

Equation 1.8

$$c_c = \frac{8 \times 10^{-36}\{\tanh(ze\psi_d/4kT)\}^4}{A^2_{11(2)}z^6}$$

where $A_{11(2)}$ is the Hamaker constant for two like particles 1 in a medium 2. This is the DLVO formulation of the Schultz-Hardy rule. Gregory, in a review, pointed out that the theoretical basis of the z^{-6} rule is weak and shows that, empirically, log c_c plotted against the counterion charge gives a linear dependance. This was recognised by Matijevic (1965) who showed that for the z^{-6} rule agreement was good for $z = 1$ or 2 but that the deviation for higher counterion charges is substantial.

The DLVO theory has provided a basis for understanding stability criteria for colloidal suspensions in a qualitative sense. The phenomena associated with the kaolin/water/electrolyte system can be described. In addition recently (Overbeek 1977, 1980) attempts have been made to modify the theory to incorporate the effects of macromolecules on the stability of colloidal suspensions. These phenomena will be discussed in a later section.

1.3.4.2 The Chemical School

The chief emphasis of the chemical school has been to consider specific chemical changes in solution (sometimes involving a pH change of 0.1 of a unit) and their effect on colloid stability. This has required consider-

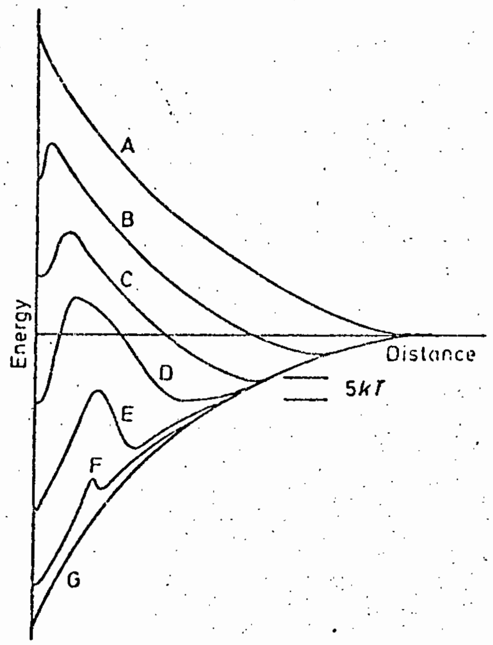


Figure 1.3: A set of potential of interaction curves (energy) B, C, D, E, and F that represent different possible solutions of the repulsion curve (A) and the v. d. Waals attraction (g). B, C, and d represent situations of net repulsion and E and F net attraction. Note the development of the secondary minimum. The 5kT energy level is indicated to represent the energy the particles possess by virtue of Brownian motion. (after Hughes)

able investigation of the behaviour of polyvalent species in solution. It is not appropriate here to detail the "approach" of this school, but rather to examine some of the criticisms of the DLVO theory that arise from their studies.

The proponents of the chemical theory, Tezak and his students, in particular Matijevic have made considerable progress in relating colloid stability to phenomena such as ion exchange, surface coordination of adsorbed species and chemisorption. In discussing the DLVO theory Matijevic (1977) states "The DLVO theory has also had negative effects. The situation (at the interface) is so complex that only the simplest systems can be handled .... These limitations (the use of the Debye-Huckel theory of strong electrolytes) have led scientists to attempt to test the predictions of the theory by matching the colloidal sols studied experimentally to the theoretical model as closely as they could ....."

More recently Lyklema (1981), discussed the problems that are involved in setting up reliable tests of the DLVO theory. He suggests that the DLVO theory is correct under the conditions for which it was derived, which are

- dilute sols, to enforce the true generation of average potentials (energies)

- only van der Waals attraction and double layer repulsion must operate

- the colloidal particles must be of a simple geometry

- the double layer must relax rapidly upon overlap to ensure thermodynamic equilibrium

A particular criticism of the theory is that essentially diffuse double layer conditions do not exist near the electrolyte concentrations that are required for coagulation. In metal-oxide systems ψ_o can be as high as tens of C/cm^2 but ψ_d is seldom more than a few C/cm^2. Thus the contribution of the diffuse part of the double layer under conditions of destabilization is small. The DLVO theory was developed for diffuse layers ($\psi_o \sim \psi_d$) with ψ_o high. This has been shown not to be the case. Thus c_c is now not considered proportional to z^{-6} but to z^{-2}. The earlier interpretation must be replaced with a dependence on z^2 (due to increasing electrolyte valence) and the increasing effect of specific adsorption (a chemical effect) leading to a potential variation of the fourth power, ψ^4. It is clear therefore that the dependence of the stability criteria on electrolyte charge is an indirect effect that is due to specific adsorption phenomena at the IHP. This understanding can go some way to explain the findings of Williams and Williams - that zeta potential computations based on estimations of surface charge were too high by an order of magnitude, as would be the case if the results of Bolland et al (1980) were compared with mobility data.

Another profound source of criticism of classical DLVO theory comes from attacks on the assumptions of continuum models especially at distances less than 30 Å from the interface. The continuum models below this value are subject to many criticisms, particularly with respect to the "subtle forces" known as structural forces and hydration forces (Lyklema 1981). These criticisms are valid when salts are present. Lyklema (1981), in particular shows the basis and relationship of these forces to classical DLVO theory and indicates their range of interaction (generally about 1nm). Another criticism of the e.d.l. theory in particular is the ad hoc manner in which modifications of the theory have been introduced. These are discussed by Ninham. These cogent criticisms represent important caveats to the application of the theory, particularly in the incorporation of further sources of attractive and repulsive potentials of interaction.

Despite these problems Overbeek (1980) has recently extended the DLVO formulation by introducing modifications that account for specific adsorption in the Stern layer. In particular he has assigned an increasing specific adsorption potential with electrolyte valence to account for the measured values of c_c at high counterion charge that were overestimated in the original theory with the z^{-6} dependence.

1.3.5 Colloid Stability in Dilute Kaolin Suspensions

The general view of the electrical double layer allows qualitative predictions of suspension behaviour to be made in different circumstances. In general the potential at the OHP (if we assume that the zeta-potential is associated with this potential) is quite low for kaolin (generally never greater than 60mV). This suggests that the failure of the GC theory for 1:1 electrolytes at high surface charge densities will not be the case for kaolin.

Thus simple GC theory could be used to explain most of the phenomena associated with Na^+ and K^+ kaolins, since little specific adsorption is expected if counterion concentrations are not excessive. This simple model breaks down with increase in electrolyte concentration. In the case of H^+ kaolinite the double layer model is more complicated as H^+ is not only a counterion but also plays a potential determining role (that is, directly modifying surface charge rather than balancing it). Thus charges on the surface that might have been electrically balanced by, say, non-specifically adsorbed Na^+ may be balanced by specific adsorption of H^+, which operates as a PDI. This may result in a net positive charge in the adsorption area. Thus in balancing surface charge (certainly on the edges of the platelets) the hydrogen-ion can be expected to reduce the surface charge density of negative charges extremely effectively.

In addition counterionic action on the faces by the ion occurs.

The generation of two types of diffuse layer of opposite charge and the resultant coagulation of the clay in the classic card house (face-edge association) structure (van Olphen; Swartzen-Allen and Matijevic; Flegmann et al) can occur under these circumstances.

A detailed analysis of the types of particle association in kaolinite suspensions has been made by Flegmann, Goodwin and Ottewill. Using a model based on the DLVO theory they showed that the barrier to face-face association in kaolin is always high. At pH 3-4 there is a net attraction resulting in face-edge association. At neutral pH, close to the p.z.c. of the edges (Williams and Williams; Nicol and Hunter; Flegmann et al) edge-edge association is favoured in the scheme of Flegmann, while Nicol and Hunter infer from their data a stronger type of face-edge association through hydroxyl adsorption on the platelet faces. This mechanism is less likely if the surface charge analysis of Bolland et al (1980) is taken into account. This work infers very low levels of anionic adsorption at neutral pH and maintains that substitutional defects in the platelet faces will mean a substantial negative charge on the face at all pH's.

This is an important feature of the colloidal behaviour of kaolin, since the instability as assessed by DLVO theory is enhanced by the amphoteric nature of the edge charges. With doubly charged ions and ions of high atomic number the likelihood of specific adsorption in the Stern layer is increased, this results in a reduction in ψ_d,which determines $1/\kappa$ the thickness of the double layer; and in addition, the diffuse layer potential decays more rapidly than with singly charged counterions. As a result Ca^{2+} kaolin suspensions are likely to be less stable than Na^+ kaolin.

The ambiguous role of the aluminium ion and pH sensitive aluminium species has been discussed with reference to the surface charge phenomena of kaolin. It is important to note that the time dependant solution of alumina from crystallite edges and the pH dependant potential determining role of aluminium ions is likely to complicate experimental investigations of kaolin colloidal suspensions. The solution of alumina from the edges at low pH, will result in the ion playing a potential determining role on the edges (essentially generating positive surface charge by protonation of Al - O^- species) (van Olphen) and it will have a counterion function, probably with a high degree of specific adsorption on the faces. The net effect, a compressed diffuse layer and a low ψ_d, will promote coagulation of the suspension. Thus where solution of alumina is not suppressed (as it can be by increasing electrolyte concentration) (Hall 1966) there will be a time dependant modification of the suspension behaviour of the clay, generally termed "aging". It has been shown that increased aluminium ion concentration in kaolin suspensions inhibits the solution of silica and silicateous species (Ferris et al).

As the pH increases the equilibrium aluminium species (neglecting coordinated H_2O) changes in the order

$$Al^{3+} \rightleftharpoons Al(OH)^{2+} \rightleftharpoons Al(OH)^{+}_{2} \rightleftharpoons Al(OH)_3 \rightleftharpoons Al(OH)_4^- \rightleftharpoons$$

and so on (Gregory 1978). In addition multinuclear hydrolysis products can be formed of which $Al_4(OH)_8^{4+}$ and $Al_8(OH)_{20}^{4+}$ are known (Hall 1965; 1966) These have higher charge than the original ions and specific adsorption may result. These polynuclear species are kinetic intermediates, but the low rates of dissolution involved can result in their persistence in solution for long periods. Of the hydrolysis products generated $Al(OH)_3$ is essentially insoluble and may precipitate on the kaolin edges or faces forming an amorphous gel-like layer. Jepson et al have postulated the formation of gel-like layers of unspecified aluminosilicates on clay crystallites.

The relative solubilities, and the time the various species endure in suspension will contribute to the time dependant nature of kaolin suspension stability, but in general it can be expected that the species will establish some form of equilibrium with the gibbsitic exposed edges and with any soluble gel-like aluminosilicates. At higher pH the likelihood of specific adsorption of aluminium hydrolysis products is reduced since the kaolin and the hydrolysed species have the same charge (which does not prevent, but inhibits, specific adsorption) and the fact that the kaolin charge density is increased as a result of the potential determining role of the OH^- ion .

In the earlier discussion of the nature and origin of surface charge it was noted that below pH 7 the charge drops to the p.z.c. at about pH 3.5. This results in a reduced diffuse layer thickness as a result of a lower ψ_d (which is more closely related to ψ_0 at low surface charge densities).

Thus the driving force for destabilization at low pH finds its impetus not only in the face-edge association but also in the reduction of the V_R term that controls the repulsive forces in classical DLVO theory by

1) specific adsorption of aluminium hydrolysis species and

2) surface charge density reduction by H^+ acting as a PDI.

It is appropriate at this point to discuss the nature of the Stern layer in oxide systems.

James and Healy (cited in Wiese, James and Healy) found that cations adsorbed at the oxide water interface are separated from the interface by one layer of water molecules, which suggests that ions maintain their primary hydration sheath when specifically adsorbed. This suggests that the IHP must be located at a distance $2\ r_w + r_i$ from the interface (where r_w and r_i are the radii of the water molecule and the ion respectively). The outer Helmholtz plane (OHP) is located at the centre of fully hydrated cations. The population of the Stern layer tends to increase with increase in concentration of electrolyte. If the electrolyte is "indifferent", (that is its only contribution to suspension destabilization is reduction in $1/\kappa$), the increase in concentration results in an increasing condensation of counterions in the Stern layer (Kitchener 1978). This is a non-specific effect that is related only to the surface potential, ψ_0 and the ionic strength, and will therefore take place at the OHP. Not all electrolytes are indifferent in kaolin suspensions and, in general, increase in atomic number and valency increases the likelihood of specific interaction at the IHP. This modifies the position of the p.z.c. (Wiese, James and Healy), generally shifting it to higher pH values, because of the reduction of surface negative charge by specific chemical interactions.

In general therefore it is noted that kaolin colloidal suspensions are destabilized

1) at low pH, by reduction of surface charge density

2) in the presence of high concentrations of electrolytes

3) by specific adsorption of high valence ions and complex hydrolysed ions

4) by the different nature of the diffuse layer on the faces and edges of kaolin at low pH leading to card house coagulation.

1.3.6 Some thoughts on the electrokinetics of kaolin suspensions

When subjected to shear forces the colloidal particle does not carry with it the whole diffuse layer. Rather a separation occurs at what has been termed the shear or slipping plane. The mobility of colloidal particles subjected to a potential difference has been related by the equation of Smoluchowski to the potential at the slipping plane, called the zeta potential, ζ . The location of the slipping plane, and its relationship to the modelistic potentials of the GCS theory has been the source of considerable debate. (Hunter and Alexander, Lyklema 1977, 1978; Hunter and Wright; Hunter).

Overbeek and Wiersma in their review state "Nevertheless the present state of the theory leaves a number of things to be desired. As outstanding examples we mention .... the difficulties concerning the inner region of the double layer (which make calculation of charge from the zeta potential rather hazardous) ..."

However specific studies of some kaolinite systems, particularly those of Hunter and Alexander indicate that the zeta potential can be equated with the potential at the OHP, ψ_d or very closely correlated with it. Thus they were able to correlate change in zeta potential with ionic strength to give results that fitted the available data better than the assumption of constant charge density in the Stern layer. These results have been confirmed for the silica/water interface by Wiese, James and Healy. Hunter later extended this approach by suggesting that the plane of shear corresponds to the plane of closest approach of the diffuse double layer ions. Many other studies, reviewed by MacKenzie, assume some relationship between the ζ-potential and ψ_d. Approaches that have not located the slipping plane at the OHP were based on the Eversole and Boardman approach (cited by Hunter and Alexander) which did not use the GCS model, but a GC model. The work of Overbeek and Lyklema which also suggested the slipping plane was in the diffuse layer was discussed and refuted by Hunter.

The basic problems of relating the ζ- potential to the surface potential are even more complex as has been shown by the analysis of Hunter and Wright (also Lyklema 1978). They have shown that the location of the slipping plane at the OHP ($\zeta = \psi_d$) and the location of the slipping plane in the diffuse layer ($\zeta > \psi_d$) give values of ψ_0 as calculated by the present theory in error by more than 100%. They suggest that the problems may be solved by postulating a concentration dependant ψ_0, that can also vary with the change in activity of PDI's with pH variation. Lyklema (1978) suggests the introduction of the concept of the porous double layer in conjunction with site binding models to solve the problem.

Therefore it is noted that while the ζ-potential is of great use in the study of coagulation, and can give an assessment of ψ_d, the exact relationship between the electrokinetically derived ζ- potential and the electrostatic model of the electrical double layer is unclear.

The variation of ζ- potential with pH for kaolinite has been determined by a number of workers (Hall (1965), Williams and Williams, Mori et al) and their results are shown below (Figure 1.4).

As can be seen the p.z.c. found by the different workers shows some variation, which may be related to the condition (aging history) of the kaolin. However the pzc. range can be considered to be between pH 3 and 4.5. This is confirmed in the assumptions made in the theoretical work of Bolland, Posner and Quirk (1979) who set the i.e.p. at pH 3.5. The results show that below the p.z.c. the net surface charge is positive.

For kaolin the charge density at the OHP measured from ψ_d was about 2% of the surface charge density calculated from the cation exchange capacity. (Hunter and Alexander). Their inference was that the majority of counterions were in the Stern Layer.

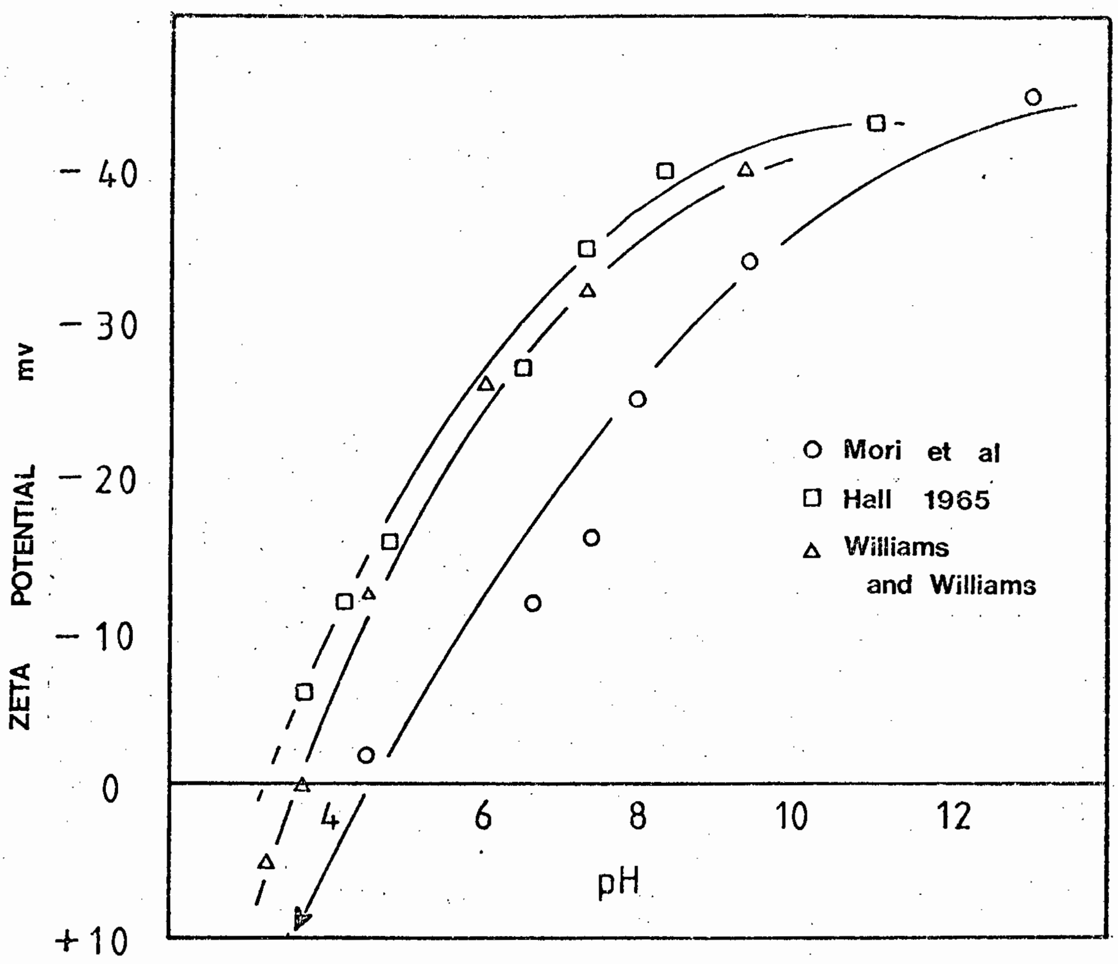


Figure 1.4: Variation of the zeta potential of kaolin with pH. These results are redrawn from Mori et al; Hall 1965; and Williams and Williams.

1.3.7 Polyelectrolyte Configuration in Suspensions

It is necessary to establish the configuration of macromolecules in solution if a true picture of the physico-chemical interactions at the interface are to be described. Akers (1971) in a review, discusses some of the phenomena as does Black (1960), relating the configuration to the understanding of flocculation. In addition a broad discussion of the development of polyelectrolyte chemistry that helps clarify the whole field and the present state of the science is available (Overbeek 1976).

For nonionic macromolecules the configuration is determined by the power of the solvent. In good solvents the molecule will have a randomly coiled extended configuration associated with a high solution viscosity. In poorer solvents the polymer molecule will assume a highly coiled configuration marked by internal chain interactions, which is accompanied by a drop in solution viscosity.

In situations where polyelectrolytes are involved the configuration changes are more marked. For example an anionic polyacrylamide in an acidic solution will behave essentially as a nonionic molecule (i.e.its properties will be determined by the efficiency of the solvent). However in an alkaline solution the carboxyl groups become ionized resulting in a net negative charge on the chain. The result is an extended more linear configuration with a degree of rigidity imparted by the electrostatic repulsion between groups. This results in an increase in viscosity of the polyelectrolyte solution.

The extent then to which a given polyacrylamide is hydrolysed will profoundly affect its dimensions in solution with change in pH. A polyacrylate is 100% dissociated at pH 6 (Michaels and Morelos). About 15% of the acrylate groups will be ionized at pH 4.

In the case of a polyacrylamide above pH 6 it will be essentially 100% ionized (Michaels and Morelos) or above pH 7 (Slater, Clark and Kitchener) with the percentage of ionized carbonyl groups falling to less than 10% at pH 4.

Thus a 40% anionic polyacrylamide can be expected to have at pH 6 about 1 in 3 segments ionized resulting in considerable internal repulsion, which will cause the chain to become extended and considerably more rigid. At pH 5 the same molecule will have about 1 in 10 segments ionized and the chain therefore will be both less extended and less rigid. Increase in electrolyte concentration tends to swamp the ionic charges and in the limit reduce the polyelectrolyte coil to an essentially nonionic conformation. At pH 6 a 10% anionic polyacrylamide will have about 1 in 12 groups ionized and about 1 in 40 at pH 5. Thus the configuration would be similar for the 10% anionic polyelectrolyte at pH 6 to the 40% anionic one at pH 5.

The role of simple electrolytes in macromolecular solutions. In the case of nonionic macromolecules electrolytes could only act by reducing the interaction between the solvent and the molecule, leading to a reduction of the molecular volume with increasing ionic strength, ultimately followed by precipitation of the macromolecule.

This was studied by Roberts et al. It was shown that significant doses of aluminium ions resulted in sedimentation of nonionic polyacrylamide above a critical dosage of the flocculant. Precipitation took place at pH 5, but not at pH 3, which suggests that it may be due to complex aluminium hydroxy species interacting with the polymer to produce an insoluble product. In the case of anionic polyacrylamides sedimentation also took place at pH 5 but at higher concentrations of aluminium ions and higher polyelectrolyte concentrations. This could be explained by the necessary charge neutralisation of the molecules of anionic polyacrylamide before precipitation requiring higher dosages of aluminium ions.

A technique used in this study to determine residual flocculant concentrations in solution depends on the turbidimetric determination of precipitated polyacrylamides (Macefield). Some researchers have indicated that charged species may crosslink with linear charged polymers and thus enhance their ability as flocculants (Black 1960).

Electron microscope studies have indicated that tangled coils of polyelectrolytes may persist in solution for long times and be responsible for bridging phenomena. In particular the work of Richardson and Rochow separately, on high molecular weight polymers (polyacrylamide and polyacrylonitrile) showed that bridges had a fibrilar morphology that had dimensions indicating that the fibrils were composed of tangled chains of polymer molecules.

Ries and Meyers independantly, later showed micrographs of polystyrene latex apparently joined by fibrilar bridges of PAM, with latex particles particularly associated with triple points. Though Ries and Meyers work was viewed with some scepticism (Napper and Hunter) Shyluk and Stow showed that aqueous polyacrylamide showed a two stage aging process associated in particular with a decrease in viscosity which would be consistent with the postulated mechanism of fibril disaggregation. This aging was accelerated by agitation, decrease in concentration and elevation of temperature. In addition the effectiveness of the polyacrylamide as a flocculant was reduced, as measured by the rate of subsidence, with flocculant aging. If this tanglinq/untangling phenomenon does not occur the reduction in flocculation ability and viscosity may be due to chain scission.

The view that flocculants may be highly tangled will complicate the analysis of the interaction of the flocculant with mineral surfaces, particularly with a view to the analysis of

i) the amount of polymer interacting with mineral surfaces
ii) the scale of the interaction in modelistic terms.

These phenomena will be discussed further when the interaction of mineral particles with flocculants (rather than flocculant configuration) is specifically discussed.

1.3.8 Adsorption of Polymers

It is not appropriate to discuss fully here the theoretical treatments of polymer adsorption. The reason for this is that the complexity of the adsorption process and the long times to equilibrium, combined with the special nature of the phenomena of flocculation make the distance between any full description of macromolecular interactions with particles in flocculation and the present state of the theory sufficiently large to merit only a superficial description. (Gregory 1978b).

In a review Stromberg compares and contrasts the theories of Silberberg and the work of Simha, Frisch and Eirich (SFE).

The picture developed of macromolecule adsorption is one of adsorbed "trains" of monomer segments separated by polymer "loops" extending into the bulk liquid phase. The model of Silberberg describes variations in the fraction of segments in adsorbed trains and loops under different conditions. An important finding of Silberberg (1962a,b) was that the adsorption energies to produce large numbers of adsorbed segments could be quite small. The apparent irreversibility of macromolecule adsorption was explained by this finding, as was the high level of adsorption from dilute solutions which results in the high affinity isotherm. However, these theoretical models describe equilibrium situations on infinite lattices and this makes their application difficult in the study of flocculation since flocculation is a process which may be complicated by the similarity of macromolecule sizes and particle dimensions (Vrij, Gregory 1973). In addition there is some doubt as to whether adsorption of flocculant to produce optimal flocculation constitutes a thermodynamic equilibrium (e.g. Jankovics). This will be pursued in the discussion of hydrodynamic influences on polymer adsorption. The theory has not, until recently, effectively considered polyelectrolyte adsorption as a generalization of the equilibrium theories of nonionic macromolecular adsorption.

This gap has been filled to some degree recently by the treatment of Hesselink who extends the work of Hoeve and Silberberg to include the adsorption of polyelectrolytes. The following discussion depends heavily on this work.

The electrical and non-electrical contributions to the adsorption are treated separately. The essential elements of the theory are discussed topically; the nature of the isotherms, the effect of polymer concentration, the effect of original surface charge, the effect of salt concentration and the degree of dissociation and molecular weight of the polyelectrolyte. The properties of the adsorbed layer are then examined. The measurable parameters of the theoretical treatment are ρ, the fraction of segments adsorbed; the nonionic energy of adsorption per segment ε ; the surface charge, σ , the degree of dissociation, α ; and other parameters, such as the surface coverage by adsorbed polymer, θ ; and the thickness of the loop layer, s .

i) At low but increasing polymer concentrations the fraction of the interface θ , covered by polymer increases slowly but, ρ , the number of adsorbed segments remains constant, i.e. the expected polymer conformation is a thin flat layer. At higher values of θ there is a fairly abrupt increase in the number of polymer segments in loops, resulting in a thicker polymer layer. The transition is sharper with increasing chain length.

ii) The adsorption of a negative polymer on a positive particle is, in general, higher than on a neutral particle, especially if the adsorption energy, ε , is low. Negative surface charge can inhibit and exclude adsorption of anionic polyelectrolytes if ε is low; but a high ε tends to mask variations in surface charge to a large degree.

iii) In general, increase in ionic strength increases adsorption. This is because of reduction in electrostatic barriers to adsorption. (This is also discussed by Gregory (1978b)). However, when charge interaction is the main reason for adsorption the adsorption will tend to decrease.

At high ionic strengths salting out effects can be important and adsorption is therefore increased. (Roberts et al).

iv) In general the amount of polyelectrolyte adsorbed, X, should decrease with increasing degree of dissociation, α . Hesselink explains this phenomenon from the viewpoint of low computed values of surface coverage for high degrees of dissociation while experimentalists cited by him attributed this to the high hydrodynamic volume of the coil.

v) The adsorption phenomena are almost independant of molecular weight with respect to the surface coverage. However the amount of polyelectrolyte adsorbed increases markedly with increase in molecular weight in the low m.w. range (1 000 - 30 000 amu). The picture at high molecular weight is less clear since the possibility of nonequilibrium effects is increased. Hesselink presents a summary of the properties of the adsorbed layer in terms of fraction of interface covered, fraction of segments adsorbed, surface charge density and the thickness of the adsorbed layer.

This formulation has the virtue of suggesting to the experimentalist simple tests of the qualitative elements of the theory. In particular, in the study of polyelectrolyte adsorption as related to flocculation, an assessment of the nature of the interaction of the flocculant with the mineral surface can be made by changing the degree of hydrolysis of the flocculant and noting the effect of this change on the levels of adsorption of flocculant. In addition, polyelectrolyte configuration can be manipulated by varying the pH, thus providing an assessment of the effect of configuration (properly interpreted with reference to hydrolysis of simple electrolytes and e.d.l. variations) on the adsorption of the polyelectrolyte.

It is necessary to be cautious, noting that Hesselink developed his treatment for 1 : 1 electrolytes (to avoid the complications of complexing in the Stern layer) and also that the bridging phenomena associated with flocculation may be non-equilibrium, and may therefore require careful interpretation.

Of importance in the study of adsorption - flocculation phenomena is the effect of the adsorbed trains of segments and the extended loops on the predictions of the DLVO theory, in particular the manner in which the V_A and V_R terms are modified.

The problem was set out in a recent paper by Overbeek (1977). Contributions to the V_R term arise from the reduction in available conformations of extended loops when the loop length (s) is less than the particle separation. This is known as the volume restriction effect. In addition when extended loops from two different particles interact the local increase in concentration gives rise to repulsion. This is the osmotic effect. The osmotic effect is quantitatively greater. Repulsion increases with molecular weight, solvent quality (which affects coil dimensions) and increase in concentration of polymer and solid.

Lyklema in a recent review (1978) argues that polymer adsorption reduces surface charge if desorption of counterions takes place in the Stern layer. This would not happen in the case of an anionic polyelectrolyte approaching a negatively charged surface. In the case of neutral macromolecules there is some doubt whether nonionic interactions with the surface would exclude, in particular, specifically adsorbed species at the

IHP. Lyklema suggests the inclusion of a term V_{sr} in the classical DLVO theory to take account of specific steric interactions of macromolecules adsorbed on surfaces. The V_A term is increased due to the increase in the effective radius of the particles due to adsorption, since the van der Waals attraction is considered to act from the new surface generated by polymer adsorption (Gregory 1978b). When considering the specific types of interactions that give rise to flocculation it is probable that the specific modifications of DLVO theory do not account for all the observed phenomena, particularly when the bridging theory of Ruehrwein and Ward is considered. However, where flocculation does not occur, e.g. stabilization by macromolecules, it is probable that the modified DLVO theory can be used. In particular the location of the shear plane (probably located at some distance from the Stern layer in these systems) with respect to the extended polymer loops, will determine whether bridging will occur or not. This has been depicted diagramatically by Gregory (1978b). (Figure 1.5)

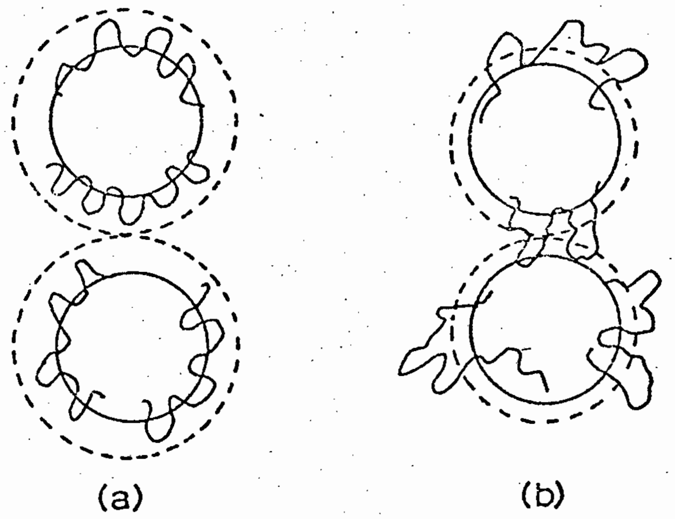


Figure 1.5: Bridging can be inhibited by the position of the shear plane.
(a) No bridging is possible since the polymer is in the unsheared layer.
(b) Reduction in the thickness of the Stern layer or the prevention of polymer collapse facilitates bridging.

The nature of the interactions giving rise to flocculation, as distinguished from coagulation, can now be discussed and thereafter the kinetics and hydrodynamics of these systems. This knowledge will permit the discussion of techniques of measuring flocculation and the examination of relevant literature concerned with experimental flocculation studies.

1.3.9 Flocculation

The mechanism of bridging flocculation was first described by Ruehrwein and Ward in 1952 (Gregory 1978a). Since that time considerable progress has been made in understanding flocculation processes and their relationship to the process of coagulation. A number of reviews are available (Gregory 1978a); Somasundaran; La Mer and Healy (1963); Napper and Hunter; Akers (1971); Vincent, Black (1960); Kitchener (1978)). In addition there are a number of studies on stabilization with polymers that provide a useful basis for comparison and evaluation (e.g. Stromberg), in water treatment (Stumm and Morgan) and more fundamental papers focusing on the nature of stability with reference to the DLVO and chemical theories of colloid stability.

Adsorption of polymers is a complex process that results from four types of interaction in the systems to be discussed here.

1) Van der Waals attraction
2) electrical double layer forces
3) steric forces associated with adsorbed polymer layers
4) bridging.

Flocculation in this study refers to those systems where bridging events critically determine the nature of the aggregated suspension, though modifications can be expected in all the terms of the "stability" expression. Somasundaran suggests the expression:

$$V = V_A + V_e + V_b + V_{sr} \qquad \text{Equation 1.9}$$

Where V_A is the Van der Waals attraction
V_e is the electrical double layer force ($\sim V_R$)
V_b is the contribution of bridging
V_{sr} is the steric contribution.

This expression is not without problems. In particular it is not clear what the nature of the forces generating the term V_b are. Further a formulation such as this stability criterion assumes that some equilibrium is established that can be characterized by definitive V_b and V_{sr} terms. The introduction of the steric term can be defended on thermodynamic grounds since the volume restriction effect and the osmotic effect can be described in terms of their free energy contributions to stability (Gregory 1978, Lyklema 1978, 1981). However the essential nature of a bridging event is that adsorption occurs on two surfaces that are not on the same particle.

In Fleers' description, reviewed by Vincent, the essential elements of bridging, in thermodynamic terms, consist of:

1) an 'adsorption attraction ' V_{aa}, for all loops of nominal length δ where δ is smaller than the particle separation, b,

2) a steric repulsion as a result of a loss of configurational entropy when a loop becomes two bridges on adsorption, and

3) a mixing term, which will result if complementary loops are generated at the second surface.

The combination of these terms results in a maximal attraction value of V_{aa} at $b = \delta$ which then reduces as b gets smaller and the configurational entropy is reduced. Above δ , V_{aa} decays rapidly as less adsorption is taking place. The "bridging contribution", V_{aa} is not easily included in the steric term.

The attraction that is described is only true for materials that are coated with flocculant. Thus any steric contributions are consquential to bridging. In any event the formulation has only a qualitative value as an essential element of the flocculation process is the type of agitation that the suspension undergoes. It is not possible to include the complex kinetic phenomena associated with agitation in an expression of this type.

Flocculation is a process depending on a number of external variables, (which may not affect the stability expression significantly) but which determine in a very profound sense the bulk physical nature of flocculation. Thus it is difficult to describe the nature of flocculation simply from the effect of polymer on the stability expression; or from implied adsorption of flocculant, bridging events and collision efficiency since these are kinetic phenomena and do not allow simple interpretation. It is appropriate to discuss the phenomenon from the point of view of its definition "the aggregation of particles by the formation of polymer bridges between the particles" and suggest certain criteria that arise from experimental observation and others from a consideration of the literature.

La Mer in his review discusses the bridging phenomenon from the point of view of fractional surface coverage. Smellie and La Mer postulated that the probability of building flocs is proportional to the surface covered by polymer, θ , and the fraction that is uncovered ($1 - \theta$). From this a rate expression is developed. This is known as the "half surface coverage" condition at which the possibility of bridging events is maximized. (Gregory 1978b). It is difficult to describe what is meant by "coverage" in these systems as the multiplicity of polymer configurations results in problems of interpretation. In addition this formulation suggests that the polymer dimensions are very small when compared with the surface area of the mineral particles in suspension. The nature of the adsorption of the polymer segments is also of prime importance (Gregory 1978b). The adsorption should not be too strong, otherwise the extended loops that participate in bridging may be too small for effective flocculation. It has been noted earlier small adsorption energies result in high segment surface coverages, because of the cumulative effect of segmental adsorption giving rise to effective irreversibility. The lower adsorption energy would favour a greater flexibility of the adsorbed polymer molecule in the conformational sense. The conformational elements of the system may be critical, as, in particular, adsorption of a rigid extended polyelectrolyte on one surface may be favoured, the equivalent adsorption of a loop or tail onto another surface, especially in conditions of high shear may be much less favoured than adsorption of a random coil under the same conditions. This element of the discussion does not appear to have been specifically raised in the literature, except obliquely by van Lierde. Walles developed an extremely simple model of flocculant adsorption. He suggested that an adsorbing macromolecule is initially adsorbed at only a few segments while the unbonded part "freely penetrates" the solution and can form bonds with other particles. He suggests that a particle with an extended adsorbed polymer chain behaves as if it has the combined radius of both the polymer molecule and the particle, but that the mass and mobility will be similar to the bare particle. Using the rate approach of Smoluchowski he developed a flocculation parameter which is the collision frequency with polymer attached relative to the collision frequency of the bare particles. These are expressed, for different chain lengths, as a ratio of chain length to particle radius. The results indicate increases in collision frequency that rise exponentially with increase in polymer chain length. This treatment must be seen as fundamentally different to that of La Mer, who did not see the problem in terms of the polymer conformation but rather in terms of "surface coverage". The model of Walles, although simple, points to an entirely different conception of floc generation that is related to polymer conformation rather than surface coverage and provides a qualitative test of the influence of polymer conformation on the flocculation process.

The influence of molecular mass on the flocculation process has also been a source of discussion. Walles suggests that, in flocculation by bridging, molecular mass is of critical importance since this will be a major factor in increased molecular dimensions. La Mer in discussing his model suggested that the greater length of loops and tails in a higher molecular mass chain would improve flocculation.

The careful work of Ash and Clayfield in flocculation of latex in a Couette mixer showed a decrease in the polymer concentration required for optimum flocculation (as measured by a turbidimetric technique) with increase in molecular weight but found that the stability of all the systems was similar. This was over the range 99 000 - 5000 000 a.m.u.

Somasundaran does not specifically discuss molecular mass. Walles suggests that in situations where charge neutralization is important molecular mass will have a diminished effect since the role of the polymer in bridging is reduced. No definitive treatment of the effect of molecular mass has been specifically applied to flocculation though much experimental evidence is available.

Charge neutralization is important in flocculation by polyelectrolytes as it modifies the V_R term significantly in the stability expresion. The adsorption of nonionic materials can result in the physical displacement of the OHP from the particle surface thus increasing repulsion between particles (Gregory 1978b). However, it is also possible to decrease the stability of systems by surface charge reduction by chemical bonding of the polymer in the Stern layer (specific adsorption). These phenomena have been described qualitatively by Lyklema (1976, 1981). With polyelectrolytes the higher charge density can facilitate or hinder specific interactions and electrostatic charge reduction, depending on the sign of the charge on the surface and the polyelectrolyte.

In general, the literature indicates that opposite charges on the surface and polymer tends to facilitate flocculation and that in ill defined systems nonionic polymers are preferred. (Kitchener 1978). However, there has been no systematic study of the effect of change in anionic character, and increasing dissociation of the flocculants over the pH range, that has been specifically related to the adsorption phenomena. However the early work of Michaels and Morelos using polyacrylamides of different ionic character showed that polyelectrolytes can be more effective than neutral polymers even when the net surface charge is of the same sign as the flocculant. However, this work needs some reinterpretation. (See Section 3.5.10).

The effect of ionic strength has been shown to be more significant on anionic polymers than on nonionic polymers (Somasundaran) in terms of adsorption but this was not interpreted in terms of measureable flocculation parameters. (Adsorption is not per se a measure of flocculation efficiency).

It has been shown that in some systems divalent or trivalent cationic species are required to promote flocculation. This process which is known as sensitisation was first postulated by Michaels and Morelos as an ionic bridging mechanism. A study (van Lierde) of the behaviour of quartz suspensions in the presence of Ca^{2+} ions and acrylate polymers indicates the quartz, which would naturally coagulate, may be dispersed by the presence of polyacrylate when it is not able to form interparticle bridges. This mechanism can be interpreted as a steric stabilization by non-rigid slightly dissociated polyacrylate forming effective bonds through the calcium bridges on the quartz surface, thus forming impenetrable layers. At higher pH the acrylate chains become more rigid and extended and some interparticle bridging takes place resulting in flocculation of the quartz. This indicates that even where "sensitisation" takes place, by the formation of ionic bridges or any other mechanism, this does not mean that flocculation always results. The facilitation of surface interaction (sensitisation) in the case of the work of van Lierde resulted in stabilization.

Also of importance in the adsorption-flocculation reaction is the quality of the solvent. In general with polyacrylamides the solubility increases with increasing anionic character. Thus a nonionic polyacrylamide would tend to be adsorbed more strongly (in the sense of nonionic bonding) than an anionic polyacrylamide on surfaces of low charge. It must be noted that this could either facilitate or hinder flocculation, depending on the nature of the adsorbed layer, and the relative concentration of flocculant and particles. This does not therefore give an indication of the efficiency of the process of flocculation.

An anionic polyacrylamide would in general have a lower adsorption on a surface than a nonionic one unless;

1) specific chemical effects promoted increased adsorption

2) conformational effects (such as chain extension) promoted a net increase in total adsorbed polymer.

Thus it can be seen that flocculation-adsorption reactions result in a complex set of interactions that can modify all four terms of the extended DLVO theory. A qualitative discussion of variables such as surface coverage, molecular mass, conformation, ionic strength and others has been undertaken. The effect of agitation as a macroscopic process facilitating floc build-up and breakdown is now discussed.

1.3.10 Hydrodynamic Considerations in Flocculation and Flocculant Adsorption

Two distinct areas need to be considered when the effect of agitation on flocculation is discussed. The first is the effect of agitation during the period of floc formation and the second is the effect of subsequent agitation on the floc structure.

1.3.10.1 The Aggregation Process

The earliest discussion of the aggregation process of fine particles is due to Smoluchowski. He considered two cases, the first where the dynamic for aggregation is Brownian motion - perikinetic aggregation; and the second where the particles are brought into contact by shear of the bulk fluid - orthokinetic aggregation.

In the first case the collision rate, b_{ij}, could be represented:

$$b_{ij} = 16 \pi D \; r_i v_i v_j \qquad \text{Equation 1.10}$$

where D is the diffusion coefficient of the primary particles radius r_i and v_i and v_j are the number concentration of the aggregates containing i and j primary particles respectively.

Brownian motions of particles do make a contribution to the flocculation process, but only in the first seconds of agitation with very fine particles (Camp.)

In a laminar shear field where particles are not in Brownian motion the collision frequency is:

$$b_{ij} = \frac{4}{3} G (r_i + r_j)^3 v_i . v_j \qquad \text{Equation 1.11}$$

where G is the shear rate ($\sec^{-1}$) and r_i and r_j are the aggregate radii of aggregates of i and j particles respectively.

The Smoluchowski formulation has been shown to be correct in a laminar shear field by Swift and Friedlander using a Couette apparatus.

A modified form of the Smoluchowski formula for laminar shear flow has been developed by Hudson to describe the rate at which uncoagulated particles are entrapped by coagula or flocs.

$$\frac{N_i}{N_o} = \exp\left(-\frac{\delta V G}{\pi}\, t\right)$$

Equation 1.12

where
N_i is the number of free particles at time t,
N_o is the number of free particles at time t = 0,
V is the volume of flocs or coagula,
δ is a measure of the efficiency of individual collisions.

Hudson notes that the free particle uptake is dependant on the floc volume, if δ , G and t are constant and this suggests that in dilute flocculating systems a minimum supernatant turbidity will in general be associated with a maximum settled bed volume.

Also, in general, increased shear rates should increase supernatant clarity if the floc volume is not significantly decreased.

Camp in an early paper, discussing coagulation, indicated that experimental evidence shows that the rate of flocculation (coagulation) is directly proportional to the shear rate and the number of particles. The root mean squared velocity gradient is directly proportional to the root of the average power input and inversely proportional to the root of the absolute viscosity so:

$$G = \sqrt{\frac{\varepsilon}{\mu}}$$

Equation 1.13

where ε is the average power input per unit mass and where μ is the absolute viscosity of the fluid. Now the rate of floc formation is directly proportional to G, (Smoluchowski) and the time required to form the floc (coagulum) is therefore less the higher G is. However, Camp recognised that higher values of G result in smaller flocs (coagula) since

$$\tau = \mu G'$$

Equation 1.14

where τ is the shearing force and G' the instantaneous velocity gradient.

Thus it can be seen that the aggregation rate is increased with increase in shear rate. The clarity of the resulting suspension should also be increased. However the floc size will be decreased because the shear forces operating on the particle are increased resulting in floc rupture.

These findings resulted from studies of coagulating systems which are qualitatively different from flocculating systems in a number of respects. However the recent experimental work of Tomi and Bagster (1978) on the galena/PAM/ water system has shown a decrease in optimum floc size with increase in stirrer speed. Rates of flocculation are so high that no reliable data on the rate of floc formation is available. However the fact that the optimum flocculant dosage decreases with stirring speed (Tomi and Bagster) and that the rate of flocculant adsorption is increased (Jankovics) perhaps serves as an indirect confirmation of the findings of studies of coagulating systems.

The more qualitative work of Linke and Booth also supports these findings.

A detailed discussion of the different elements of the agitation contribution to the flocculation process is now undertaken.

1.3.10.2 Flocculant Adsorption

Jankovics showed increased rates of polymer adsorption on calcium phosphate with increase in stirring rate.

The stirring system was a pyrex coated magnetic stirrer bar in a volumetric flask. The stirring speed range was 2.2 - 8 revolutions per second. The effect of molecular mass was also investigated. He showed that the rate of adsorption decreased with increase in molecular mass. The level of maximum adsorption was a constant number of flocculant molecules which indicates that the maximum adsorption is a function of the number of polymer molecules rather than the molecular mass of the polymer in the bulk liquid. It ought to be noted that the long agitation times resulted in deflocculation of the slurry.

Linke and Booth in their classic paper of the flocculation of silica by PAM's found that increased agitation time resulted in excess flocculant adsorption from the bulk liquid. On the basis of their results they state "In flocculated systems, so called 'adsorption isotherms' are thus fictitious, and are strictly a function of the degree of agitation imposed on the mixtures."

This statement suggests that flocculant adsorption is not at an equilibrium at optimum flocculation, and that the degree and duration of agitation profoundly modifies both the adsorption of flocculant and the experimentally determined parameters of flocculation.

Tomi and Bagster have shown recently (1978) that in the galena/PAM/water system high stirring rates resulted in less polymer adsorption for optimum flocculation properties. However, floc sizes were reduced (as expected from the work of Camp).

Healy suggests that the adsorption of PAM on quartz was lower when the rate of agitation was increased (from mild to violent) which was confirmed in the study of Bagster and Tomi.

Healy could find no increase in adsorption with longer agitation times as found by both Tomi and Bagster, and Linke and Booth earlier.

It must be noted that there is no contradiction in these results. Two distinct phenomena are being observed:

a) The initial adsorption of flocculant resulting in the generation of an "optimum floc." The optimum floc requires lower flocculant adsorption the higher the stirring rate.(The flocs will however be smaller).

b) After the initial adsorption of flocculant Linke and Booth and Bagster and Tomi observed degradation of flocs which was associated with adsorption of excess flocculant from the bulk liquid. This process may take place at all agitation rates but will occur much more rapidly at higher rates of agitation.

In the case of Jankovics stable flocs were generated initially but the rate of breakdown decreased with increasing flocculant molecular mass.

To summarize:

1) The rate of flocculant adsorption increases with increased stirring rate.

2) The optimum flocculant dosage decreases with increased stirring rate.

1.3.10.3 Floc Size

Tomi and Bagster, have noted that floc size at "optimum" flocculant concentration decreases with increase in stirring rate. Jankovics noted that the end result of long agitation times was a deflocculated suspension. These two findings essentially incorporate two different elements of flocculation phenomena as related to agitation.

The first is the mechanism of floc formation which, it has been suggested, is analagous to coagulation in particle mechanical terms. However, should a floc break down under shear the possibility of reformation (above the optimum flocculant concentration) is small (Tomi and Bagster). Thus in conditions of prolonged agitation the flocculation process is distinctly different from coagulation phenomena (in that ruptured coagula can reform).

Thus the floc size (or mean floc size) in any system will be a mixture of contributions from the initial process of aggregation, the amount of degradation as a result of the agitation conditions, and the amount of residual flocculant in the bulk liquid (to be discussed later).

Therefore the effect of shear conditions leading to floc rupture will be discussed more fully below.

1.3.10.4 Floc Degradation under Agitation

Various studies of flocculating systems have included some examination of the effect of agitation (Linke and Booth; Healy; Reich and Vold; Thomas; Hannah et al. Tomi and Bagster (1978a) McCarty and Olsen). However, often the methods used allow no quantification of the agitation parameters.

General findings that may be noted are:

1) reduction in floc size with increase in stirring time
2) reduction in floc size with stirring intensity
3) reduction in settling rate with stirring time.

Other studies, in particular those of Tomi and Bagster; Aragman and Kaufmann and Parker, and reviews of Somasundaran; and Spielman, have given some understanding of the influence of mechanical agitation and have discussed mechanisms of floc breakdown.

In general, both coagulating and flocculating systems have an upper limit of aggregate size associated with each shear rate which will be determined by the forces holding the aggregate together. In order to better analyse flocculation and the effect of agitation the nature of the fluid behaviour in stirred tanks is discussed below.

1.3.10.5 Turbulence in Stirred Tanks

Turbulence phenomena are complex and their mathematical description is beyond the scope of this study. (Spielman).

Turbulence as defined by Taylor and von Kaumann (cited by Hinze) is "an irregular motion which in general makes its appearance in fluids, gaseous or liquid, when they flow past solid surfaces or even when neighbouring streams of the same liquid flow past one another." Turbulent motion is irregular in time and space.

The irregular nature of turbulent flow results in velocity fluctuations due to the generation of eddies in the fluid.

Thus the instantaneous velocity of the fluid U has a contribution $\bar{U}$ which is the mean value of the bulk flow and u the instantaneous fluctuation at a point due to turbulence thus:

$U = \bar{U} + u$, where $|u|$ becomes a measure of the intensity of the turbulence.

In general the intensity is more usually measured

$$u' = \sqrt{\bar{u}^2}$$

Another important concept in the examination of turbulent systems relies on the analysis of the turbulence in terms of a spectrum of eddy sizes whose properties in different size ranges may be different. Thus, for instance, experimental studies have shown that small eddies are profoundly affected by the viscosity of the fluid and are responsible for the dissipation of energy because of their decay. Their size may be associated with a "wave number" (to extend the spectral analogy) which will be high because of their small "wave length." An indication of their size is given by the dissipation microscale λ_g. In addition there exists an integral (or macro) scale which it can be shown is the order of the size of the energy containing eddies (which generally have lower wave numbers than the energy dissipating eddies).

Another parameter ε may be defined which is the total energy dissipation in the turbulence and which is equal to the work input per unit time and mass, ε , in stable homogeneous systems.

The work input generates the energy containing eddies and the dissipation occurs in the eddies of the order of λ_g.

At high Reynolds number* Kolmogoroff (cited by Hinze) made simplifying assumptions about regions of the turbulent spectrum. He indicated in his first hypothesis that high wave number eddies are independent of external variations. They depend only on the kinematic viscosity ν , and the energy dissipation rate ε . This range was therefore called the universal equilibrium range. Kolmogoroff defined a microscale:

$$\eta = \left(\frac{\nu^3}{\varepsilon}\right)^{\frac{1}{4}} \qquad \text{Equation 1.14}$$

on dimensional grounds and a macroscale l_e which is of the same order as the integral scale.

The integral scale has a wave number $k_e = {}^1/_{l_e}$ and similarly the microscale has a wave number k_d.

*the Reynolds number is a dimensionless number that defines the relationship between the inertial and viscous forces in a fluid. A high Re suggests turbulent conditions and a low one laminar shear flow.

The high Re ensures that $k_e <<<< k_d$.

Turbulent Reynolds numbers may be defined (Hinze) such that:

$$Re_\lambda = \frac{u'\lambda_g}{\nu} \quad \text{and} \quad Re_l = \frac{u' l_e}{\nu}$$ Equation 1.15 and 1.16

Also $$\varepsilon = 15\nu \frac{u'^2}{\lambda_g^2}$$ for dissipation (1.17)

$$\varepsilon = A \frac{u'^3}{l_e}$$ for work input (1.18)

Where A is a numerical constant of the order of unity.

We may thus define the relationships between the Kolmogoroff parameters and the Eulerian parameters such that:

$$Re_l = A/15 \quad Re_\lambda^2$$ Equation 1.19

$$\lambda_g / \eta = 15^{\frac{1}{4}} \quad Re_\lambda^{\frac{1}{2}}$$ Equation 1.20

$$l_e / \lambda_g = A/15 \, Re_\lambda$$ Equation 1.21

$$l_e / \eta = 15^{-\frac{3}{4}} A \, Re_\lambda^{3/2}$$ Equation 1.22

Kolmogoroff's second hypothesis was that at very high Re there exists a subrange of the universal equilibrium range such that the effect of the viscous component is reduced so as to be negligible and the phenomena depend only on ε. This is known as the inertial subrange. The wave number criterion is such that the wave number k of the inertial subrange be

$$k_d << k << k_e$$

Experimental evidence has shown that the conditions for the existence of the inertial subrange are that $Re_\lambda > 1\ 500$ or $Re_l > 1.5 \times 10^5$.

1.3.10.6 Stirred Tanks

When an impeller agitates a tank of fluid turbulence arises from sharp velocity discontinuities adjacent to liquid streams discharged from the impeller blades (Davies). There are also boundary and form separation effects from the blades themselves. The power input, P, in stirred tanks is expressed in terms of a dimensionless power number, Po,

where $$Po = \frac{P}{N^3 L^5 \rho}$$ for baffled tanks (Equation 1.23)

or $$Po = \left(\frac{P}{N^3 L^5 \rho}\right)\left(\frac{1}{N^2 L}\right)^{\left(\frac{a - \log Re_t}{b}\right)}$$ for unbaffled tanks (Equation 1.24)

Where N is the number of impeller revolutions in unit time

L is the impeller diameter

Re_t is the Reynolds number for stirred tanks $\left(\frac{NL^2}{\nu}\right)$

a,b are constants related to the impeller type

ρ is the fluid density

ν is the kinematic viscosity.

The power input per unit mass of fluid, P_m, is equivalent to the energy dissipation rate ε discussed earlier, and can be calculated using

$$P_m = Po\ N^3\ L^5 / \pi a_t^2\ H$$ Equation 1.25

(where $\pi a_t H$ is the fluid volume)

where a_t is the tank radius

H is the fluid air interface height

Now $\varepsilon = A \frac{u'^3}{l_e}$

so $u' = (l_e)^{1/3} (Po\ N^3\ L^5 / \pi a_t^2\ H)^{1/3}$ Equation 1.26

and $l_e \sim 0.08 \text{ to } 0.1\ L$ (Davies)

hence $u' = 0.43\ NL^2\ (Po/\ \pi a_t^2 H)^{1/3}$ Equation 1.27

which reduces to $u' \propto NL$ in geometrically similar tanks (since Po is the order of 1). U for the impeller discharge stream can be calculated using

$V_f = CNL^3$ where Equation 1.28

V_f is the volumetric flow rate

C is the constant (0.4 - 0.6)

This is reduced to a velocity by dividing by the swept area of the impeller.

Thus $U \simeq 0.6\ NL^3\ /\ \pi\ (L/2)^2 \ \sim 0.8\ NL$ Equation 1.29

Close to the blades however the velocity may approach the blade peripheral velocity, πLN, and u' can reach 0.5 U so that the maximum order of u' is about NL. Pipe flow gives an approximate relation for the fluctuation velocity of energy dissipating eddies, $u_d \simeq 2.2\ NL\ (Re)^{-0.22}$.

1.3.10.7 The Implications for Floc Rupture

Stirred tanks can be divided into three zones which are characterized energy dissipation relative to the mean value. These regions are summarized in a table and diagram from Tomi and Bagster (1978a).

Table 1.1: Fractional volume of impeller zones and energy dissipation factors.

Zone	Fractional Volume	Energy Dissipation Factor
bulk	0.9	0.25
impeller	0.095	5.4
impeller tip	0.005	50

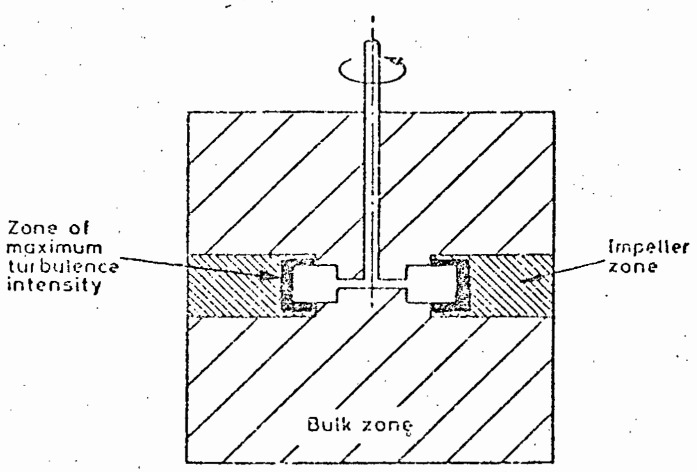


Figure 1.6: Diagramatic representation of the 3 zones in an impeller stirred tank. The fractional volume of the three zones is in Table 1.1. (after Tomi and Bagster 1978a)

A similar analysis due to Davies gives a factor of 70 near the impeller. The higher values of energy dissipation near the impeller result in lower values of η probably as low as 5 μm compared with 30 - 45 μm in the bulk of the tank. This suggests that turbulent disruption of flocs probably happens close to the impeller. Thomas discussed the phenomenon of turbulent floc disruption and he suggested that floc disruption is due to a pressure difference across the aggregate close to the turbulent eddy. Using as a basis analyses of turbulent disruption of droplets in imimiscible liquids he suggested that the mechanisms of rupture would be:

1) Floc extension and rupture (low relative viscosity)
2) Failure due to fluid shear stress exceeding the strength of the floc.

Thomas assumed that the Kolmogoroff criteria applied.

His analysis showed

$d_{max} \propto \nu^{-3/2} \quad \varepsilon^{-5/2}$ in the inertial subrange Equation 1.30

and

$d_{max} \propto \left(\frac{\nu}{\varepsilon}\right)^{\frac{1}{2}}$ in the viscous range Equation 1.31

Tomi and Bagster more recently have considered the rupture of aggregates in stirred vessels. Also assuming the Kolmogoroff hypothesis, they have developed failure criteria for large aggregates, small aggregates and aggregates of intermediate size. Working from the presupposition that aggregates are homogeneous in terms of structure and shape (i.e. $\tau_{crit} = p(d)$) they found:

1) $d_{max} \propto \varepsilon^{-1}$ in the inertial range

$p(d) \sim \rho u'^2$

where: p(d) is the force required to rupture the floc and
d_{max} is the maximum floc diameter.

2) rupture criteria independent of d in the viscous range

$$p(d) \sim \mu\left(\frac{\varepsilon}{\nu}\right)^{\frac{1}{2}}$$

3) $d_{max} \propto \varepsilon^{-\frac{1}{2}}$ in the intermediate range

$$p(d) \sim \rho d^2 \left(\frac{\varepsilon}{\nu}\right)$$

The equations for the viscous range and intermediate range are regarded by this author as erroneous for reasons given below. The assumption that the Kolmogoroff hypotheses hold for impeller speeds below 1 000 rpm in tanks is uncertain and that, certainly, the second hypothesis is extremely unlikely to hold in this region.

Tomi and Bagster showed a reasonable correlation of theory with the data of Reich and Vold which was undertaken at high stirring rates in a blender.

In Tomi and Bagster's analysis of their own experimental results (at much lower stirring rates) they could not correlate floc sizes with either the viscous or inertial forms of their analysis. The arbitrary introduction of the parameter λ_g which is representive of the region of highest energy dissipation (but does not suggest a rigid separation of inertial and viscous effects, or indeed the separation of energy containing eddies from energy dissipitating ones), cannot be justified. The magnitude of λ_g in their study is the same order as l_e (about 0.1L) which suggests that neither of Kolmogoroff's hypotheses apply and therefore the postulation of different criteria giving rise to three rupture conditions is not valid. (This will be discussed further in the presentation of results).

Thus while it is certain that the floc sizes generated in stirred tanks are a function of the turbulent conditions particularly related to the region close to the impeller, analyses based on the Kolmogoroff hypotheses are not appropriate at agitation rates <1 000 rpm.

Floc degradation has been shown by Tomi and Bagster; and Healy to be a slow process and this suggests that at long agitation times the structure of aggregates is still being modified. This results in a weakening of the floc structure followed by turbulent disruption of the floc, under the constant shear conditions applied.

Spielman, similarly, comments on the range of validity of the inertial subrange though he is not aware of the work of Bagster and Tomi. He indicates that the assumption is sometimes made to allow analysis of results. Specific hydrodynamic interactions are ignored in analysis of rate processes in turbulent coagulation.

Another mechanism has been suggested for floc degradation. Rather than disruption occuring by a process of shear into two large fragments, a mechanism of surface erosion on a particle scale is suggested. In particular Parker developed equations for flocs smaller and larger than the microscale η, of the form

$$d_s = C/G^{\ell} \qquad \text{Equation 1.32}$$

where C is a floc strength coefficient and ℓ depends both on the breakup mode (erosion or rupture) and the eddy scale leading to disruption. The coefficient C depends strongly on an ill defined and immeasurable parameter "floc surface shear yield strength" (Spielman). In addition the analysis is complicated by the same assumption of the Kolmogoroff criteria which cannot be applied in the low shear regions in flocculating systems. However, surface erosion may play a part in floc breakdown. The difficulty of defining the nature of the turbulence (without simplifying assumptions) and the time dependant nature of floc disruption in flocculation (as opposed to coagulation) causes the difficulties in interpretation. Indeed Tomi and Bagster in their development of a criterion for rupture of small aggregates observe "One would therefore predict that at a critical intensity of turbulence τ_{crit}, ... all aggregates within the size range are ruptured ..... In general, this behaviour is not observed in practice."

The primary advantage of the current interest in the hydrodynamic aspects of flocculation may be a stricter control of agitation parameters in flocculation studies. In addition it may result in an approach to the subject from the angle of floc size-density relationships and the effect of agitation on these parameters. (Michaels and Bolger)

To Summarize:

1) Although various researchers have studied the effect of agitation on floc size and floc degradation quantification of the agitation parameters has been neglected except in recent studies.

2) The analysis of floc disruption in turbulent conditions has suggested that the mechanism of floc rupture is due to the pressure difference across flocs in turbulent eddies (of the same order of magnitude as the floc) exceeding the yield shear of the floc. An erosion mechanism is also proposed.

3) Since floc degradation is a slow process it is probably due to the mechanisms suggested above coupled with internal rearrangement of the floc under the fluctuating shear forces of turbulent eddies, resulting in a weakening of the structure followed by disruption.

1.3.11 The Organisation and Presentation of Experimental Studies

The investigation of the literature concerned with the measurement of flocculation on the one hand and the hydrodynamic dimension of flocculation on the other indicated that no study in which agitation has been quantified and controlled also embraces the traditional measures of flocculation. Thus in the first instance it was necessary to develop a stirring system that gave results that could be considered representative of stable conditions of flocculation. This in turn necessitated the development of a method of recording floc structure. A photographic method was developed in conjunction with two stirring systems, one based on a magnetic stirrer and the other on a four blade impeller. The stirring systems were then evaluated on the flocculation performance of the Na^+ kaolin treated with a nonionic polyacrylamide.

These experiments led to the conclusion that the impeller stirrer was the best basis for further studies of flocculants and the flocculation of kaolin.

Three different homoionic forms of the local kaolin (Heckroodt) were prepared* and the performance of 6 flocculants evaluated under standard conditions of agitation. A particular advantage in the case of the 5 polyacrylamide flocculants was the availability of a simple method of residual flocculant determination (Macefield) that permitted measurement of flocculant adsorption. Thus the experimental work focussed on the evaluation not only of flocculation as assessed by classical measures of flocculation, but also the interplay between agitation, adsorption of flocculant and the assesment of floc structure. The effect of pH and ionic strength was also studied to assess the importance of these parameters and also to give greater insight into the particular adsorption - flocculation reactions at the molecular level.

A note is included on digital image analysis of photographic floc images which was done to quantify the essentially qualitative findings based on the photographic records presented in the body of the thesis.

The literature review of studies specifically concerned with flocculation of kaolin immediately precedes the experimental studies of the 6 flocculants. The investigation of the agitation systems is more logically placed after the literature review of the hydrodynamic elements of flocculation.

---

* see Appendix 1

CHAPTER TWO

DEVELOPMENT OF EXPERIMENTAL METHOD

2.1 Floc Photography

There are few instances in the literature where changes in the flocculation-adsorption parameters have been correlated with the visual appearance of the flocs on a microscopic and a macroscopic scale in a manner that allows comparison and evaluation (Tomi and Bagster 1980). The method of floc photography detailed in Appendix 3 was developed initially (for use with a stereo optical microscope) in order to minimize the effects of convection generated by heating from the light source. It was then adapted for use with a camera mounted on a copy board for more routine recording of floc sizes.

The primary motivation for generating the photographic record was the change in floc size with flocculant dosage as well as the changes in appearance of the flocs. More troublesome to evaluate is the degree of association between flocs and only preliminary statements can be made about this aspect. An additional problem in the presentation of the optical micrographs, in particular, is the loss of depth of field that results from the use of only one optical path in taking photographs as compared with stereo viewing of the flocculated kaolin. Incredibly detailed, interlocking, fine flocs are reduced to woolly clouds as the three dimensions are projected onto the plane. One solution to this problem would have been the provision of stereo pairs of these structures but unless this technique becomes more firmly established such sophistication is considered unnecessary. Essentially two types of floc structure or "morphology" can be distinguished using the stereo-optical microscope. These are presented as Figures 2.1 and 2.2. The first is the "woolly" structure mentioned above which is in fact an interlocking network of extremely fine flocs. This network is easily disrupted by the mildest agitation but reforms within about 10 seconds after the liquid stops moving. Thus a thin layer of slurry distributed over a petri-dish will appear to coalesce into a structure of flocs with largely solid free liquid in between. This first type of structure is generally associated with low dosages of flocculant (0.1 - 0.5 mg/g kaolin). The second type of floc structure is associated with higher dosages of flocculant. It is characterized by loose aggregates of individual or discrete flocs that are considerably larger than the fine flocs that make up the woolly structure of

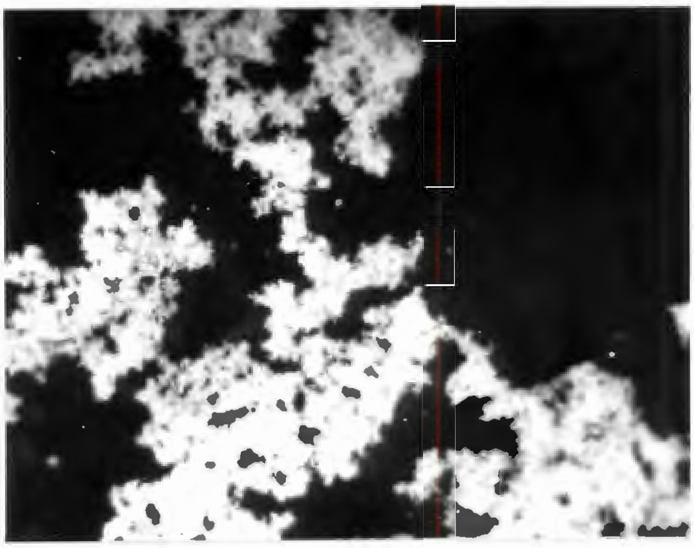


Figure 2.1: Micrograph of 'woolly' floc structure. This is a projection of a three dimensional network of small associative flocs onto the plane.

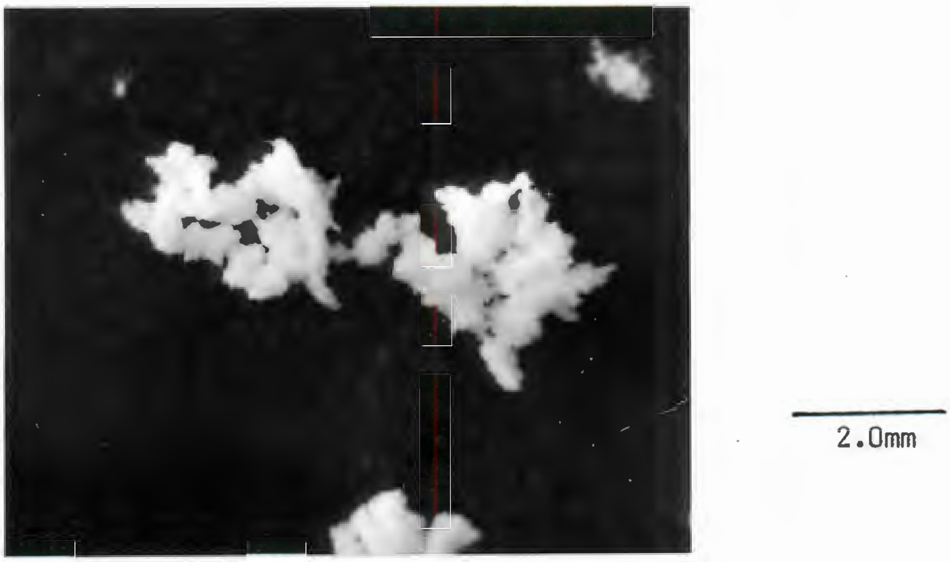


Figure 2.2: Micrograph of coherent 'discrete' flocs. Note the higher reflectivity of the flocs.

Fig. 2.1. They are easily distinguished as they have a higher reflectivity due to their greater coherence and have a denser more bulky conformation that distinguishes them from the networked woolly morphology.

Two other groups of structures need to be mentioned. They are both associated with the transformation of floc structure with agitation. The first is a 'fluffy' precursor of the discrete flocs generated with longer periods of agitation and the second a disrupted discrete floc structure that is associated with long periods of agitation. Both these structures will be easily recognised in the section in which they are discussed.

Floc photography was also used to generate suitable photographs for subsequent areal image analysis of the floc size distributions using the camera mounted on the copyboard. This necessitated, in the case of low flocculant dosages, a low concentration of flocs to prevent the spontaneous aggregation of flocs mentioned above. Hence photographs like Fig. 2.3 were taken. Fig. 2.4 shows a more concentrated suspension that has aggregated into floc bundles leaving patches of clear fluid between them. By contrast a photograph (Fig. 2.5) of a flocculated sample with a high dosage of flocculant is shown. The flocs are more reflective and are essentially discrete, individual flocs. Where appropriate, in the presentation of results, photographs of floc structures will be included and will be used in the discussion to evaluate flocculation-adsorption mechanisms.

Micrographs presented in this thesis are all at the same magnification which is indicated on the appropriate pages by means of a scale bar equivalent to 2 millimetres.

In the case of the photographs the scale bar represents 2 centimetres.

Figure 2.3: A low concentration of individual flocs of the 'woolly' type.

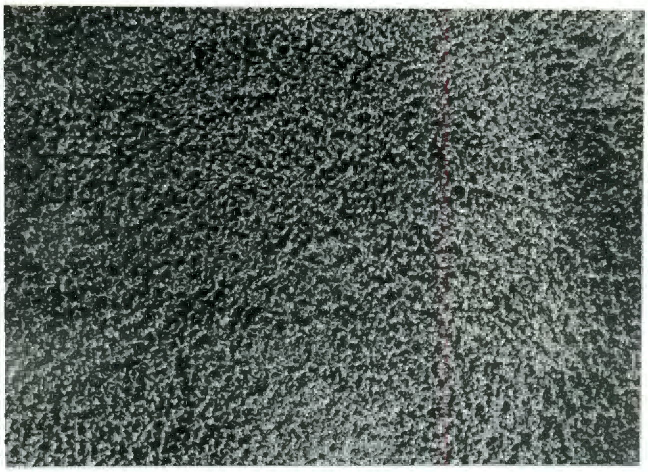


Figure 2.4: At a higher concentration of solids the flocs associate to form aggregates that are easily disrupted by agitation.

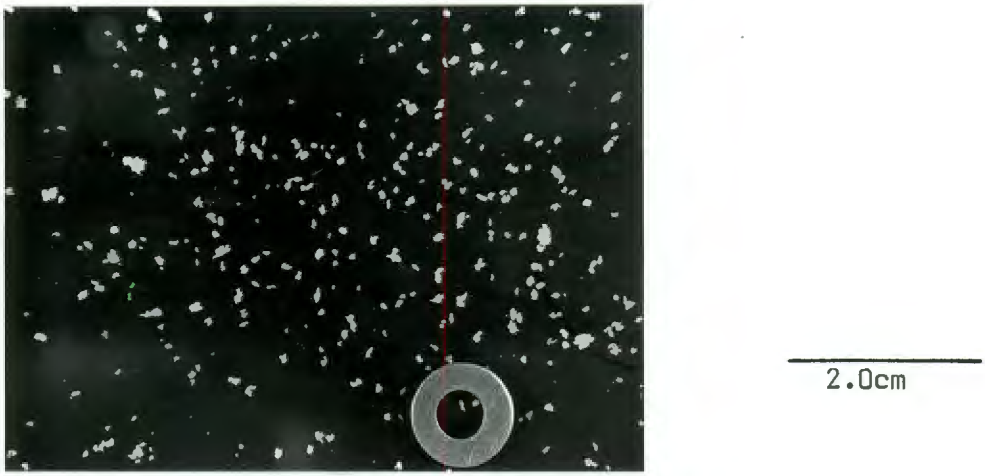


Figure 2.5: Higher dosages of flocculant produce flocs that are more reflective and that have a larger average floc size.

2.2 THE EFFECT OF SHEAR CONDITIONS ON THE ADSORPTION OF FLOCCULANT, FLOC STRUCTURE AND FLOCCULATION PARAMETERS.

2.2.1 Analysis of the Agitation Systems.

The experimental details are recorded in Appendices 2 and 4. It is first important to describe the stirring systems used here in terms of the parameters examined in the literature review. Two types of stirrer were used for the bulk of the experiments - a magnetic stirrer and a 4 bladed impeller type stirrer.

The details are tabulated below:-

Stirrer	Speed	Axial Diameter	Swept Volume	Impeller
	r.p.m.	mm	mm^3	
Magnetic	960	25.5	3 400	Teflon coated bar
Impeller	240	50	24 500	4 bladed impeller

Assuming that the Kolmogoroff hypotheses hold, the following data can be recorded which describe the conditions of the suspension when agitated.

	Magnetic	Impeller
Re_1	123	122
ε	25.6 watts/m^3	1.60 watts/m^3
η	14µm	28µm
λ_g	307µm	615µm
l_e	2.5mm	5mm

The symbols represent turbulence criteria described and defined in Section 1.3.10.5.

Of these data l_e is assumed to be 0.1 L and u′ = NL (Davies) and the rest are calculated from measured parameters and the assumed values, where l_e is the Eulerian macroscale and u′ the instantaneous turbulent intensity. N and L are stirrer criteria:- N is the rpm and L the stirrer diameter.

Approaching the system from the point of view of the stirred tank the following data can be recorded as defined in Section 1.3.10.6 .

	Magnetic	Impeller
Re_t	10 000	10 000
n	0.08	0.08
Froude correction for unbaffled tank	1.15	0.98
Po	1.4	1.2
P_m(mean)	0.56 watts/m^3	0.24 watts/m^3
P_m(impeller zone)	16 watts/m^3	1.00 watts/m^3
P_m(max. intensity)	329 watts/m^3	20.00 watts/m^3

Comparison of the value derived from the turbulence condition for energy input, ε , and the volumetric power number, P_m indicates that they are of the same order in the tank but lower by a factor of 1.6 for the impeller stirrer which may reflect the choice of l_e. However it does reflect that the energy input is by volumetric displacement from the impeller and it also suggests that the energy dissipation in the bulk is far less than in the impeller zone. Thus it can be seen that floc disruption events will take place near the impeller and floc building at regions remote from the highly turbulent and inhomogeneous conditions near the impeller. The floc size at any time will reflect the interplay between these processes.

It is also worth noting that the energy input in the magnetic stirrer is significantly higher in all regions than the impeller stirrer, but that the Reynolds numbers which are a measure of the turbulence are the same. This arises from the radial velocity of the two impellers being different but the actual velocity of the impeller tips being the same.

2.2.2 The Accuracy and Variability of the Experimental Results

Before consideration of the experimental results specifically it is appropriate to discuss the accuracy of the results presented in general terms rather than detail these before or during the presentation of the results themselves. This is done here because the methods used throughout this study remain the same in their essentials.

2.2.2.1 Flocculant Adsorption

This was determined by difference from the flocculant in the supernatant. Linke and Booth had shown that this is a valid procedure in their determinations of flocculant adsorption. The accuracy of each result is within 1% of the initial concentration added. However it is possible that there is some variability due to small weighing and decanting errors in the preparation of the kaolin for flocculation. The trends of the results and their internal and comparative consistency suggest these errors are small.

2.2.2.2 Supernatant Turbidity

Each point on the supernatant turbidity graphs represents, of course, a separate determination requiring a weighed kaolin sample and preparation of a suspension (1% w/w concentration). The turbidimeter used in this study has 4 scales for measurement of turbidity. In general in this study the higher three scales were used. Lower turbidities thus show lower variability and also higher accuracy. In spite of this the general trend of the results show remarkable consistency in all cases except the 1mg/g sample stirred with the magnetic stirrer (Fig. 2.2.3) where it can be seen that the lower order results have been favoured. However, fortunately the general trend can be deduced from the results of the lower and higher dosages of flocculant in the system.

2.2.2.3 Settled Bed Height

The settled bed height data are the least satisfactory from the point of view of accuracy in the study of the two agitation systems, but this problem was much less pronounced in the studies of the effect of the 6 different flocculants on H^+ and Ca^{2+} kaolins (Section 3.2). In the case of the stirring systems analysis only the most general statements can be made on the basis of the settled bed height data. In the case of higher dosages of the n-PAM with the Na^+ kaolin the extremely large floc size also came to play a role, in that the packing of the settled bed became a critical factor and large variations in settled bed arose at each increase in dosage (Fig. 2.2.6). For this reason no attempt was made to predict what trend was being followed in this instance. Fortunately most flocs generated in this study were something like an order of magnitude smaller and therefore similar problems did not arise in the case of H^+ and Ca^{2+} kaolins. It can thus be said that the accuracy of the settled bed results in the flocculant studies is good; probably better than ±0.2mm for each individual result with the accuracy increasing somewhat at lower dosages.

2.2.3 Results of Agitation Time - Flocculation Experiments.

Fig. 2.2.1 and 2.2.2 record the adsorption of neutral polyacrylamide (n-PAM) for 4 different flocculation dosages for the magnetic stirrer and the impeller stirrer on a Na^+ kaolin. At all the flocculant concentrations the total adsorption is achieved within an hour, except in the case of the 4mg/g dosage for the impeller stirrer, the limit being reached more rapidly the lower the initial concentration.

A number of things can be noted from these graphs :

1) The additions of 1,2 and 4 mg/g are characterized by a 'plateau' in adsorption, of some minutes duration, lower than the maximum possible adsorption for a given dosage.

2) The plateaux are less well defined in the case of the magnetic stirrer.

3) At additions of 2 mg/g and 4 mg/g the initial rate of adsorption is lower for the magnetic stirrer but the plateau adsorption is higher than that of the impeller stirrer.

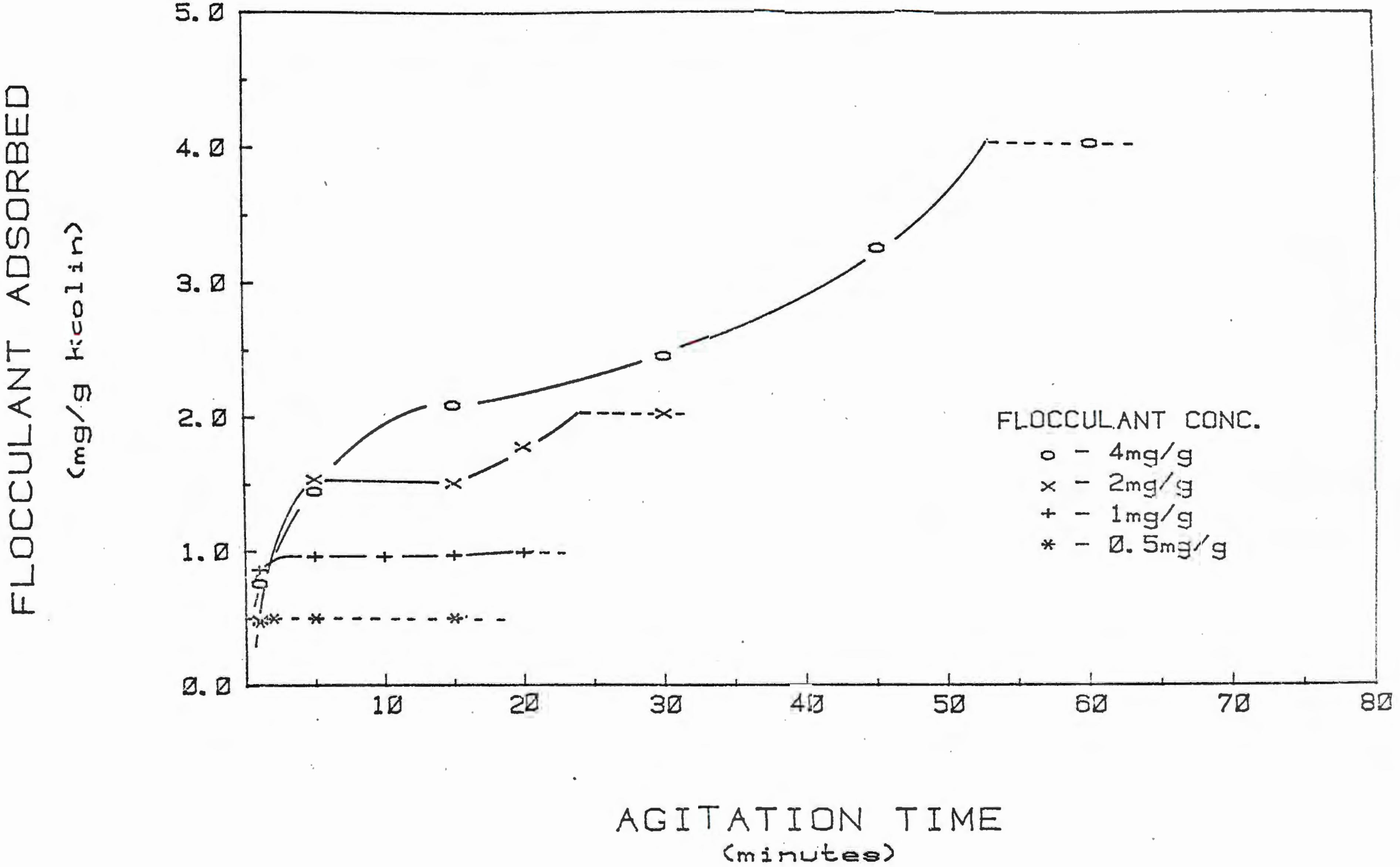


FIGURE 2.2.1

FLOCCULANT ADSORBED vs AGITATION TIME for MAGNETIC STIRRER

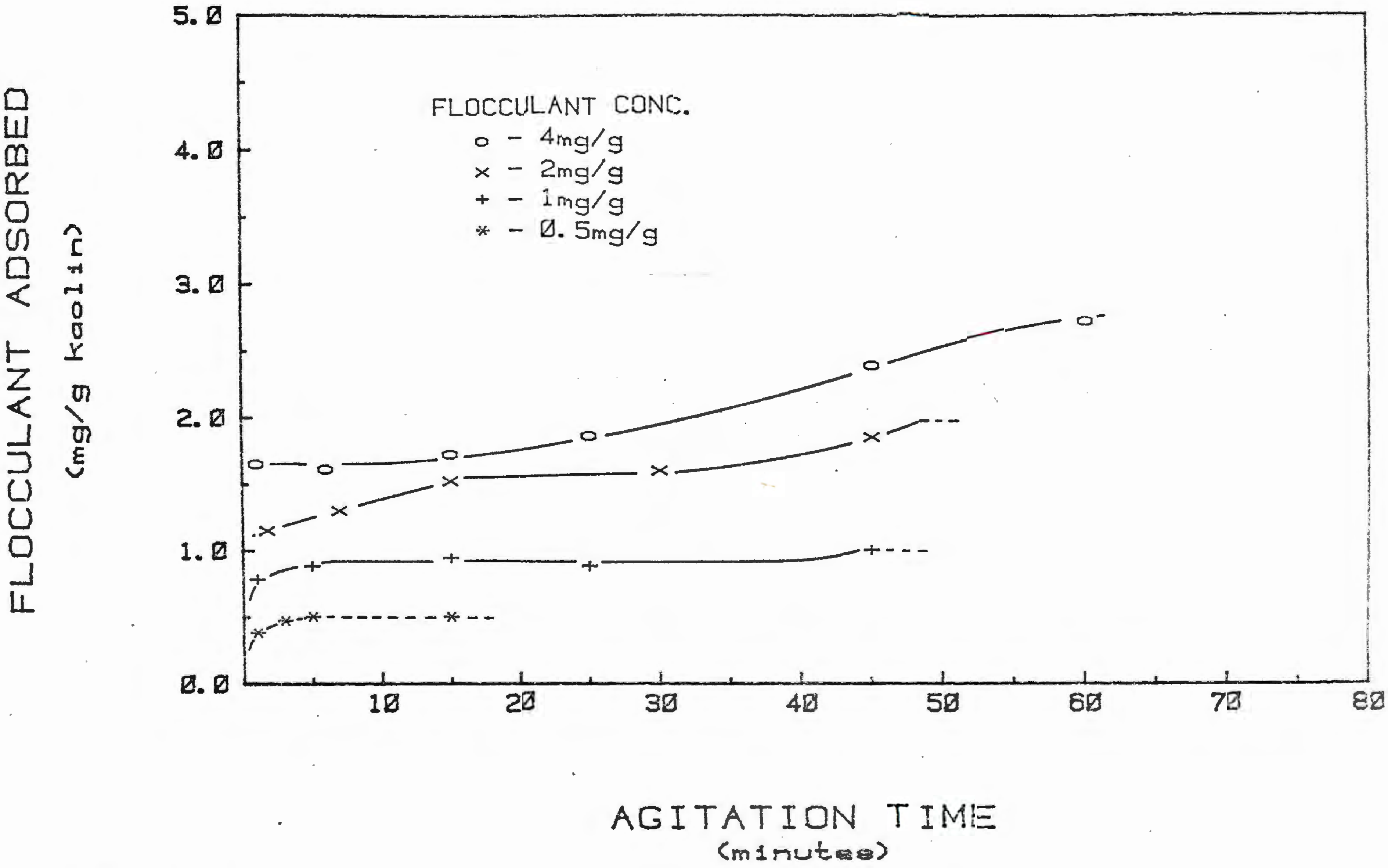


FIGURE 2.2.2

FLOCCULANT ADSORBED vs AGITATION TIME for IMPELLER STIRRER

4) The duration of the adsorption plateau appears to be reduced with higher initial PAM concentrations.

5) In the case of the 4 mg/g addition the period following the plateau adsorption may be characterized by an acceleration of the rate of adsorption. This is particularly apparent for the magnetic stirrer.

Figures 2.2.3 and 2.2.4 record the supernatant turbidity of the flocculated suspension after 15 minutes (Appendix 2) at the four different initial concentrations of flocculant for the magnetic stirrer and the impeller stirrer respectively.

The following can be noted from these graphs :

1) If the turbidity minima are considered for the two stirrers it is clear that the minima decrease as the dosage is increased reaching a minimum for the 2 mg/g dosage with a small increase in the case of the impeller stirrer at the 4 mg/g dosage. In the case of the magnetic stirrer the supernatant turbidity may not have reached its minimum value at the 4 mg/g dosage. The magnitude of this turbidity value is very similar to that of the 2 mg/g value.

2) The higher the concentration of flocculant the longer the minimum turbidity endures. The minimum is achieved at a later time.

3) In the case of the magnetic stirrer the turbidity of the supernatant increases with stirring time for all dosages of flocculant except the 4 mg/g after the minimum.

4) With the impeller stirrer the minima in turbidity at higher flocculant dosages appear more stable, but a higher magnitude of turbidity is recorded than is the case with the magnetic stirrer.

When comparing the turbidity results with data of the adsorption results there are no obvious correlations except that, in general, higher levels of adsorption result in lower turbidities. In addition it seems that the

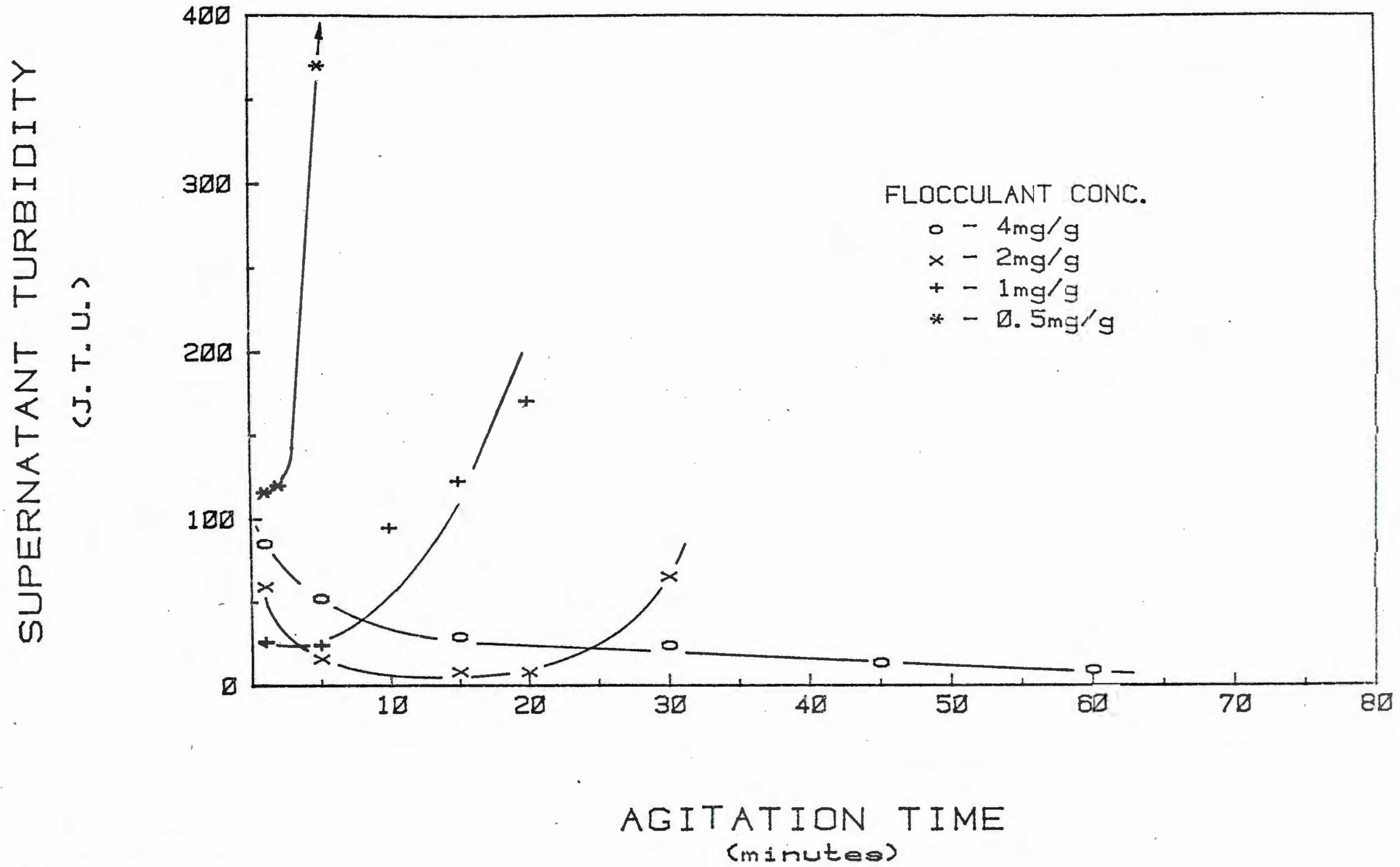


FIGURE 2.2.3

SUPERNATANT TURBIDITY vs AGITATION TIME for MAGNETIC STIRRER

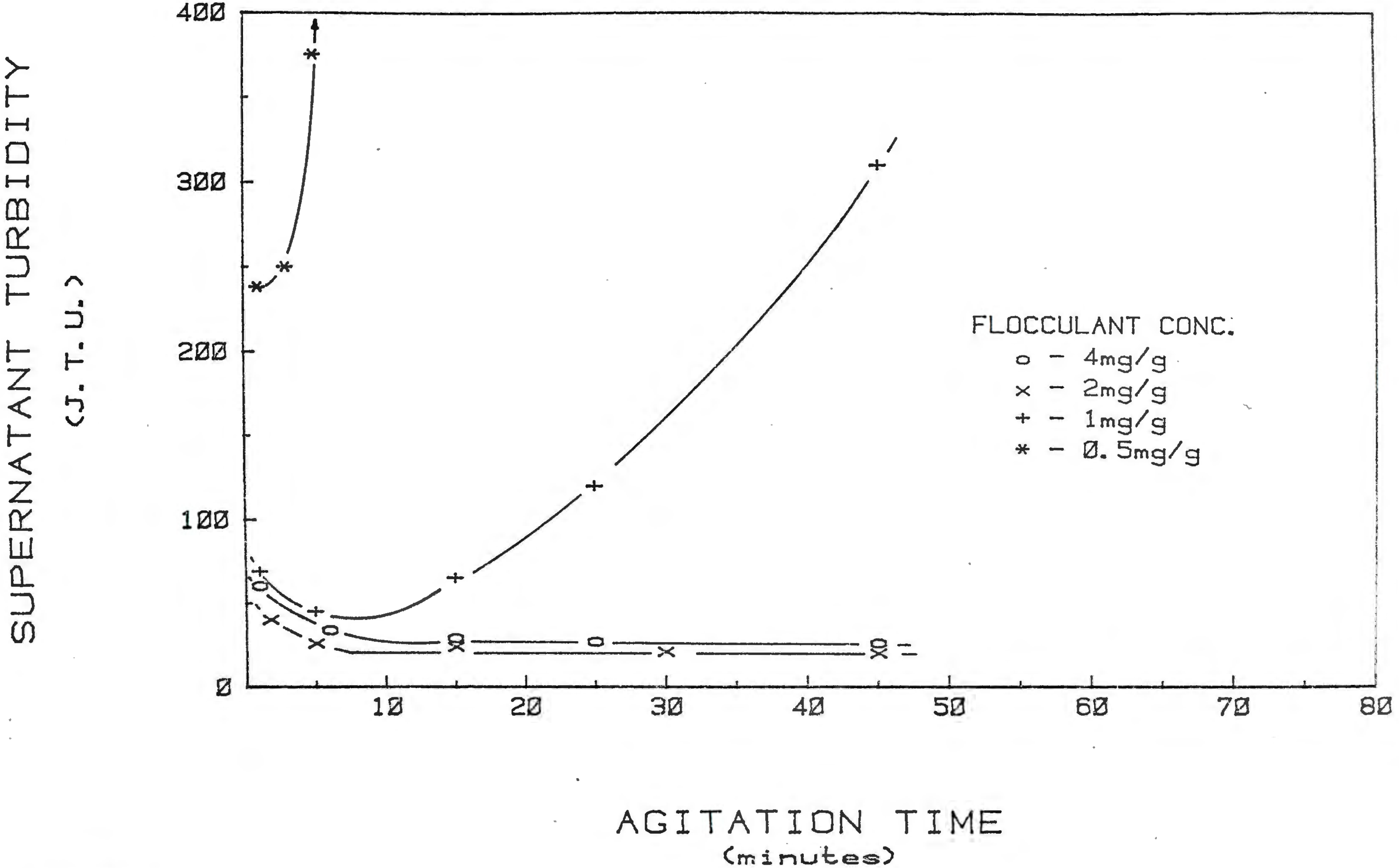


FIGURE 2.2.4

SUPERNATANT TURBIDITY vs AGITATION TIME for IMPELLER STIRRER higher impeller speed (of the magnetic stirrer) leads to lower turbidity minima where flocculant adsorption levels are very similar (i.e. at low flocculant concentrations).

Figures 2.2.5 and 2.2.6 show the settled bed heights versus agitation time of the Na^+ kaolin for the magnetic and impeller stirrers with the same form as used previously for flocculant adsorption and supernatant turbidity.

The following points may be noted :

1) The total change in settled bed height is generally greater in the case of the magnetic stirrer.

2) The settled beds of the samples stirred with the impeller are more stable with the exception of the 1 mg/g flocculant dosage, and the 4mg / g sample (see Section 2.2.2).

The reason for the variability in the results for the 1 mg/g dosage is to be found in the change in behaviour of the flocs close to the 1 mg/g dosage. In the subsequent section it will be seen that the settled bed height is at a maximum at the 1 mg/g dosage. The reasons why this maximum occurs will be found in the discussion of the present data and the results and discussion of the subsequent chapter.

3. With the exception of the lowest flocculant dosages the bed heights tend to decrease with increasing initial flocculant concentration. Again note the anomalous result for the 1 mg/g impeller stirred sample.

In comparison with the other data presented the following can be noted :

1) The plateaux in settled bed heights do not correspond directly to plateaux in adsorption-time data.

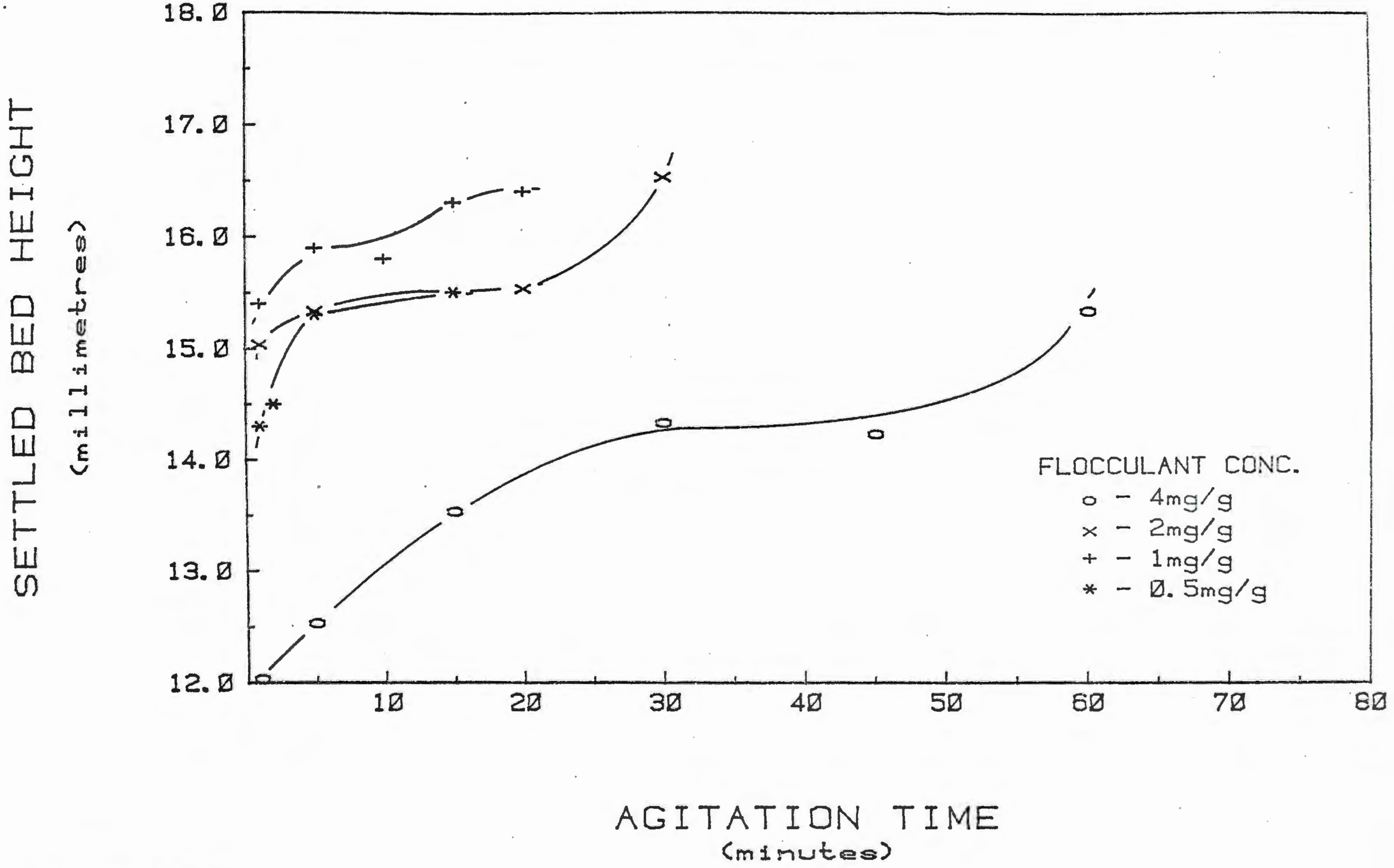


FIGURE 2.2.5

SETTLED BED vs AGITATION TIME for MAGNETIC STIRRER

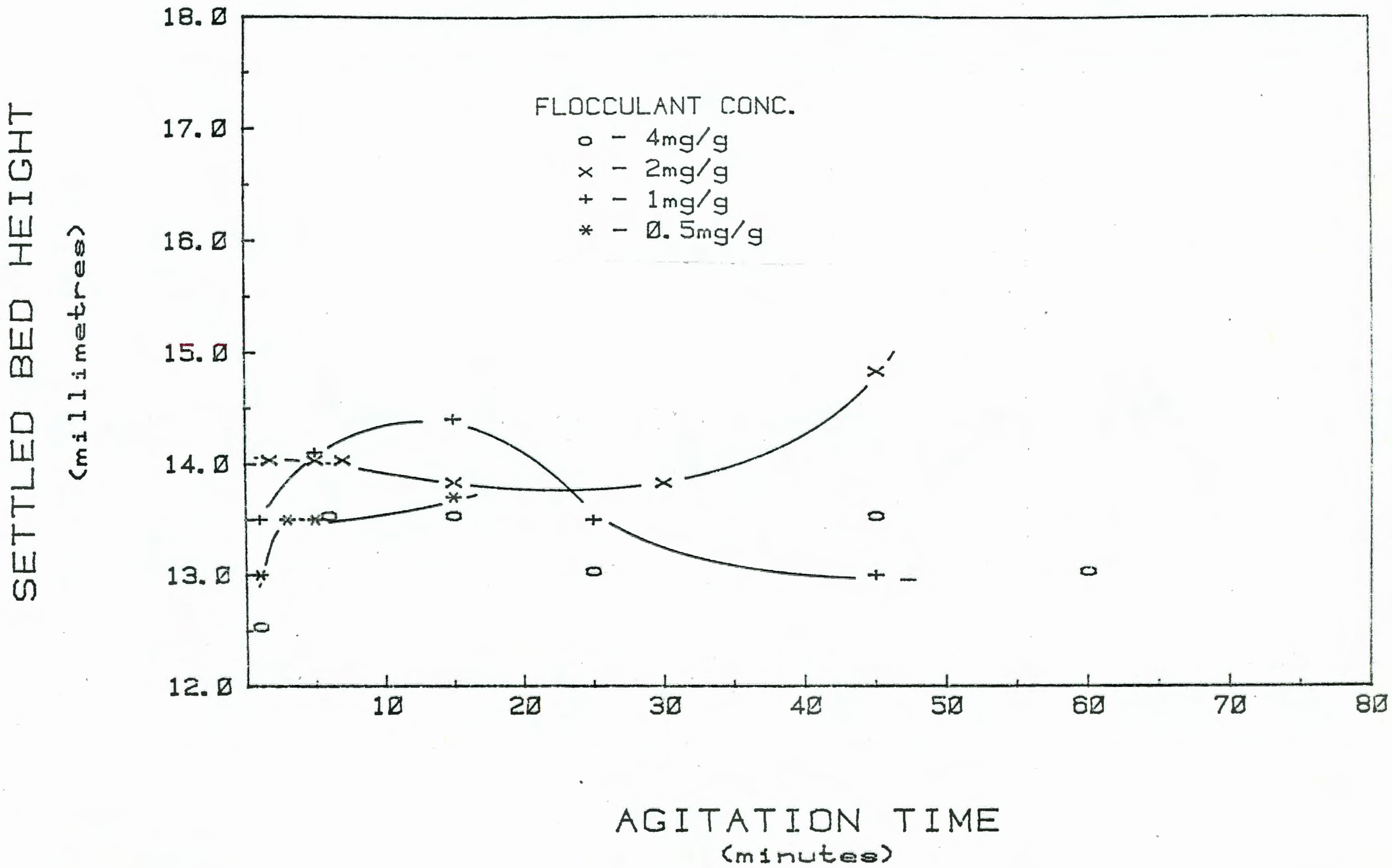


FIGURE 2.2.6

SETTLED BED vs AGITATION TIME for IMPELLER STIRRER

2) In the case of the magnetic stirrer there is a marked increase in settled bed height when the maximum adsorption is achieved (though the 1 mg/g result does not show this).

This is not the case with the impeller stirrer.

Floc structure deterioration can be observed in the case of both the impeller and magnetic stirrer photographically.

It will be noted from Fig. 2.2.7 that the damage caused by the magnetic stirrer results in a progressive reduction in the size of the flocs, with substantial disruption having taken place already at 15 minutes. In the case of the impeller stirrer (Fig. 2.2.8) there is a slight but noticeable reduction in size from 1 - 5 minutes, no substantial reduction to thirty minutes, and some obvious disruption by 60 minutes.

These two sets of photographs were taken with the camera mounted on the copy board. The flocculant dosage concentration was 2 mg/g.

Another series of photographs was taken using the stereo-optical microscope (Figure 2.2.9). This was in order to get a better impression of the change in floc structure. This series of five photographs shows the progressive change in structure with the impeller stirrer. The flocculant concentration was 4 mg/g. At 10 seconds the flocs consist of almost a single blanket which shows no evidence of disruption. At 2 minutes the blanket has been disrupted into aggregates of smaller, but still coherent, flocs. At 15 minutes there is evidence of small flocs but the field is occupied predominantly by large coherent flocs. The pattern is similar at 45 minutes. At 1 hour the process of disruption has advanced with the damage being evidenced by fibrilar appendages on most of the flocs, with evidence of disrupted fragments more obvious.

It is clear that there is some association between the plateau region of flocculant adsorption and the stability of the flocs as evidenced by the photographic record.

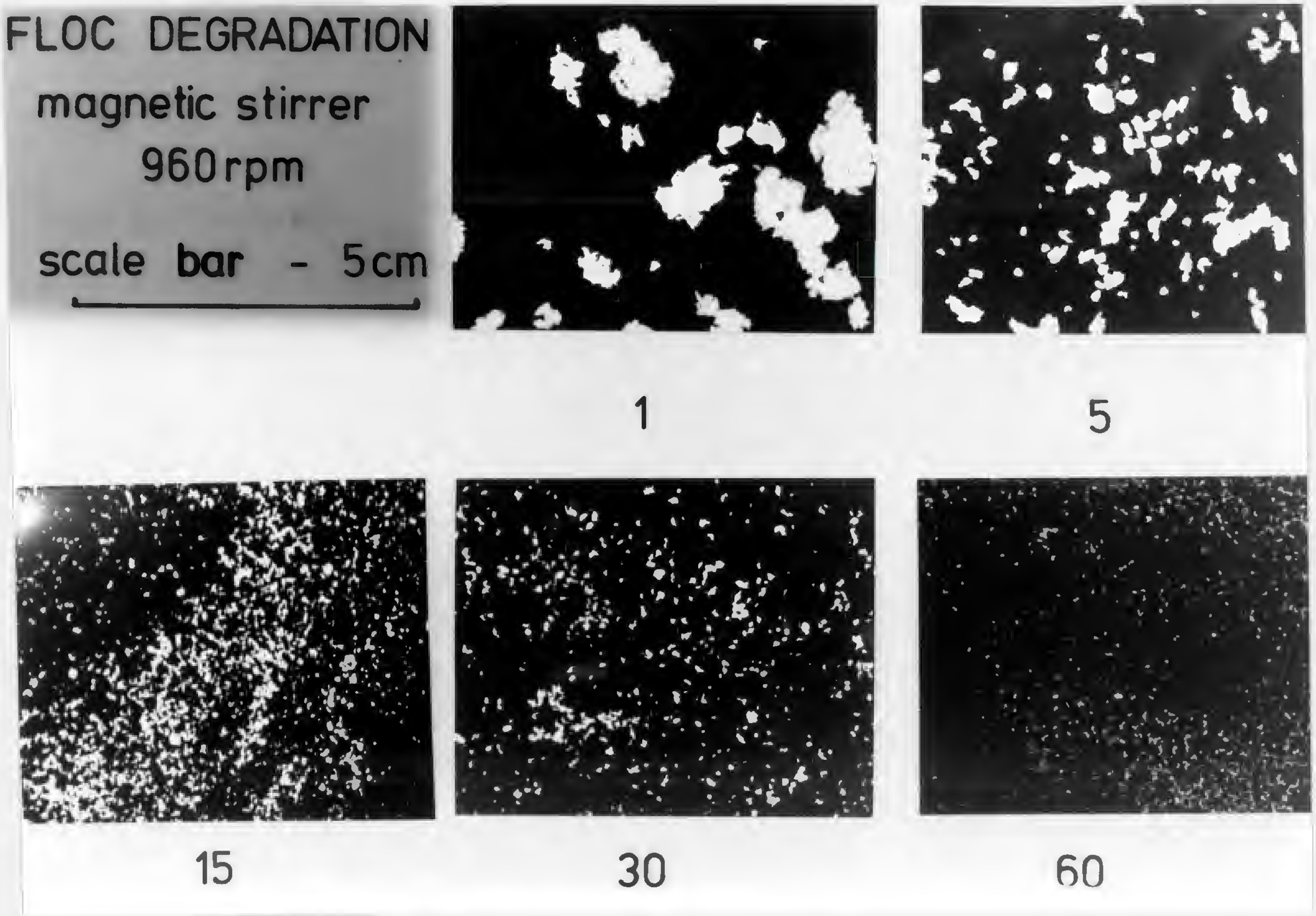


Figure 2.2.7: Floc degradation on agitation. The agitation times in minutes are shown beneath each photograph.

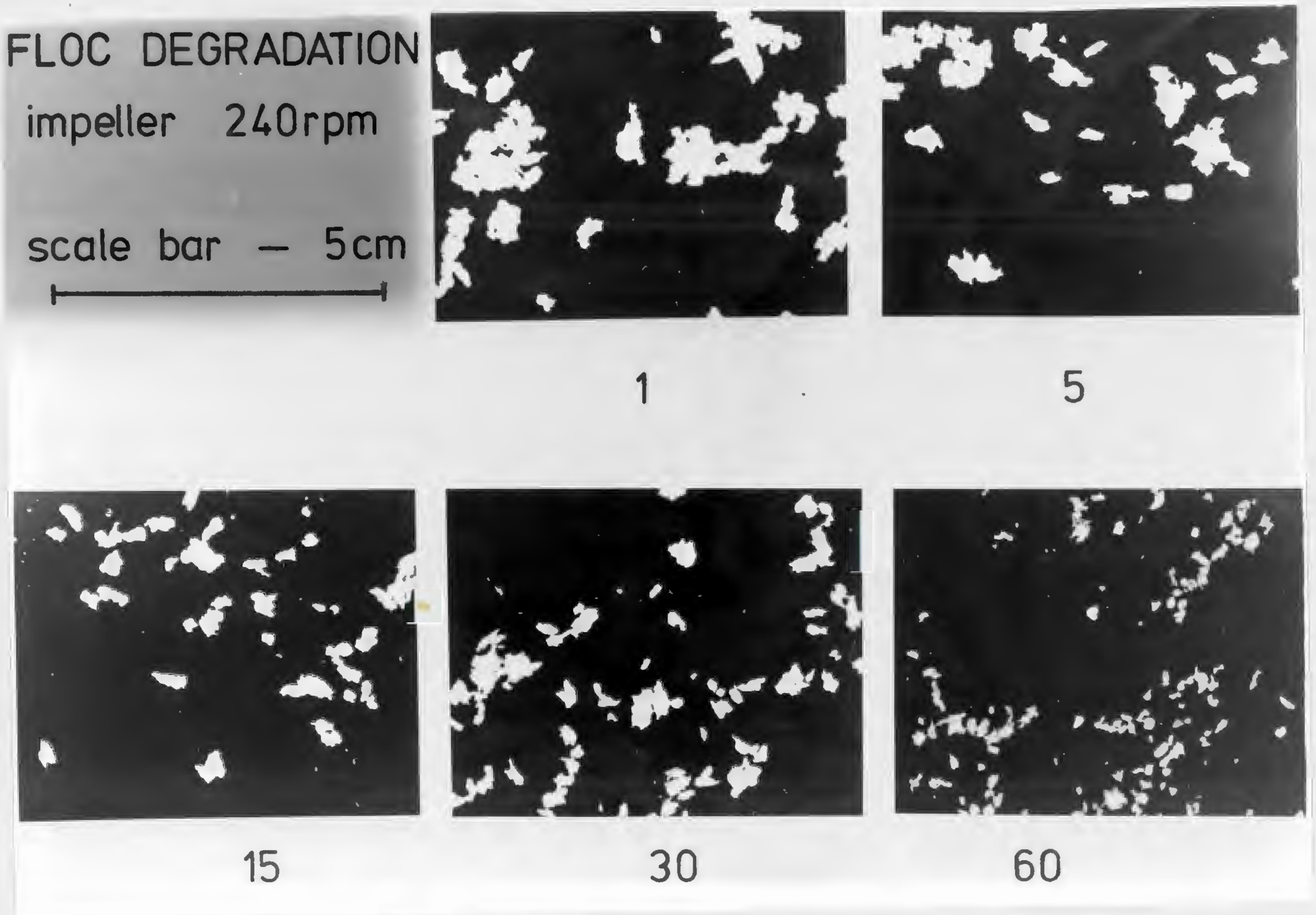
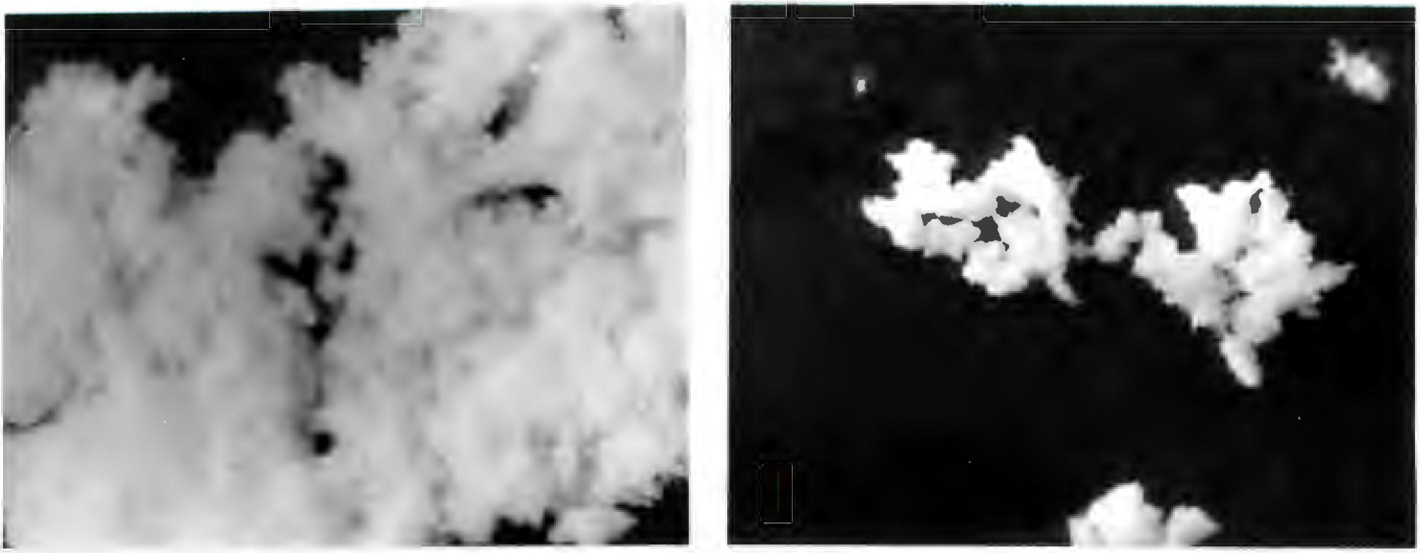
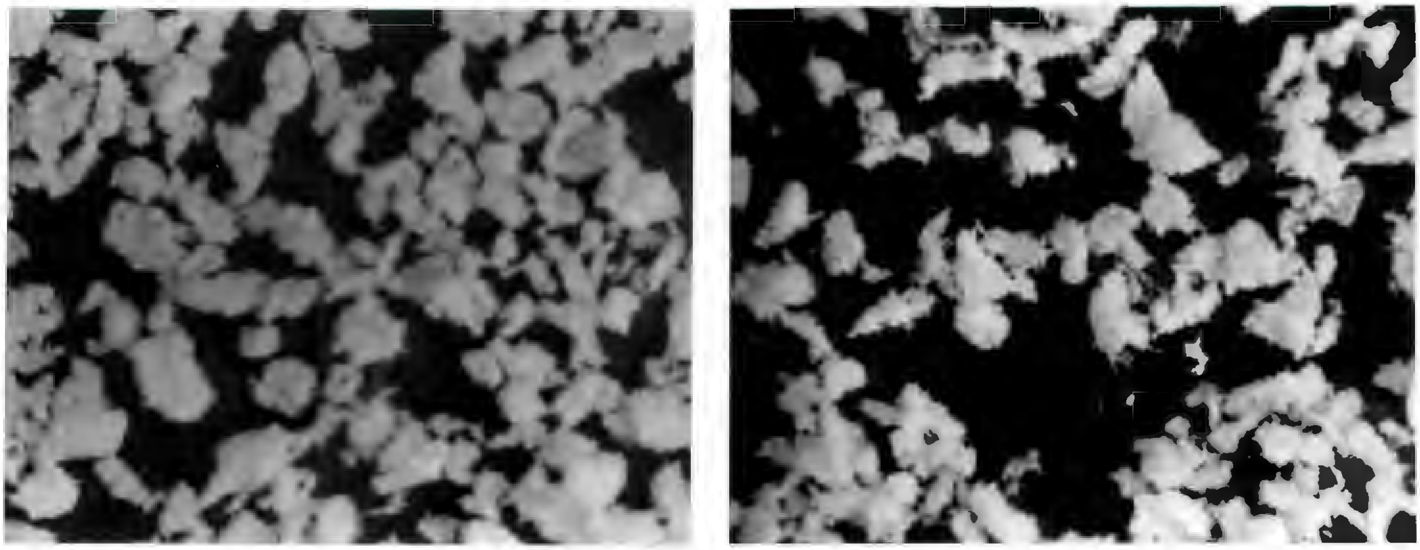


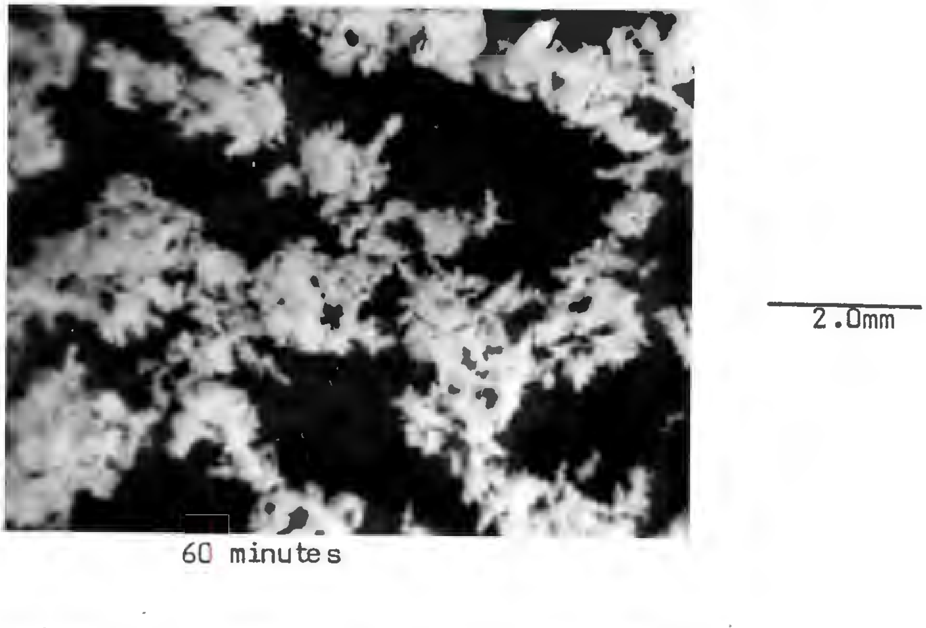
Figure 2.2.8: Floc degradation on agitation in the impeller stirrer. Agitation times in minutes are shown beneath each photograph.



10 seconds 2 minutes



15 minutes 45 minutes



60 minutes

Figure 2.2.9: Na^+ kaolin treated with n-PAM. Dosage 4mg/g. Micrographs showing the effect of agitation on floc structure.

It is the power input in the zone of maximum impeller intensity that gives rise to the different levels of floc breakdown that can be observed photographically and in the various parameters that give an indication of the degree of flocculation. This basis for the interpretation of the stirring results will be pursued in the discussion.

2.3 Discussion

On agitation floc structure and flocculant adsorption are affected by energy input and flocculant dosage. In addition classical measures of flocculation give insight into these processes.

2.3.1 Effect of Energy Input

The stirring systems designed to evaluate the effects of agitation were characterized by almost equal values of Re_1 but very different magnitudes of power input. If the criteria that give rise to floc rupture are related only to the instantaneous condition of the suspension then an equilibrium floc structure would be established rapidly, following initial floc formation. However, if the process is related to the total amount of energy per unit volume of suspension that is put into the system, floc breakdown that is time dependent could be expected. Time dependent floc degradation is observed in the case of magnetic and impeller stirrers. The magnetic stirrer, when analysed, has approximately twice the mean volumetric power input of the impeller stirrer. However in the maximum intensity zone the volumetric power input is about 16 times that of the impeller stirrer. Since rupture events are most likely to occur in this region the more rapid breakdown of floc structure in the magnetic stirrer is easily understood.

The observation that the process is time dependent and also relatively independent of the Reynolds number derived from the turbulence criteria indicates that the assumption of homogeneous turbulence in stirred tanks at moderate impeller velocities is not an adequate explanation of floc rupture phenomena. A more profitable approach is the empirical description of the stirring system based on the work of Rushton et al as developed by Davies. The use of volumetric power numbers, P_m, and the analysis of the tank as comprising of three regions, as described, provides the soundest basis for deciding which stirring system will be more aggresive in terms of floc degradation. To reduce power input (and therefore inhibit floc degradation) in the zone of maximum intensity the volume swept by the impeller should be increased as much as possible and the radial velocity reduced. This may not however be the best basis for forming flocs initially.

2.3.2 Stirring and Flocculant Adsorption

The experimental variables discussed here are the two different types of stirrers, and the time for which the flocculated suspension was stirred. The most obvious result in terms of the stirrers is the generally higher adsorption that occurs in the magnetic stirrer. In the case of the 2 mg/g and 4 mg/g dosages the difference is significant. The shape of the curves at these dosages is also different. The rate of flocculant uptake is more rapid for the impeller stirrer although the plateau level is lower. These results must be interpreted in terms of a model of agitation-adsorption and floc structure. The adsorption data at long times indicates that there is a relationship between floc degradation and increase in adsorption. This was clearly noted from macroscopic and microscopic evidence of the floc structure. At the plateau regions there is a stable floc structure and no adsorption under agitation. It is therefore not inconsistent to assume that the initially rising portions of the adsorption-time graphs for the magnetic stirrer and the 2 mg/g dosage for the impeller stirrer are due to floc instability which results in increased adsorption until stable flocs (at the adsorption plateau) are formed.

Thus the duration of the adsorption plateau appears to be reduced when the concentration of unadsorbed flocculant is higher since the probability of flocculant adsorption on exposed surfaces, following degradation events, is increased. The process of redispersion of material then proceeds. The 2 mg/g impeller stirred adsorption-time data can also be understood in these terms of excess flocculant adsorption. The initial level of adsorption is low (close to 1 mg/g) and increases slowly to a similar plateau level to the sample dosage of 4 mg/g. This transition can be understood as a progression from the stable adsorption plateau at 0.87 mg/g for the 1 mg/g dosage to the higher plateau for the 4 mg/g dosage which results from the presence of the flocculant excess.

The plateau at the 4 mg/g dosage in its turn also terminates as flocculant adsorption increases following degradation of the flocs.

These results are substantially in agreement with the work of Jankovics who showed increased level of adsorption with increase in stirring speed which indicates greater floc durability at lower speeds. Jankovics did not however observe the characteristic plateau region (except perhaps with the higher molecular mass flocculants) found in this study. It should be said therefore that the plateau region is not a necessary characteristic of polymer-mineral interaction at all stirring speeds but it does give evidence of stable flocs that are not significantly degraded during agitation over the plateau region of adsorption as is confirmed by the photographic record.

The study of Tomi and Bagster (1978) and Healy showed lower levels of flocculant adsorption at higher stirring rates, but decreased floc size. In the present study the problem has been constructed differently. The impellers were chosen to have identical tip velocities but different rotation rates (the magnetic stirrer being 4x that of the impeller stirrer). This was done to identify what the critical variable is in agitation. The results of the present study suggest that it is not a turbulence controlled mechanism but rather one that is controlled by the energy input into the system in the region close to the impeller. The lower initial adsorption of flocculant with the magnetic stirrer confirms that the findings of reduced flocculant adsorption at short times with increased impeller speeds are correct, but it should be noted that in the presence of excess flocculant breakdown of flocs can result in higher levels of adsorption.

It is also interesting to note that for the impeller stirrer the plateau level of adsorption for the 2 mg/g dosage and the 4 mg/g dosage is very similar suggesting that the adsorption at a stable level may be due to a combination of the initial concentration and the prevailing turbulent condition of the stirrer. This area would require further investigation.

2.3.3 Agitation and Flocculation Parameters

The two flocculation parameters, settled bed height and supernatant turbidity can provide insight into the effects of agitation. The change in the settled bed heights of the kaolin agitated with the magnetic stirrer provides an independant assessment of the floc disruption process. The general increase in bed height with time suggests a floc density reduction with disruption of the flocs.

The analysis of variations in bed height is however complicated since at low flocculant dosages small compressible flocs form which result in lower settled bed heights. At intermediate flocculant dosages the flocs become discrete and more rigid and hence there is an increase in bed height. Higher dosages still cause an increase in floc density resulting in a decrease in bed height. An analysis of the reasons for this view will be presented in the discussion in the subsequent section, but it will be assumed in the discussion of the present results.

The most notable finding with respect to the settled bed heights of the Na^+ kaolin is the smaller total change in bed height of the impeller stirred kaolin across the dosage range. With the exception of the 1mg/g dosage which is at the point of the change in floc behaviour noted above and the 4mg/g dosage the heights at each dosage do not vary more than 0.5mm in the plateau region. By contrast the plateau conditions in the case of the magnetic stirrer are foreshortened presumably by disruption of the flocs (seen photographically) as a result of the higher energy input of the magnetic stirrer.

The bed heights of the flocs generated in the magnetic stirrer are higher suggesting a lower floc density. However, there is, for the higher dosages, a general decrease in bed height with dosage which is an indication that the density increases with dosage. These results did not indicate whether it would be more profitable to use the impeller stirrer as the basis of the experimental technique if any reliable measures of bed height were to be made. Plateau conditions however were observed to exist for the impeller dosages (except 1mg/g and 4mg/g) at about 15 minutes, which facilitated the choice of agitation system when supernatant turbidities were considered.

Figure 2.3.1 is a diagram of the supernatant turbidity minimum for the range of flocculant dosages. The time of achievement of the minimum in minutes is recorded and the time to which the minimum persisted. As has already been noted the minima generated with the magnetic stirrer are

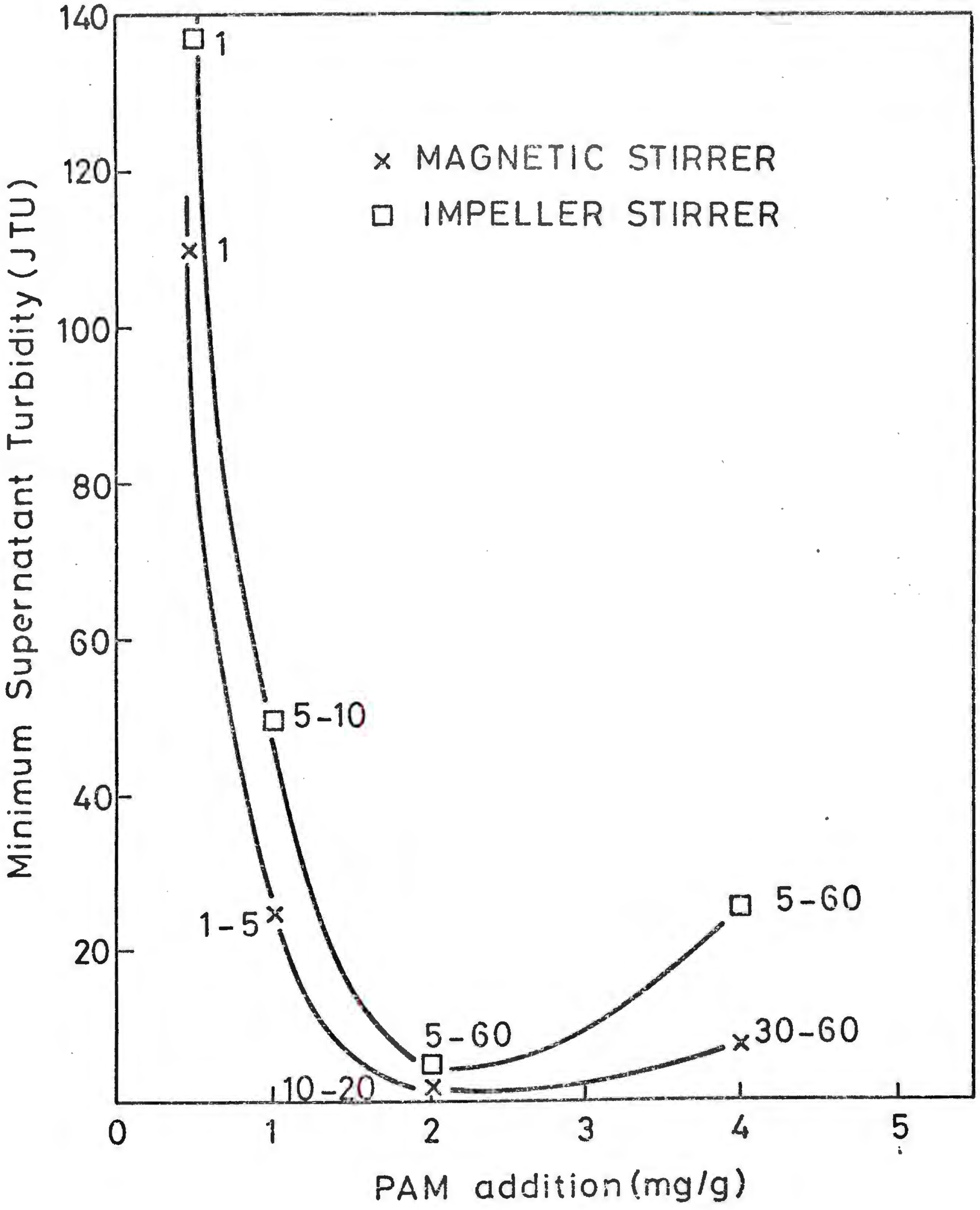


Figure 2.3.1: Minimum supernatant turbidity achieved at increasing concentrations of n-PAM. The approximate starting and finishing times of the minimum are indicated at each dosage.

lower. The lowest minima for the stirrers are achieved at 2 mg/g dosage and they persist for at least 10 minutes. This suggests that the minimum turbidity is achieved at higher dosages than is the case for the settled bed maximum ($\sim$1mg/g). The length of time that the minimum persists for is strongly a function of the flocculant dosage. This suggests that at low dosages a particle erosion mechanism may be operating to resuspend some mineral particles, but without excess flocculant adsorption since there is inadequate excess flocculant available. As the flocculant concentration increases the statistical chance of a particle escaping an effective bridging event is reduced and thus floc disruption does not allow resuspension of flocculant-free mineral particles, but some may adsorb excess flocculant and be resuspended (stabilised).

The first process (of particle erosion) is reduced by increasing the dosage but the second becomes more favourable so a minimum in supernatant turbidity ensues under the competition of these two processes.

The lower minima of the magnetic stirrer can possibly be related to the analysis of Hudson for the case of settling. Since the floc volume (as indicated by the settled bed height) is higher for the magnetic stirrer across the dosage range there is more efficient capture of particles by the settling floc bed. It is probable that future kinetic studies will provide a better basis for understanding this phenomenon.

The turbidity minima for the impeller stirrer appeared to be more enduring, particularly at about 10-15 minutes. Since this represented a similar pattern in at least some of the settled bed results and since the adsorption results confirmed this it was decided that the impeller stirrer was a better basic apparatus for the examination of flocculation using a variety of flocculants and different homoionic forms of the kaolin under standard conditions of agitation.

CHAPTER THREE

THE FLOCCULATION OF KAOLIN

3. THE FLOCCULATION OF KAOLIN

3.1. Literature Survey

3.1.1 The Extent of the Literature

Studies involving the flocculation of kaolinite are numerous, (Dollimore, Horridge and Owens, Dollimore and Horridge 1971, 1971/1972, 1972, 1977, 1973; Black, Birkner, and Morgan, 1965, 1966; Micheals and Bolger; Sakaguchi and Nagase; Bhatty, Dollimore, and Zahedi; Linke and Booth; Th. Stutzmann and B. Siffert; Packham 1965; Schamp and Huylebroeck; Jankovics; Roberts, Kowalewsha and Friberg; Micheals and Morelos; McCarty and Olsen).

In addition there exist many studies of the flocculation of quartz, silica and other minerals with polyacrylamides and polyacrylates (van Lierde; Dixon et al; Kane, LaMer and Linford 1963; 1964; Slater and Kitchener; Slater, Clark and Kitchener; Healy; and others).

More general papers have also appeared discussing the nature of flocculation from an experimental background (Healy and LaMer; LaMer, Friend and Kitchener; Slater and Kitchener; Slater, Clark and Kitchener; Dollimore, Griffiths and Miller). In addition some papers deal with the nature of adsorption on kaolinite as related to its electrical and chemical behaviour in suspension (Mortensen 1957, 1959). There are also a number of reviews (Vincent; LaMer and Healy; Akers 1972; Gregory 1978). This body of literature provides a background against which further research into flocculation and flocculation-adsorption reactions can be conducted.

The most extensive body of work into the kaolinite-polyacrylamide system is that of Dollimore and his co-workers. In order to assess the literature the findings and insights of these researchers will be detailed and then compared and contrasted with the other literature mentioned above.

3.1.2 Floc Sizes

The earliest paper in the series was concerned with the floc sizes of kaolin flocculated by polyacrylamide. Average floc radii using 3 empirical relationships were computed. The floc radii were similar for the cationic and anionic polyacrylamides and smaller for the neutral polyacrylamide.

Settled bed volumes were in the order water < anionic < cationic < neutral with pH about 4.9. The polymer concentration used to determine floc radii was the optimum flocculant dosage for the specified solids content. The flocculant demand was in the order anionic < cationic < neutral.

3.1.3 Refiltration as a measure of Flocculation

The filtration of kaolin treated with polyacrylamide was next examined (Dollimore and Horridge 1971/1972). The particular consideration here was the applicability of the refiltration theory of Smellie and LaMer (LaMer) to flocculation studies. This theory based on the Kozeny-Carmen equation and Smoluchowski's coagulation theory has a basic relationship of the form :

$$\frac{P_o^{\frac{1}{2}}}{(Q - Q_o)} = A + B P_o$$

where :

Q rate of filtration through the flocculated bed.
Q_o rate of filtration through the unflocculated bed.
P_o flocculant dosage (p.p.m.)
A, B constants.

Smellie and LaMer indicated that A/B is equal to P_m, the optimum flocculant concentration. A suitable plot gives A and B and hence P_m can be calculated. Dollimore and Horridge introduced a further variable P_e, which was the dosage for the maximum refiltration rate. Six polyacrylamide flocculants were used (3 anionic, 2 cationic and 1 neutral) all with molecular weights of the order of 3×10^6. They found that for anionic polymers the data fitted the theory reasonably well but that the calculated values of P_m, the optimum flocculant concentration, did not agree with the measured values. P_e, the concentration for the maximum rate of refiltration was coincident with the concentration producing the maximum rate of fall of the interface in settling tests.

The results for the neutral and cationic polyacrylamides did not fit the theoretical formulation so P_m could not be predicted. The authors saw some usefulness in the test however since the maximum refiltration rate was coincident (with the anionic polyacrylamides)with the maximum rate of fall of the interface. The most cogent criticisms of the refiltration theory remain those of Slater and Kitchener. These criticisms are as follows (Slater and Kitchener) :

1) three adjustable constants in the theory
2) an unjustifiable mathematical correction
3) the assumption of constant floc size in the cake and in free settling.
4) the assumption that the filter cake height is constant for different flocculant dosages.
5) the assumption that maximum refiltration rate is coincident with optimum flocculation (which Slater and Kitchener showed was not valid for fluorite and an anionic flocculant).

Their work is frequently cited in discussion of appropriate methods to measure flocculation (Akers 1978; Kitchener (1978); Vincent). It seems generally accepted now that the refiltration theory is in the formal sense a failure. However (Dollimore and Horridge, 1978) have suggested that its usefulness as a test is not related to L, (the length of the bed, which LaMer and Smellie considered a constant, or, E, the voidage of the bed which is the controlling parameter but L_e, the effective length of the bed to the suspension fluid, which suggests that the maximum refiltration rate is related to the formation of "large loose flocs", which will be associated with high filtration rates because L_e will be low. In a study of vacuum filtration of kaolin slurries (Estcourt) flocculated with polyacrylamide it was shown that increase in flocculant concentration results in decreasing cake resistance to zero with a subsequent small decrease in filtration rate which was attributed to viscosity changes in the supernatant fluid, and not to specific cake resistance increase.

At the limit filtration took place through a fairly compressible bed by filtrate flowing around floc superaggregates, which are not compressed substantially themselves.

Below polymer dosages of 0.6 mg/g of kaolin the rate of filtration decreased with addition of flocculant when compared to the untreated slurry. This suggests the effective fluid volume of mobile filtrate was reduced initially by the creation of flocs, and that the formation of larger more coherent flocs with increase in polymer concentration resulted in a macroporous pathway for filtrate to move through the filter cake. In addition the greater strength of flocs generated at higher dosages may result in a less compressible bed (Kitchener; disputed by Dollimore and Horridge 1972).

3.1.4 pH Variation and its effect on Flocculation

Dollimore and Horridge in further work (1973) on kaolin flocculated with polyacrylamide, investigated the relationship between flocculation parameters and pH. Here the simple relationship noted earlier between filtration rate and sedimentation rate broke down when projected along the pH axis. A maximum refiltration rate was noted at pH 5.8 for kaolin treated all with types of polyacrylamide and this coincided with a maximum in the sedimentation rate for the neutral polymer. The anionic polymer had a maximum sedimentation rate at pH 4.5 - 5, and the cationic had two peaks, one at pH 4.5 - 5 and one at pH 9.5 - 10, with a trough at pH 5.8. However the maxima in settled bed volume are coincident with the maximum in refiltration rate along the pH axis. Thus the earlier research indicates that maximum refiltration rate at a constant pH of 4.9 is coincident with a minimum in settled bed volume (although the minimum is frequently not pronounced) which was interpreted as the most effective condition of flocculant adsorption. However as their later results indicated (1973) the relationship between settled bed minimum and sedimentation rate maximum breaks down. At pH 5.8 the sedimentation maximum is coincident with the settled bed maximum for a neutral polyacrylamide. There is little modification of the light transmission curve. At pH 9.5 there is again coincidence of the settled bed maximum at the maximum sedimentation rate and little modification of the light transmission curve. It would seem therefore that the phenomena giving rise to the measured settled bed volume above a pH of about 5.5 are related in a different way to the sedimentation rate than those that operate below a pH 5.5. This may be due to changes in particle association phenomena as is suggested by Dollimore and Horridge. It is notable that there is always a maximum in the settled volume vs flocculant dosage graphs that is coincident with a maximum in light transmission, although it becomes less pronounced with increasing pH.

To summarize, along the pH axis the obvious relationship is between the refiltration rate and the settled bed volume, while along the polymer concentration axis it is between the sedimentation rate and the refiltration rate and secondly between light transmission and the settled bed volume. The relationship between settled bed volume and refiltration rate in the situation where pH is varied suggests that the permeability of the bed is an important criterion in refiltration.

3.1.5 Flocculant Adsorption

The work of Dollimore and Horridge did not involve the recording of the amount of polymer adsorbed. The work of Black, Birkner and Morgan (1965) approached the flocculation of kaolin from a water treatment perspective. Thus much lower particle concentrations (33 mg/litre) were used and settling velocity and filtration parameters were not measured. The amount of polymer adsorbed was measured as was the electrophoretic mobility of the particles and the residual turbidity of the suspension. Two hydrolysed polyacrylamides (PAM) were used at pH 7 in a synthetic water at an ionic strength of about 0.5M. The 4% hydrolysed PAM which they designated HPAM - 4 produced a minimum turbidity at 7.19 mg/g kaolin while the HPAM - 30 produced an equivalent minimum turbidity with a dosage of 0.33 mg/g kaolin. Almost all the flocculant was absorbed at these dosages.

An analysis of Dollimore and Horridge's results has been tabulated:

		Dosage for maximum light transmission mg/g	
Type	Flocculant Designation	Clay RT	Clay SPS
Anionic	A 150	0.20	0.30
Anionic	A 130	0.20	0.30
Anionic	A 100	0.30	0.35
Neutral	S 20	1.00	1.65
Cationic	C 100	0.35	0.40
Cationic	C 110	0.40	0.50

As can be seen the dosage level is very similar for the anionic flocculants in the two different studies (Dollimore and Horridge worked with 10% solids suspensions) but the much higher level of adsorption with the less anionic HPAM - 4 than with the neutral flocculant used by Dollimore and Horridge cannot be easily explained.

3.1.6 Exchangeable Cation.

Dollimore, Horridge and Robinson later (1977) investigated the effect on flocculation behaviour resulting from modification of the exchangeable cation on the clay surface. The used Na^+, K^+ and Li^+ forms of the clay and used a nonionic flocculant of molecular mass 3×10^6. The pH was controlled at 5.8.

The dosage required to produce the optimum filtration and sedimentation rates was the same for the three homoionic forms (2.1 mg/g kaolin) which is higher than the dosage that was required at pH 4.9 (1.65 mg/g). The sedimentation rate maximum was the highest for the Li^+ kaolin and then the K^+ followed by Na^+. This order was paralleled in the filtration rate data. Dollimore and Horridge interpreted these results in terms of the hydration of the cations, since the water vapour adsorption experiments showed the same order $Na^+ > K^+ > Li^+$, suggesting the modification of the amount of water associated with the particle or floc results in differences in the settling rates. This must be regarded as an extremely tenuous interpretation since, as has been pointed out, the interior water in a floc is immobilized during sedimentation (Sutherland). Thus only the surface of the floc is encountering the shear forces that result in the sedimentation process. In addition it is not made clear what role is played by the adsorbed flocculant, which modifies the shear plane location on adsorption (Gregory 1978). It is also not made clear whether

a) size differences in the flocs rather than hydration process, or
b) density changes in the flocs themselves (due to the differences in repulsion, ψ_d, and polymer conformation)in the presence of different ions.

are responsible for the changes in settling rate. No other work appears to have been done on the role of the exchangeable cation in flocculation although other studies discuss the effect of ions such as Al^{3+}, Na^+ and Ca^{2+} at different ionic strengths (Roberts et al; Black Birkner and Morgan 1965; Micheals and Morelos). However Mortensen (1957) investigated the relationship of the exchangeable cation and anion on kaolin to the adsorption of hydrolysed polyacrylonitrile and found, in general, an increase in adsorption with increasing valence of the cation and related those findings to the normal lyotropic series indicating that the major effect of the cation was in the reduction of the zeta-potential of the clay particles. This is related in turn to the degree of hydration of the cations and the persistence, in particular, of the outer hydration sheath in the Stern layer. They generalized this finding to say that the adsorption of polyelectrolytes increased with decreasing zeta potential of the mineral.

The H^+ kaolin, exhibited a higher level of adsorption than expected. Unfortunately there is no evidence that pH was controlled in these experiments and, as has been mentioned, this can be expected to have a profound effect on the adsorption of polyelectrolytes. However, increased adsorption with decrease in surface charge can also be deduced from the theory of Hesselink.

In a later paper Mortensen (1959) showed that increasing ionic strength resulted in an increase in the adsorption of polyacrylonitrile. In addition the behaviour of 1 : 1 and 2 : 1 electrolytes was considerably different (from the shape of the adsorption-electrolyte concentration results). This suggests that different mechanisms give rise to the adsorption. The 1 : 1 electrolytes decrease the zeta potential and the 2 : 1 electrolytes may become involved in particle polymer ionic bridges. The role of the anion was shown to have some significance. However the results of Mortensen give no further insight into the differences in flocculation behaviour observed by Dollimore el al (1977). The role of the exchangeable cation in flocculation by polymers and polyelectrolytes requires further elucidation, in particular, in the understanding of the differences of flocculation behaviour that may be observed with different cations.

A detailed study of the effect of hydrolysed aluminium ions (Roberts et al) on the sedimentation of kaolin in the presence of polyacrylamides (as measured by light transmission of the supernatant) showed, initially, an improvement in flocculation with increase in aluminium ion concentration. This improvement depended on the polyacrylamide concentration at higher dosages of Al^{3+} ions at pH 5. The three types of polyacrylamide (cationic, nonionic, anionic) showed an increase in sensitivity to the aluminium ions in the order cationic < nonionic < anionic. The best performers were the nonionic polyacrylamides at median dosages of aluminium ion (5 - 20 ppm). At pH 3 with an anionic polyacrylamide (which will be effectively nonionic) the addition of aluminium ions has no effect on the sedimentation behaviour. The difference in behaviour may be related to the precipitation of an hydrolysed aluminium ion of high charge on the surface at pH 5, thus reducing the ψ_d to a low value resulting in improved flocculation. At higher dosages however the particle charge is reversed (Packham; Roberts et al) and flocculation becomes less efficient due to restabilization of the kaolin with a positive surface charge. This was shown from electrophoretic mobility measurements. This explains why at pH 5 the anionic flocculant is still very efficient at high aluminium dosages, while the cationic form becomes progressively less efficient due to mutual repulsion between the polycation and the positively charged kaolin surface. Thus at pH 3 the destabilization mechanism is double layer compression, but at pH 5 adsorption of hydrolysed aluminium ions is the important mechanism. Black (1960) suggests that highly charged flocculants might be crosslinked by oppositely charged ions and that this might modify their flocculation efficiency. It was noted that polyanions and neutral polymers could be coagulated at pH 5 (Roberts et al) by comparatively low dosages of aluminium ions suggesting the formation of a polymeric ion - organic polymer complex. This also suggests that flocculation may be activated by such links between the particle surface and the polyion as has been suggested for the Ca^{2+} ion (Van Lierde; Gregory 1978; Black, Birkner and Morgan 1965). This did not occur at pH 3.

3.1.7 Effect of Molecular Mass

Other elements of the flocculation of kaolin remain to be investigated. The role of the flocculant molecular mass has been much discussed (Dixon et al; Gregory 1973, 1969, 1978; Akers 1972; Ash and Clayfield; van Lierde; Kitchener 1978; Walles; Stutzmann and Siffert; Schamp and Huylebroeck; Linke and Booth; Jankovics).

Some researchers found an increase in flocculant (mass basis) required for optimum flocculation (as determined by settling rate) with increase in flocculant molecular mass (Linke and Booth). Others found no definite relationship between molecular mass and flocculant demand (Stutzmann and Siffert) although this was not related to specific flocculation parameters. Akers (1972) in a review mentions that the approach of Silberberg has shown that there will be little dependance on molecular mass above 500 000 a.m.u. Kitchener in a review mentions that flocculation and floc strength are improved by high molecular mass flocculants. This is supported (Jankovics) by a study that showed deflocculation on prolonged agitation is much less rapid with higher molecular mass flocculants. A careful study (Ash and Clayfield) showed that flocculants of higher molecular mass flocculated a latex slurry optimally at lower dosages but that the floc stability decayed more rapidly at excess dosages. This seems to contradict the assertion of Gregory (1978) that increased flocculant molecular mass increased the breadth of the flocculation region (as a function of dosage) and that the rate of flocculation increased. Schamp and Huylebroeck, in the study of PAM adsorption on kaolinite concluded that increasing molecular mass resulted in lower levels of adsorption (presumably in the limit) which contradicts the finding of Jankovics that the molar adsorption in the limit is a constant (and therefore that total mass of flocculant adsorbed increases with increase in molecular mass).

3.1.8 The Contribution of Agitation

It is important to note that the major changes observed with molecular mass variation occur from low to intermediate molecular masses (100 - 50 000) and that the normally higher molecular masses found in the flocculation of kaolin with polyacrylamides tends to result in far smaller variation in behaviour. (Gregory 1978; Dixon and La Mer). However the contradictory nature of the evidence raises the problem of identifying the cause of the variations. A partial solution may be found in the variety of methods of agitation used in different studies. The most careful and well defined system used was that of Ash and Clayfield who used a Couette Mixer. Others used a variety of systems, for example -

a) end over end rotation at 12 rpm for 1 hour (Gregory 1968)
b) "shaken for an appropriate time" (Schamp and Huylebroeck)
c) thoroughly mixed (Linke and Booth)
d) magnetic stirrer (Jankovics)

Other researchers, not primarily concerned with the influence of molecular mass, apply a wide variety of techniques of agitation generally based either on repeated inversions of a settling cylinder (e.g. Dollimore and Horridge) or based on a mechanical stirrer or stirrers in parallel (e.g. Packham).

The variety of methods based on inversion and their justification is based on the criterion of reproducibility and their relationship, in general, to the jar test.(Hudson and Wagner). As such these tests differ from those where mechanical stirrers are applied, where the intention is often to explore such parameters as floc degradation, optimimum retention time in flocculators and so forth. The effect of agitation on flocculation was noted early (LaMer and Healy; Healy; McCarty and Olsen) the general finding being a decrease in settling rate with increased mixing time (LaMer and Healy; McCarty and Olsen). Filtration rate increased with stirring to a maximum; the filtration rate being higher the lower the rotational velocity of the impeller in the range 15 - 60 rpm (LaMer and Healy). More recently Tomi and Bagster with a carefully designed apparatus based on a baffled stirring system and have shown :

1) that the optimum flocculant dosage decreases linearly with the logarithm of the stirring speed,
2) the optimum floc size decreases with increase in stirring speed (as measured by optical transmission during agitation).

Unfortunately these results cannot be compared directly with traditional measures of flocculation, such as the supernatant clarity, settling rate, settled bed volume or refiltration data which constitute the bulk of the literature on flocculation of kaolin.

Thus the improvement of the scientific control of the experimental variables has not yet resulted in information that can be meaningfully applied to the data already at hand in the literature.

3.1.9 Electrophoretic Mobility

A further aspect of flocculation studies, in particular those involving model systems and dilute suspensions has been the measurement of the electrophoretic mobility of the flocculated species and the examination of the effect of flocculant adsorption on the mobility or the surface potential as determined by potentiometric titrations. (Szczypa et al; Dixon et al; Healy; Gregory 1969; Kane et al (1964); Black, Birkner and Morgan 1965, 1966). In particular the work of Black et al, and Szczypa et al provides a basis for interpeting the interactions of high molecular mass materials on surfaces. It has been shown that anionic flocculants do not substantially modify the mobility (Black et al 1965 and Black 1960) and may cause it to increase or decrease while still flocculating the material (Black et al, 1965, 1966; Healy; Dixon et al).

The electrophoresis studies have contributed significantly to understanding the flocculation of kaolin with anionic materials. A nonionic flocculant was shown to have no effect on the surface potential of calcium carbonate, suggesting that interaction is through hydrogen bonding (Szczypa et al).

Cationic flocculants generally reverse surface charge which then increases up to a limiting positive value that seems to be a function of the flocculant type. Flocculation occurs at mobilities close to zero, and in the negative range. Restabilization occurs with higher dosages of cationic flocculant. (Black et al 1965 and 1966). Thus electrophoretic mobility studies on kaolin are only expected to be useful in the flocculation context with

1) cationic flocculants

2) monitoring mobility changes with ionic strength changes, the addition of specific ions (Roberts et al) and pH variation.

In the case of colloidal minerals some of these changes can be inferred from the state of the sedimenting unflocculated material as is suggested by Parks. In the particular case of kaolin the study of Flegmann et al has shown that maximum bed volumes of untreated material can be associated with the isoelectric point due to face-edge coagulation being favoured.

Frequently assessment of the state of aggregation of unflocculated kaolin suspensions can provide an indication of the charge phenomena giving rise to that state.

The measurement of flocculation has to some degree resulted from the development of arbitary procedures that give reproduceability. Other studies measuring properties such as floc size and agitation parameters frequently do not incorporate these procedures and thus comparisons are difficult.

In addition a wide range of particle concentrations are used (depending on the emphasis of the individual study) and on occasion contradictory results are reported. Nevertheless in the kaolin-polyacrylamide system a number of studies have been conducted that provide a basis for further investigation, in particular, of the areas of the relationship of floc size, agitation, and adsorption data to the classical measures of flocculation. Other studies in different systems will allow some assessment of the findings of such an investigation.

3.2 Investigation of the Effect of Flocculant Type on Flocculation

A series of flocculants were provided by Allied Colloids Limited, of which 6 were chosen to form the basis of the investigation. They are described below in Table 3.1 (Alston)

A series of experiments were conducted using different initial flocculant concentrations (0.1, 0.5, 1, 2, 4 mg/g) and monitoring the adsorption of flocculant, supernatant turbidity, settled bed height, floc size (photographically) and floc density-size distributions.

The experiments were conducted at the "natural" pH of the kaolin in suspension and the pH was monitored to ensure that there were no large changes over the period that the experiments were conducted (about 2 years). Additionally care had to be taken to control the time the kaolin was in suspension, prior to treatment with flocculant to avoid complications of differential aging. The study of the effects of agitation on the stability of flocs, and the consistency of experimental results of flocculation efficiency led to the choice of the impeller stirrer as the most appropriate apparatus, with a stirring time (following treatment) of 15 minutes being chosen because of the stability of the Na^+ kaolin - n-PAM system at this time for flocculant dosages of 1 mg/g and above.

There were three homoionic kaolins chosen to investigate the effect of the flocculants on the flocculation process. These were Na^+ kaolin, H^+ kaolin and Ca^{2+} kaolin. The H^+ kaolin was chosen because of its acidic condition and because as a singly valent cationic form it could be compared and contrasted with the Na^+ kaolin which has a natural pH in the alkaline range. The Ca^{2+} kaolin was used primarily to test the hypothesis of ionic bridging with hydrolysed polyacrylamides by comparison of the flocculation behaviour with that of the singly valent forms.

TABLE 3.1

Allied Colloids Flocculants	percentage anionic(a) or cationic (c)	Molecular Mass	Type	Designation in thesis
Magnafloc 139	10 (a)	5 - 10 x 10^6	polyacrylamide	low m.w. 10-HPAM
Magnafloc E24	10 (a)	10 - 20 x 10^6	polyacrylamide	10-HPAM
Magnafloc 155	20 (a)	10 - 20 x 10^6	polyacrylamide	20-HPAM
Magnafloc 156	40 (a)	10 - 20 x 10^6	polyacrylamide	40-HPAM
Magnafloc 351	0	10 - 20 x 10^6	polyacrylamide	n-PAM
Magnafloc 140	10 (c)	5 x 10^6	unknown - probably polyethyleneimine	cationic

The pH's of the three types of kaolin when in suspension are tabulated below :

TABLE 3.2. : pH of Homoionic Kaolins

Homoionic Type	pH
Na^+	9.86 ± 0.04
Ca^{2+}	9.44 ± 0.03
H^+	5.00 ± 0.1

At these different pH's the settled bed height of the untreated materials (which is a measure of the degree and type of aggregation) increased in the order $Na^+ < Ca^{2+} < H^+$. The clay concentration chosen for the experimental work was 1% w/w at the time of flocculant addition. This clay concentration was chosen since it allowed the most representative range of flocculant concentrations to be investigated and compared with meaningful measures of flocculation efficiency. The full description of the experimental procedure is appended (Appendix 4 and 5).

3.2.1 Flocculant Adsorption

Figure 3.1 shows the adsorption vs initial flocculant concentration for the nonionic polyacrylamide (n-PAM). The shape of the graphs is a curve with initial slope close to unity with a knee at about the 1 mg/g flocculant dosage. The initial slopes decrease in the order $H^+ > Ca^{2+} > Na^+$ and the level of adsorption at high initial concentration is $Ca^{2+} > H^+ > Na^+$.

Figure 3.2 shows adsorption vs initial flocculant concentration for the 10% anionic polyacrylamide (10-APAM).

The initial adsorption is almost total up to about 0.5 mg/g with the slopes decreasing in the order $H^+ > Ca^{2+} > Na^+$.

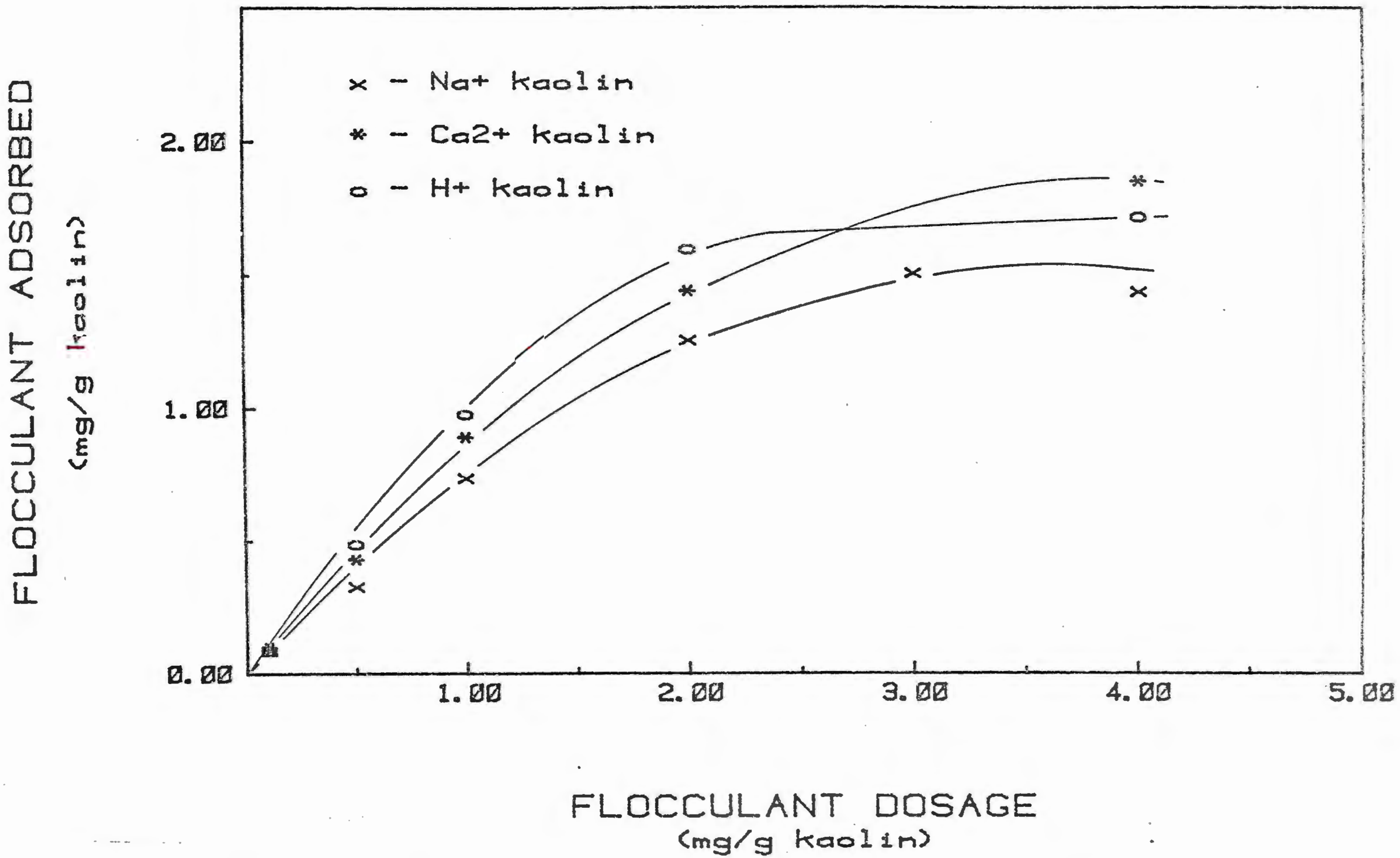


FIGURE 3.1

ADSORPTION vs. DOSAGE for NONIONIC POLYACRYLAMIDE

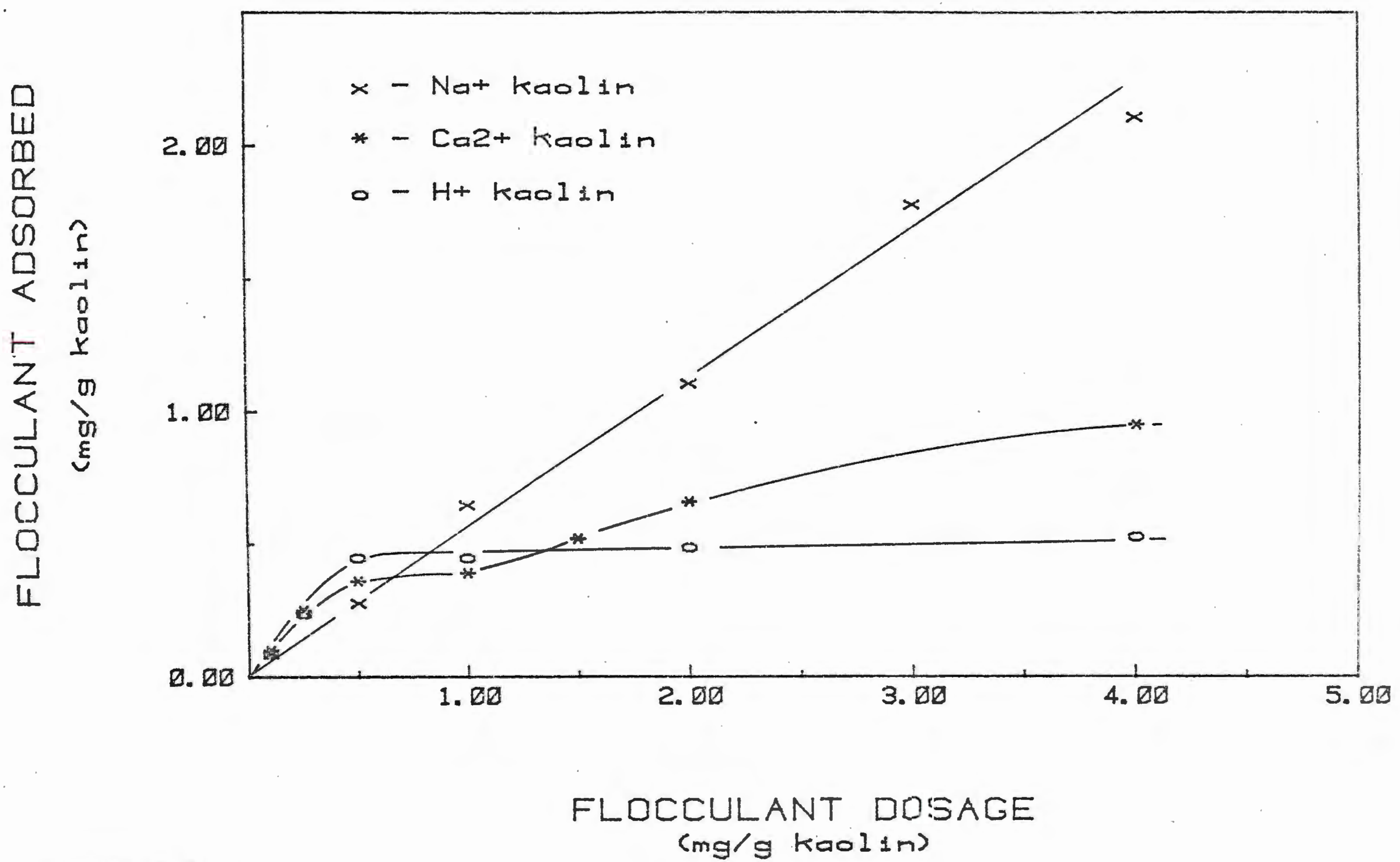


FIGURE 3.2

ADSORPTION vs. DOSAGE for 10% ANIONIC POLYACRYLAMIDE

The sodium kaolin has an almost linear relationship for flocculant adsorption vs dosage, the slope being about 0.6. The Ca^{2+} kaolin has a knee in the region 0.5 - 1.0 mg/g flocculant dosages and subsequently appears to be reaching a plateau at 1 mg/g. The H^+ kaolin adsorbs flocculant to a plateau at 0.5 mg/g which appears to be extremely stable.

Figure 3.3 shows the adsorption dosage curves for the 20% anionic PAM. The lowest levels of adsorption are difficult to determine but the indications are that there is almost no region of initially almost total adsorption with the Ca^{2+} and H^+ kaolins although plateau conditions are not apparent below 2 mg/g flocculant added. At 1 mg/g and above the adsorption levels are decreasing in the order $Na^+ > Ca^{2+} > H^+$ which follows the pattern established for the 10-APAM above the 2 mg/g flocculant dosage, though it does not reflect the order of the levels of adsorption of the n-PAM (i.e. $Ca^{2+} > H^+ > Na^+$). The Na^+ kaolin has not reached a plateau of adsorption at the 2 mg/g dosage and visually the suspension is effectively dispersed.

Figure 3.4 shows the adsorption-addition data for the 40-APAM. The characteristics of the adsorption are similar to those of the 20-APAM except that the 40-APAM seems to be slightly less strongly adsorbed, as is the case for the Ca^{2+} and H^+ kaolin. The order of decreasing level of adsorption, $Na^+ > Ca^{2+} > H^+$, is preserved.

Figure 3.5 (low m.w. 10-APAM) should be compared with Figure 3.2. Low levels of flocculant dosage result in the observed almost total adsorption decreasing in the order $H^+ > Ca^{2+} > Na^+$. This order is reversed at higher levels of flocculant addition (4 mg/g). When compared with Figure 3.2 the following can be noted :

1) the levels of adsorption are higher in the case of the H^+ and Ca^{2+} kaolin with the low m.w. flocculant
2) this is reversed for the Na^+ kaolin
3) the H^+ kaolin does not achieve its distinctive plateau adsorption (Fig. 3.1, 2, 3, 4) with the low m.w. flocculant.

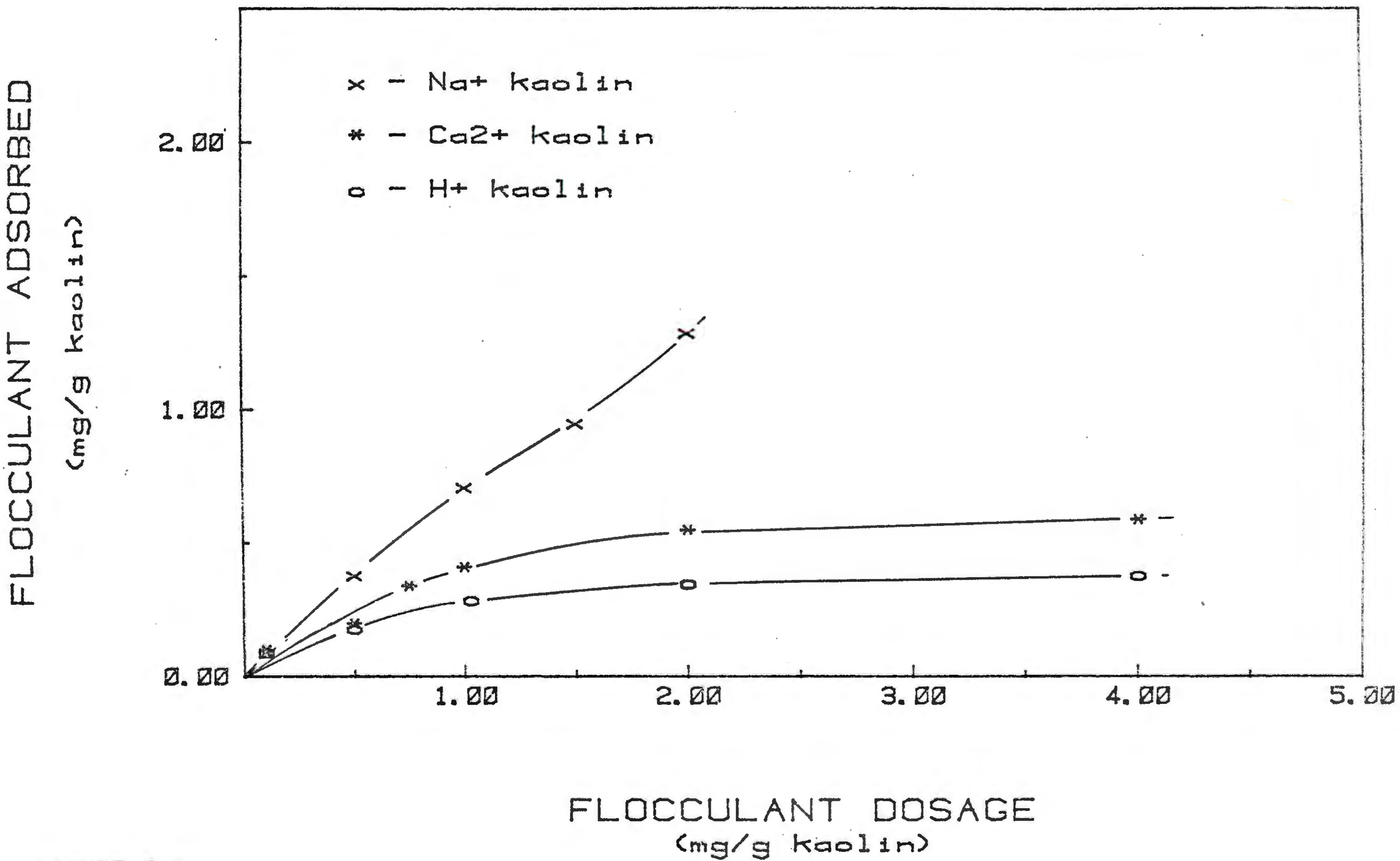


FIGURE 3.3

ADSORPTION vs. DOSAGE for 20% ANIONIC POLYACRYLAMIDE

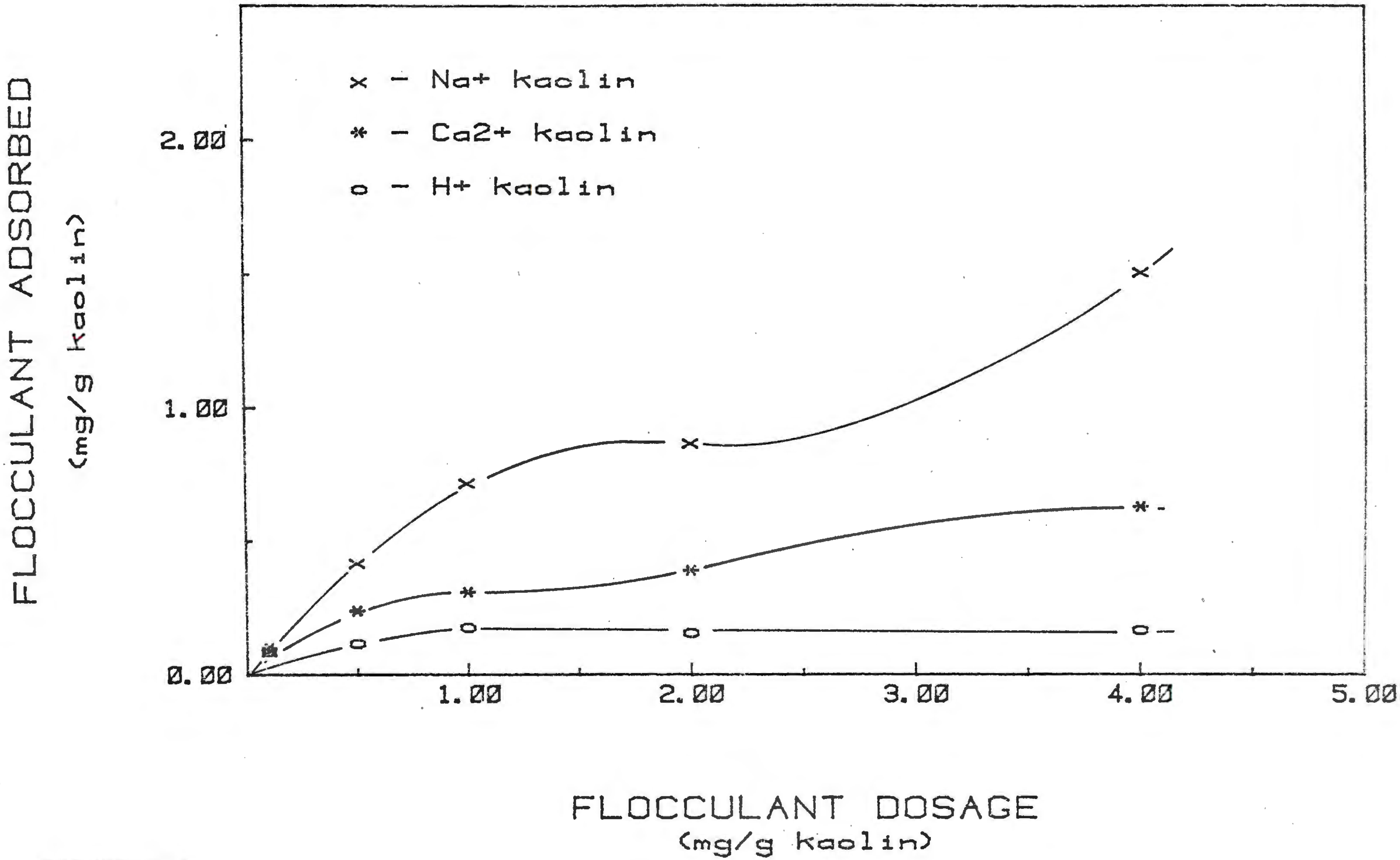


FIGURE 3.4

ADSORPTION vs. DOSAGE for 40% ANIONIC POLYACRYLAMIDE

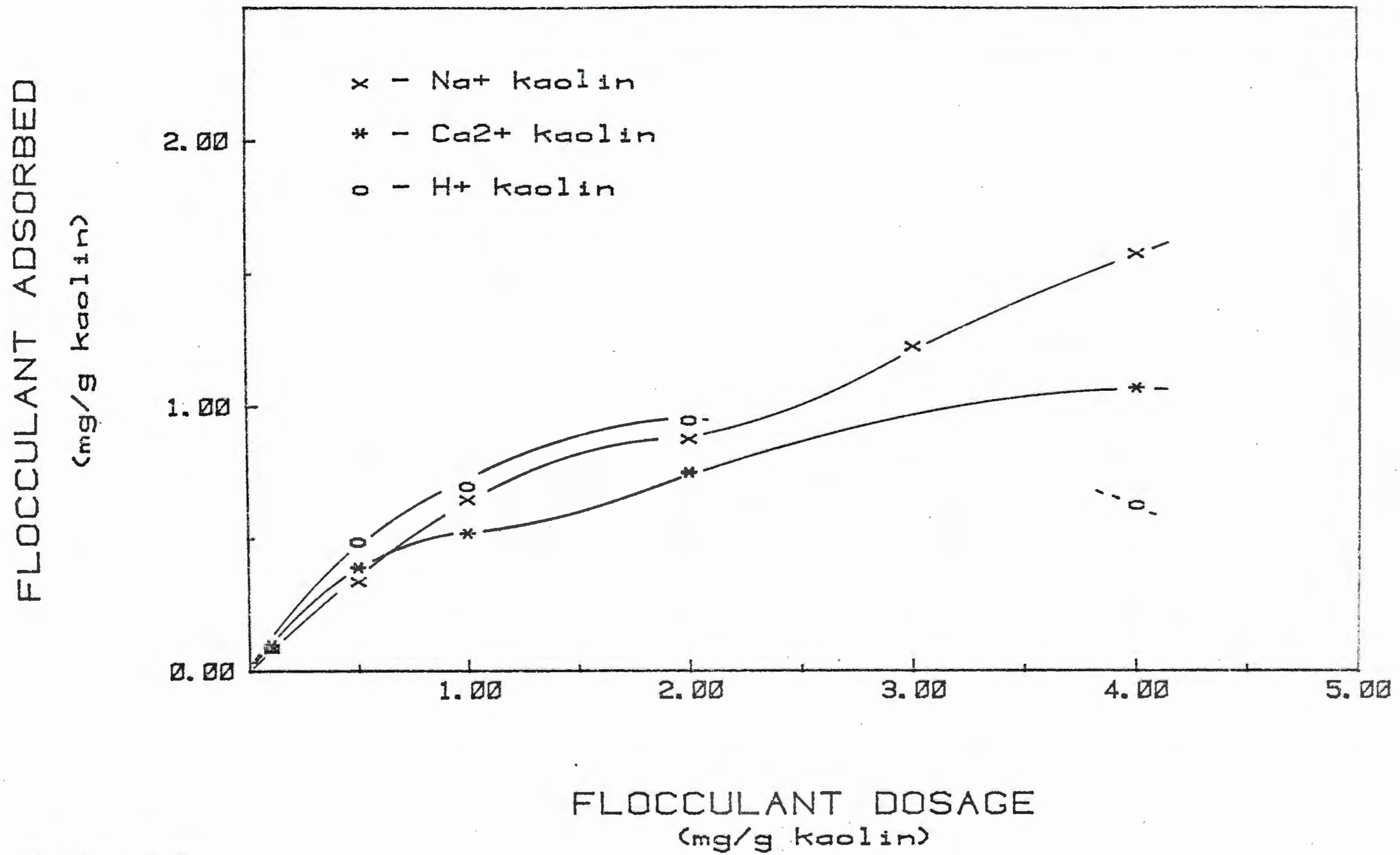


FIGURE 3.5

ADSORPTION vs. DOSAGE for low m. w. 10% ANIONIC POLYACRYLAMIDE

Another way of examining these results is to concentrate on the individual homoionic forms of the kaolin and to note the differences in flocculant adsorption. This is done in Figures 3.6, 3.7 and 3.8 for the Na^+, Ca^{2+} and H^+ forms respectively. The Na^+ kaolin shows similar adsorption of all flocculants at a dosage of 0.5 mg/g which persists though less markedly at 1 mg/g. At 2 mg/g the low m.w. 10-PAM and the 40-APAM have a somewhat lower level of adsorption than the other three. There is an increasing adsorption with increasing concentration for all the flocculants with the exception of the nonionic polyacrylamide. It may be noted that the degree of dispersion of the kaolin in the case of the 20-APAM is so high that the adsorption cannot be determined for 4 mg/g dosage of flocculant.

The Ca^{2+} kaolin (Fig. 3.7) exhibits a reduction in the level of adsorption with increasing anionic character in the order n-PAM > low m.w. 10-APAM > 10-APAM > 20-APAM > 40-APAM. This separation is less distinct at intermediate concentrations for the low m.w. 10-APAM, 10-APAM and 20-APAM, but the distinction becomes clear at higher concentrations. In the case of the H^+ kaolin (Fig. 3.8) the separation is even more distinct and the order of decreasing adsorption is the same. This order is not reflected in the case of the Na^+ kaolin.

It is now appropriate to record the two measures of flocculation used in this study and their relationship to the adsorption data. This will be done using the same form of presentation by first considering each flocculant in isolation with the three homoionic forms of the kaolin for the supernatant turbidity.

3.2.2 Supernatant Turbidity

The first method used to determine the efficiency of flocculation was the determination of supernatant solids by turbidimetry. This was done after 15 minutes as described in the experimental methods (Appendix 4).

Figure 3.9 shows the graph of supernatant turbidity vs flocculant dosage for n-PAM. As can be seen the turbidity drops off rapidly to a minimum value followed by a gradual increase or maintenance of the low value.

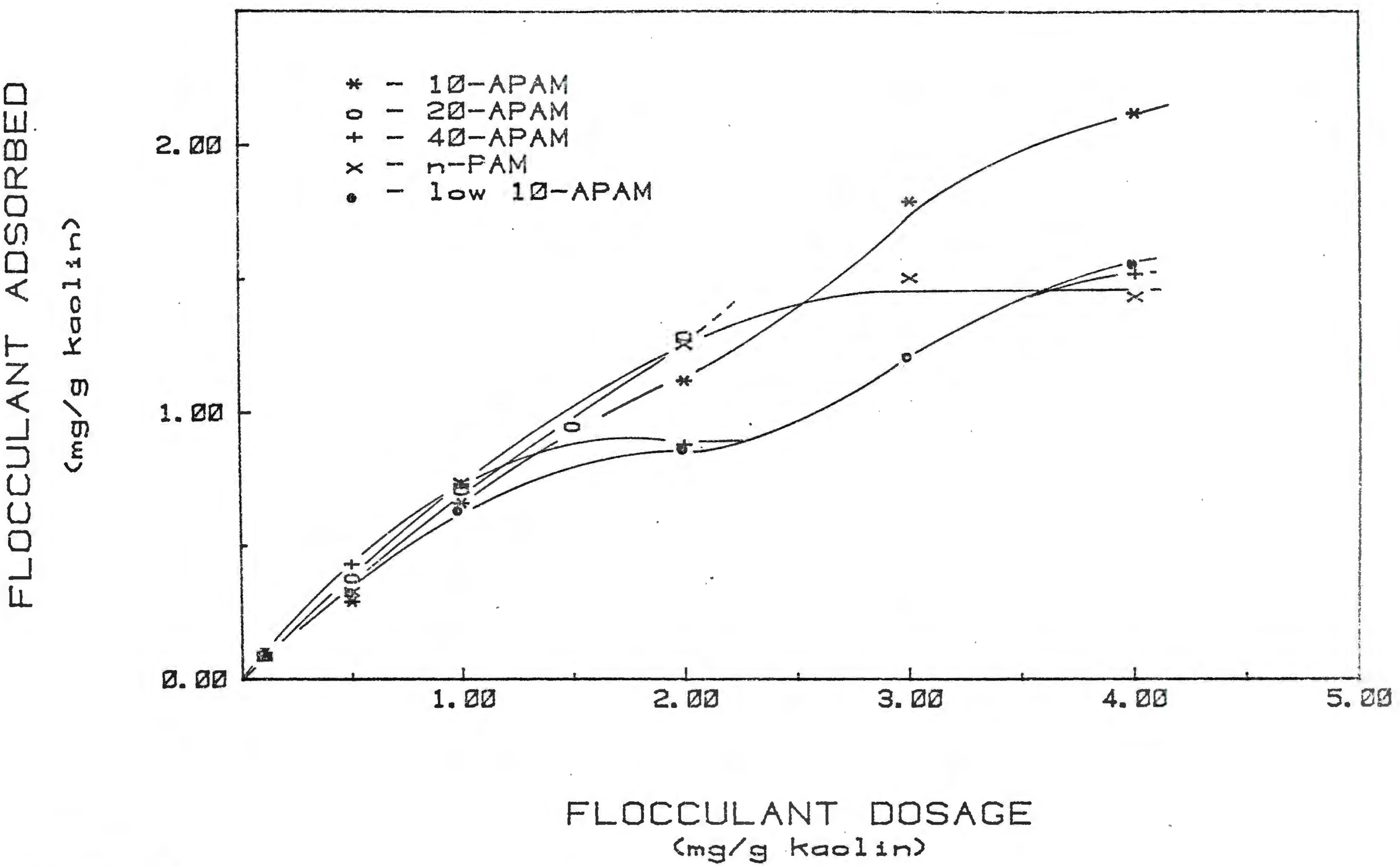


FIGURE 3.6

ADSORPTION vs. DOSAGE for Na+ KAOLIN

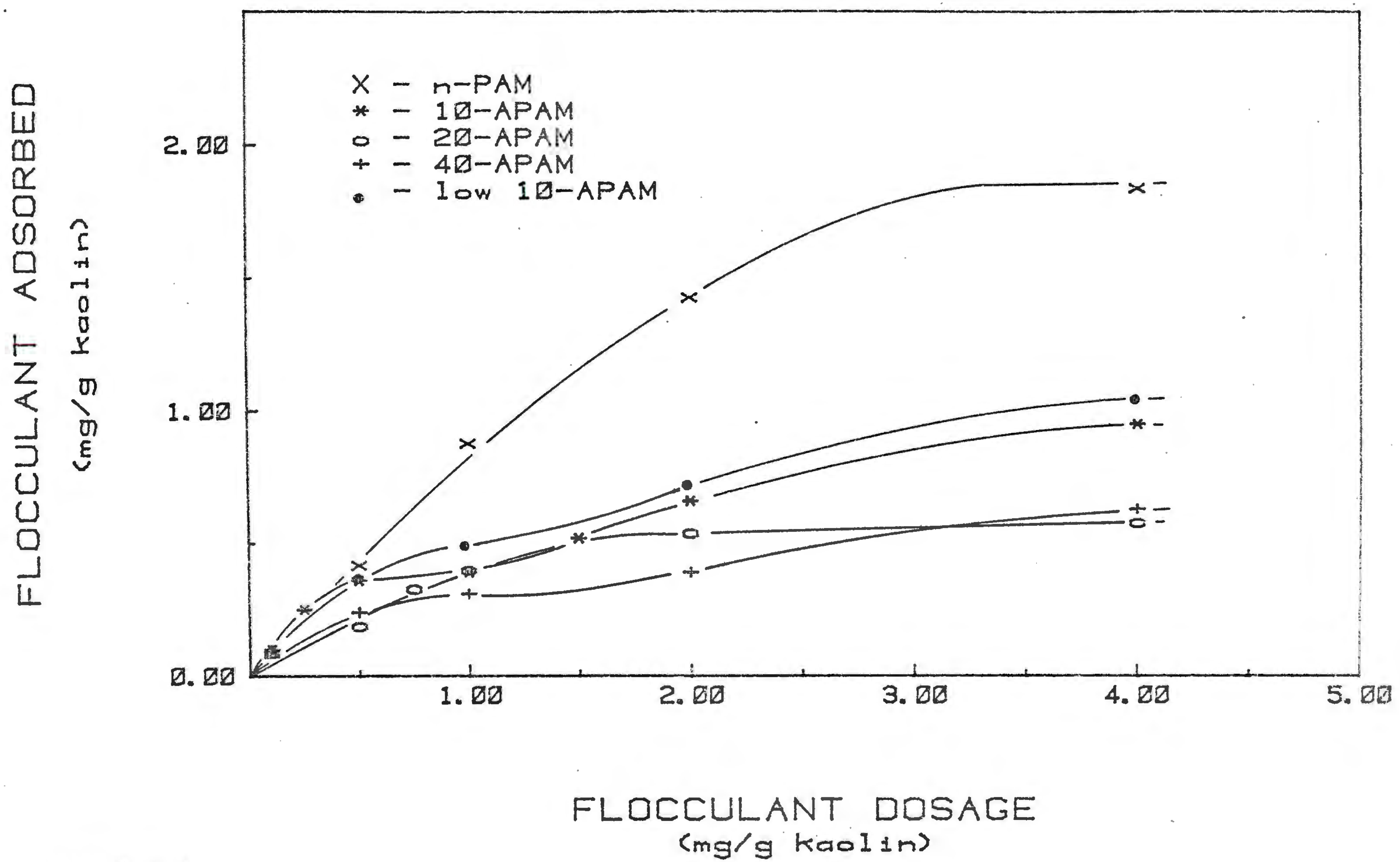


FIGURE 3.7

ADSORPTION vs. DOSAGE for Ca^{2+} KAOLIN

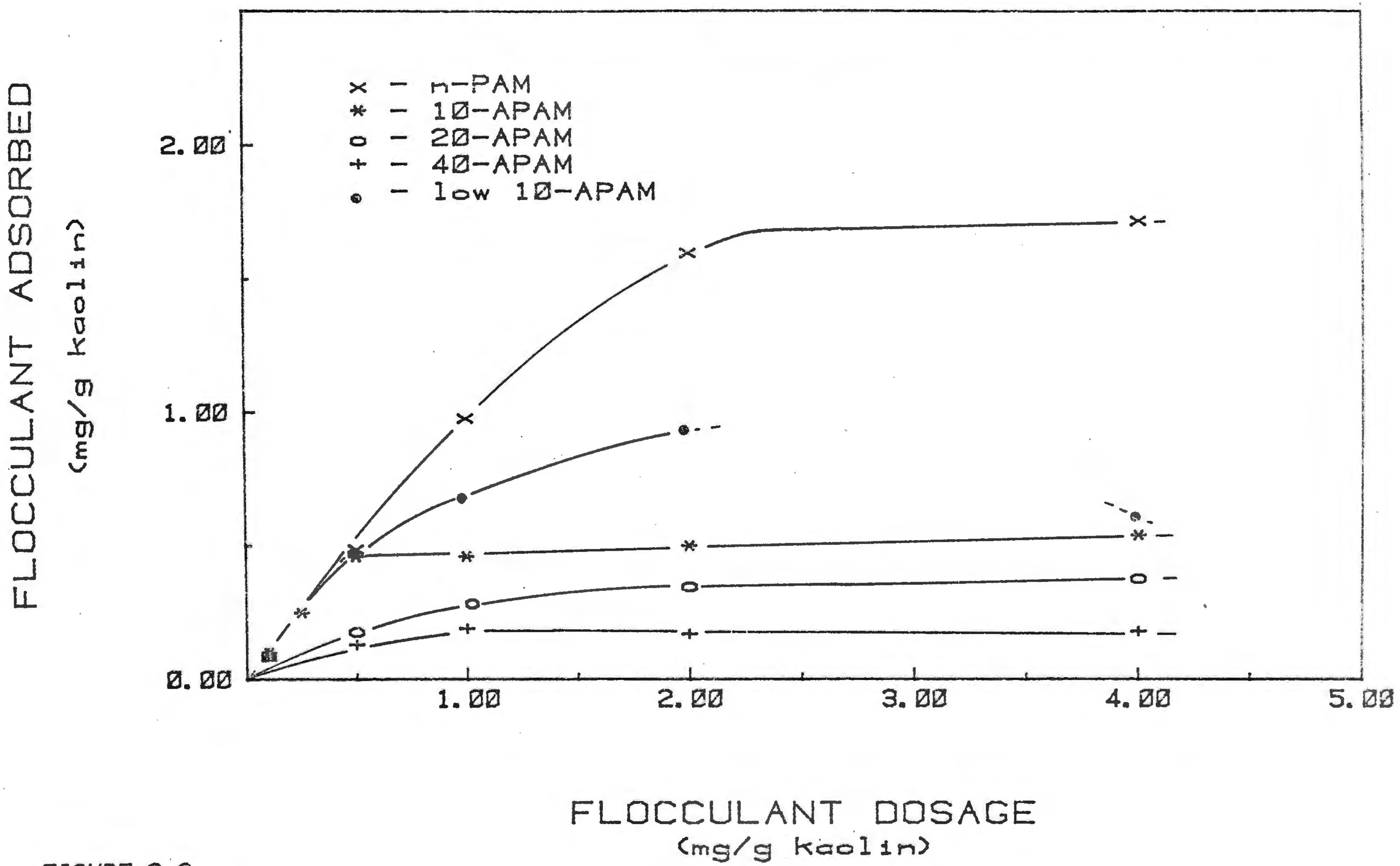


FIGURE 3.8

ADSORPTION vs. DOSAGE for H+ KAOLIN

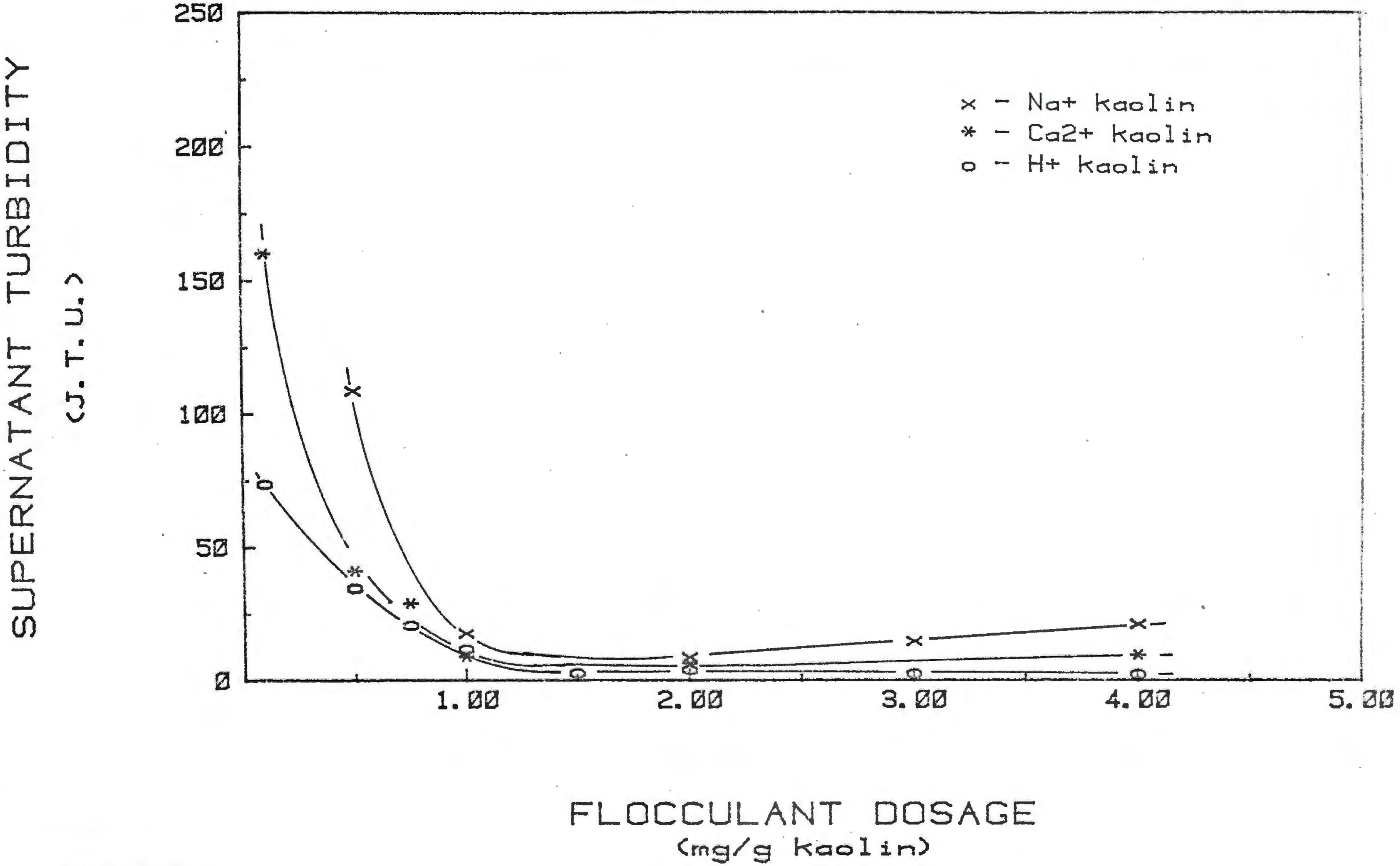


FIGURE 3.9

SUPERNATANT TURBIDITY vs. DOSAGE for n-PAM

The absolute value of turbidity achieved in the minimum is lowest for the H^+ kaolin, higher for Ca^{2+} and highest for Na^+. However the total decrease in turbidity is greatest for the Na^+ kaolin which is well dispersed in its untreated state. It will be noted that for all the subsequent flocculants except the cationic the turbidity of the Na^+ kaolin is not recorded. This is because in no instance did the turbidity of Na^+ kaolin fall below 500 J TU when treated with anionic flocculants. Thus this measure of the state of flocculation was not able to indicate changes in aggregation of the Na^+ kaolin. Visually however it was still possible to detect changes in the suspension but this is difficult to record or quantify as an empirical assessment of flocculation.

Figures 3.10, 3.11 and 3.12 show the turbidity - flocculant dosage diagrams for 10-APAM, 20-APAM and 40-APAM. The general pattern of the behaviour is similar but it is noted that the minimum trough becomes narrower with increasing anionic character. The higher concentration flocculant additions result in an increasing turbidity. The position of the minimum moves to lower initial flocculant concentrations. The H^+ kaolin always achieves the lowest turbidity which is of the order of 10 JTU and the increase in turbidity at higher dosages does not exceed 40 JTU. The Ca^{2+} kaolin has an increase in minimum turbidity with increasing anionic character in the order n-PAM < 10-APAM < 20-APAM < 40-APAM, with a generally bigger increase in turbidity at higher dosages than that of the H^+ kaolin, up to about 120 JTU over the range of flocculant concentrations studied.

Figure 3.13 shows the turbidity vs flocculant addition results for the low m.w. 10-APAM. Compared to Figure 3.10 (10-APAM) it can be seen that the shape of the graphs is very similar, but that the low m.w. variety does not result in such a large increase in the turbidity at dosages beyond the minimum turbidity achieved.

Figure 3.14 shows the turbidity vs flocculant addition results for the cationic flocculant. It is immediately recognizable that the basic pattern of the results is considerably modified in the presence of a cationic flocculant. The separation between the Na^+ and the Ca^{2+} and H^+ forms of the kaolin is marked. The slope indicating the rate of decrease of turbidity with increase in flocculant concentration is considerably reduced. It ap-

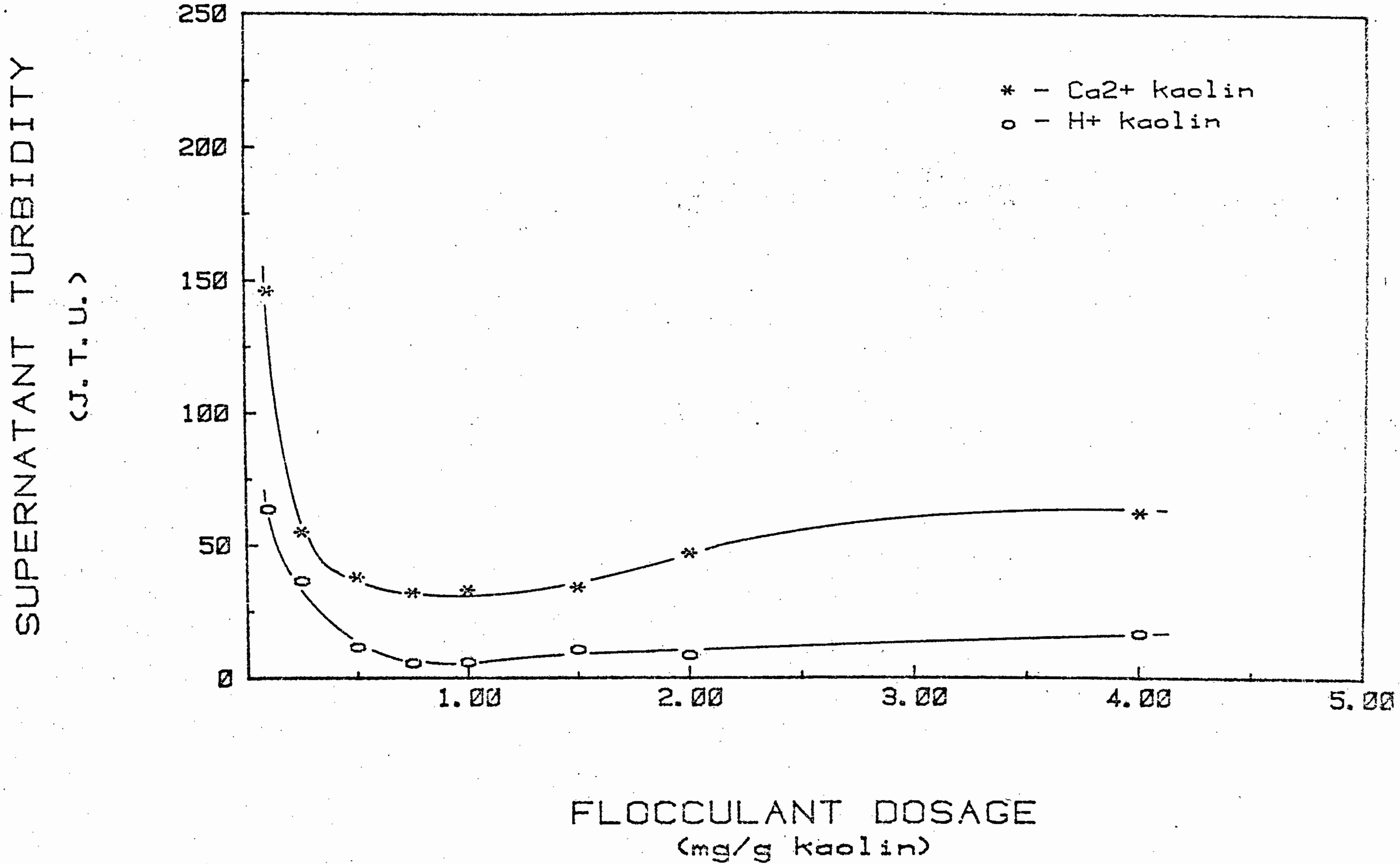


FIGURE 3.10

SUPERNATANT TURBIDITY vs. DOSAGE for 10-APAM

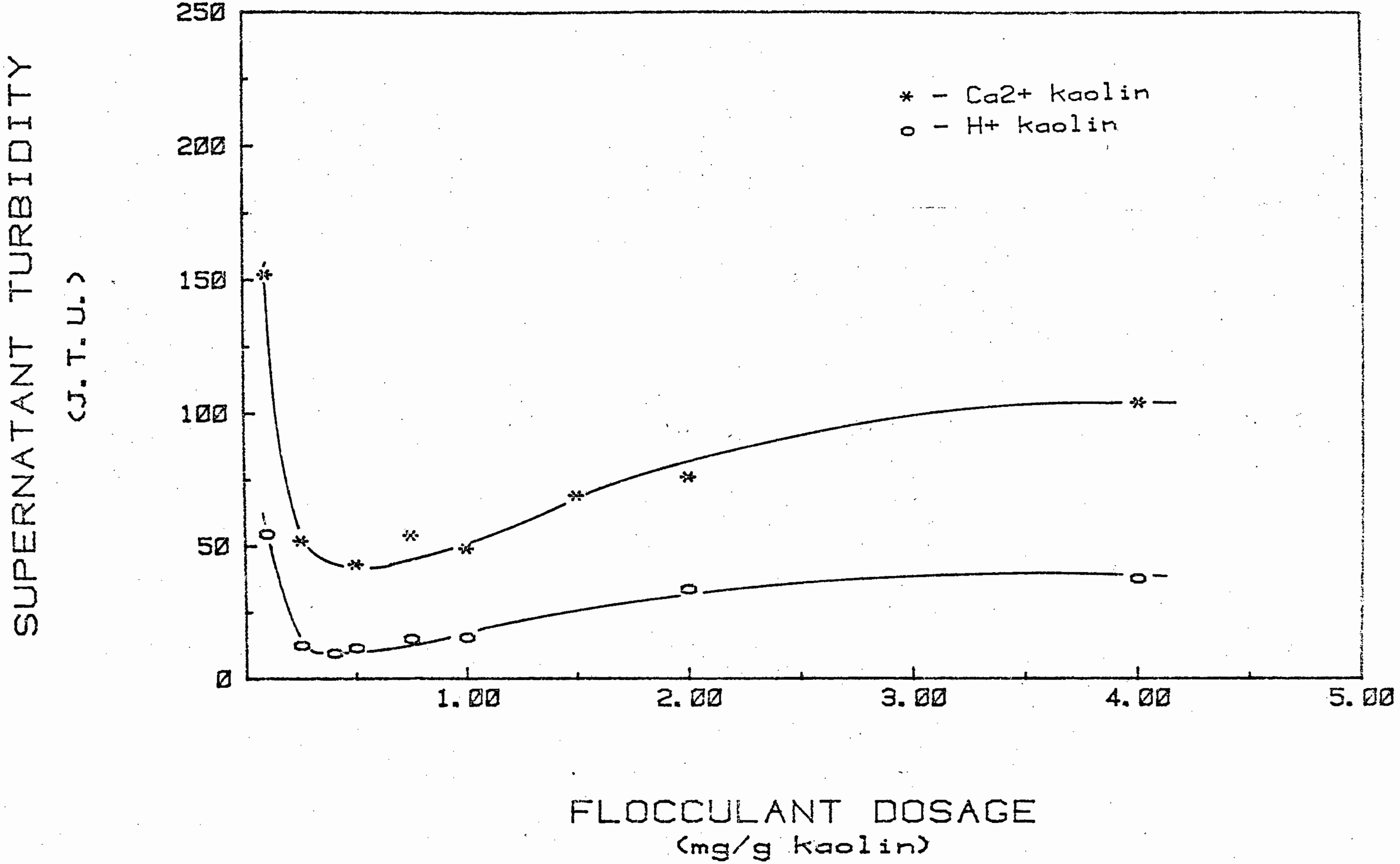


FIGURE 3.11

SUPERNATANT TURBIDITY vs. DOSAGE for 20-APAM

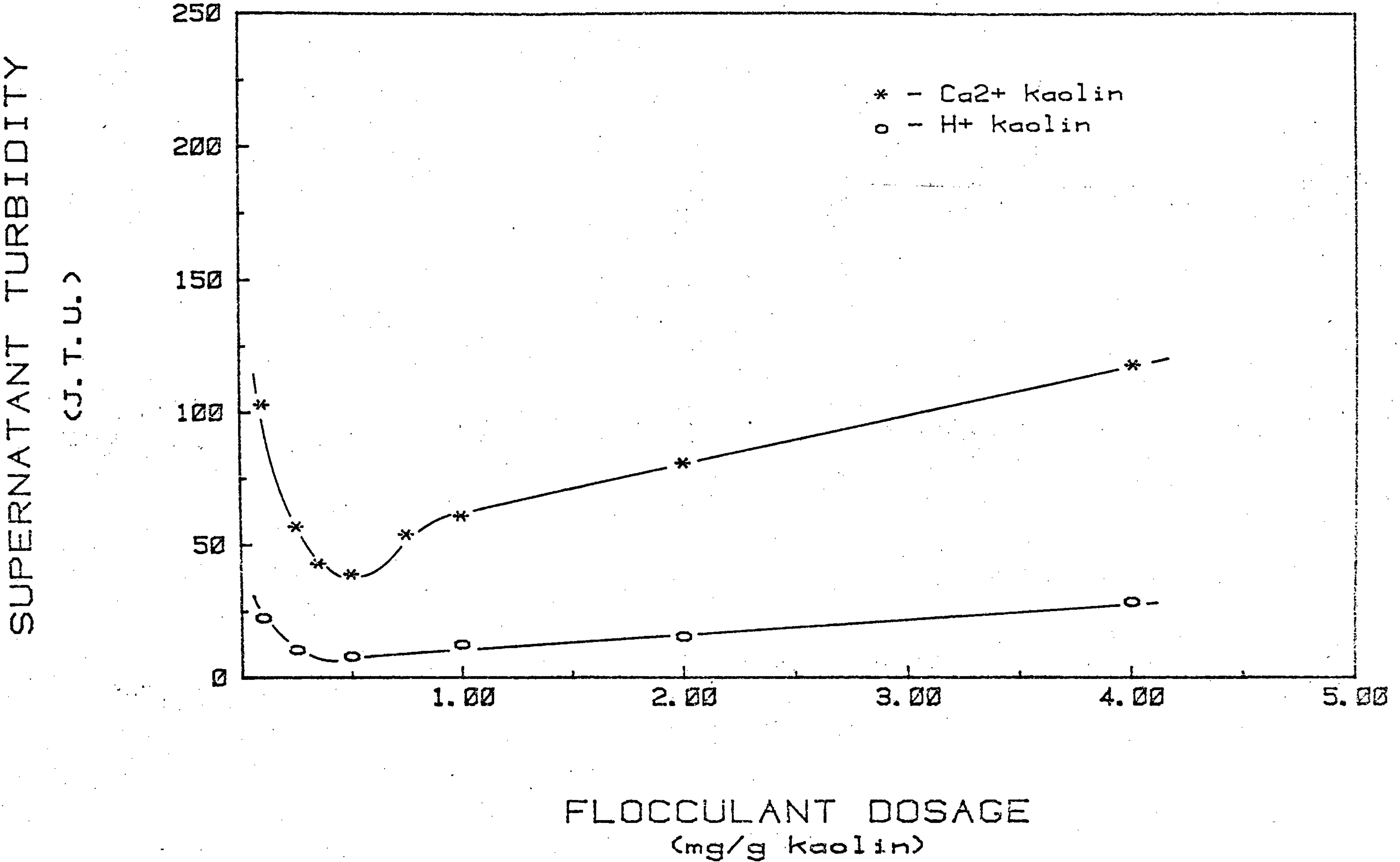


FIGURE 3.12

SUPERNATANT TURBIDITY vs. DOSAGE for 40-APAM

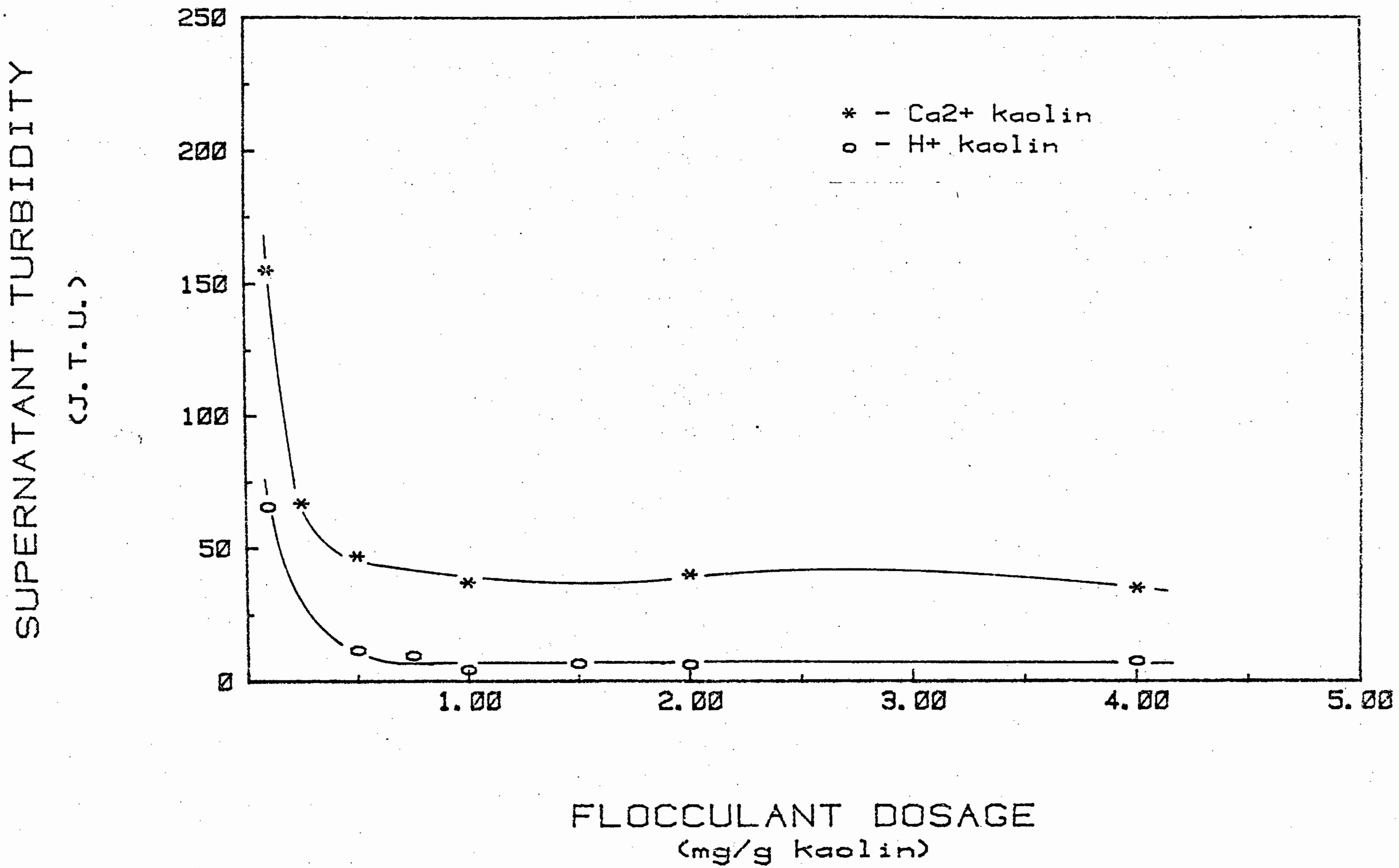


FIGURE 3.13

SUPERNATANT TURBIDITY vs. DOSAGE for low m.w. 10-APAM

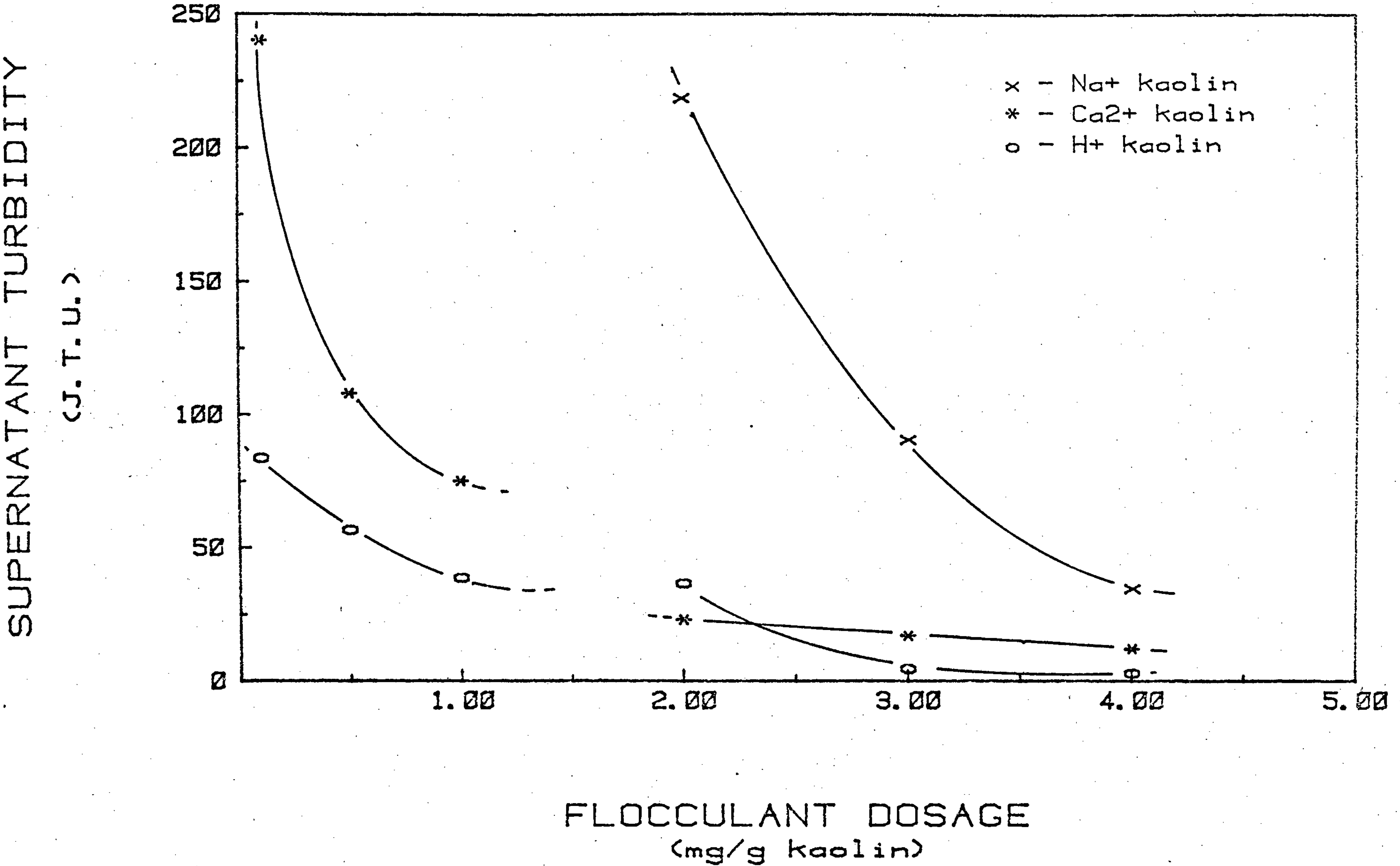


FIGURE 3.14

SUPERNATANT TURBIDITY vs. DOSAGE for 10% CATIONIC FLOCCULANT pears from the results for the Ca^{2+} and H^+ kaolins that there may be a point of inflection in the turbidity-flocculant dosage graphs. This has been recorded in the construction of the graphs since the variations shown are in excess of the normal variability of the results. It is noted however that similar points of inflection would possibly be masked by the rapid decrease in turbidity with anionic and neutral flocculants.The low level of turbidity achieved is comparable to that for Ca^{2+} and H^+ kaolin treated with the neutral polyacrylamide. The Na^+ kaolin has not achieved a minimum at a dosage of 4 mg/g.

Figures 3.15, 3.16, 3.17 show the results plotted for the Na^+, Ca^{2+} and H^+ homoionic forms respectively (note the change of scale in Figure 3.17). Most notable for all the kaolins is the increasing rate of turbidity reduction in the order cationic > neutral > increasing anionic character. This is particularly evident for the H^+ kaolin and the two useful results for the Na^+ kaolin. There is a gradual increase in the minimum turbidity with increasing anionic character up to 20% with the minimum turbidity for the 40-APAM being similar to that of the 20-APAM. The minimum turbidity for a given anionic flocculant seems to be relatively independant of molecular mass. The width of the minimum decreases in the order n-PAM > 10-APAM > 20-APAM > 40-APAM for the Ca^{2+} clay and in the order n-PAM > 10-APAM > 20-APAM ∿ 40-APAM for the H^+ kaolin.

3.2.3 Settled Bed Heights

The essential characteristics of the settled bed height data when plotted against flocculant dosage are shown in Figure 3.18. This is for the 20-APAM with the H^+ kaolin and Ca^{2+} kaolin. With this flocculant, as with the other anionic flocculants, it is not possible to include results for the Na^+ kaolin since stable settled beds were not formed after 15 minutes of settling, or the beds were so diffuse and the suspended material so concentrated that no adequate measurements could be made. The essential characteristic of the curve is the increase in bed height to a maximum with a subsequent decrease to a plateau value. This pattern of results was generally observed for all the flocculants except the cationic one. In addition it is noted that the plateau value of the Ca^{2+} kaolin is lower than that of the H^+ kaolin. This is also generally observed for the different flocculants.

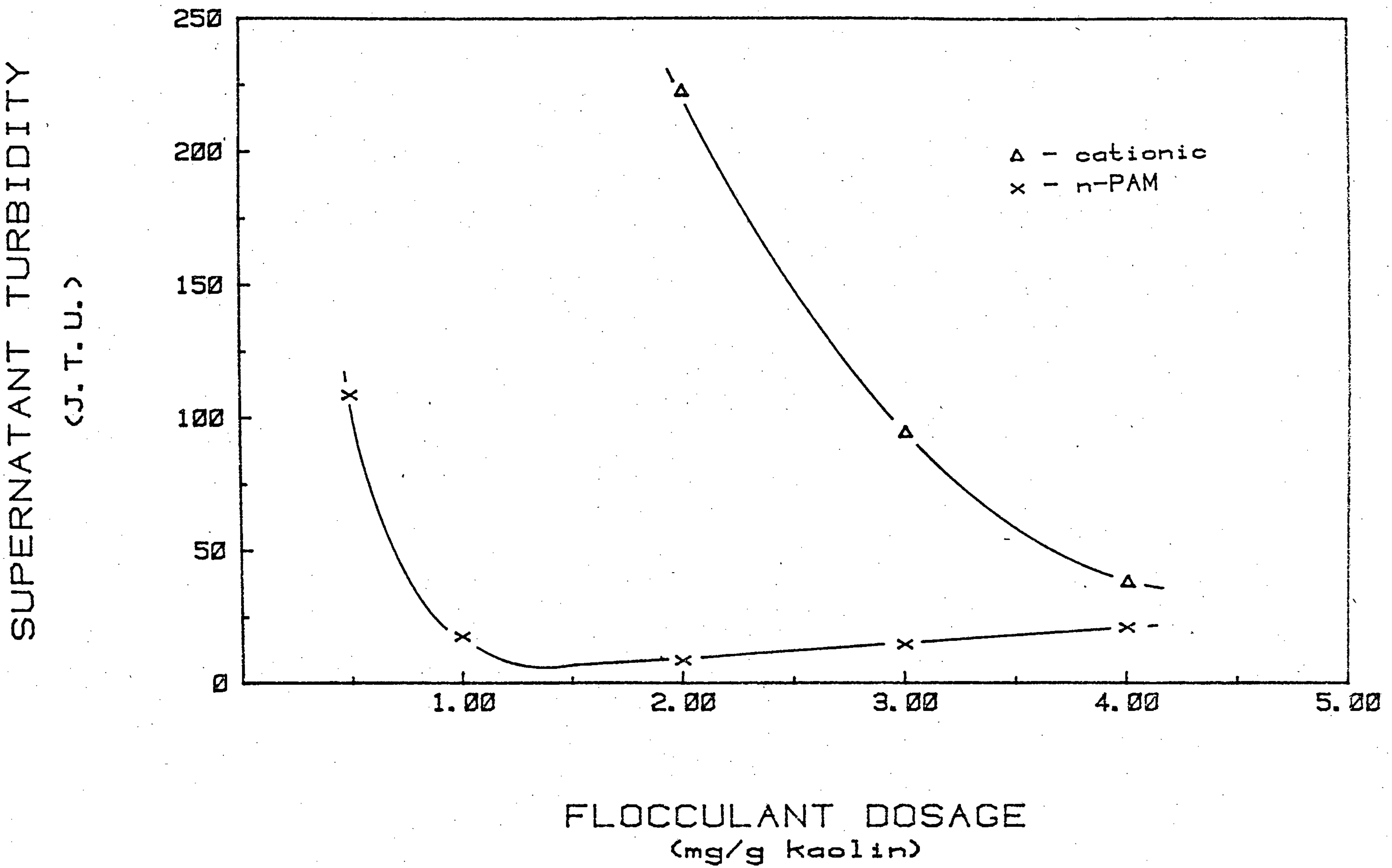


FIGURE 3.15

SUPERNATANT TURBIDITY vs. DOSAGE for Na+ KAOLIN

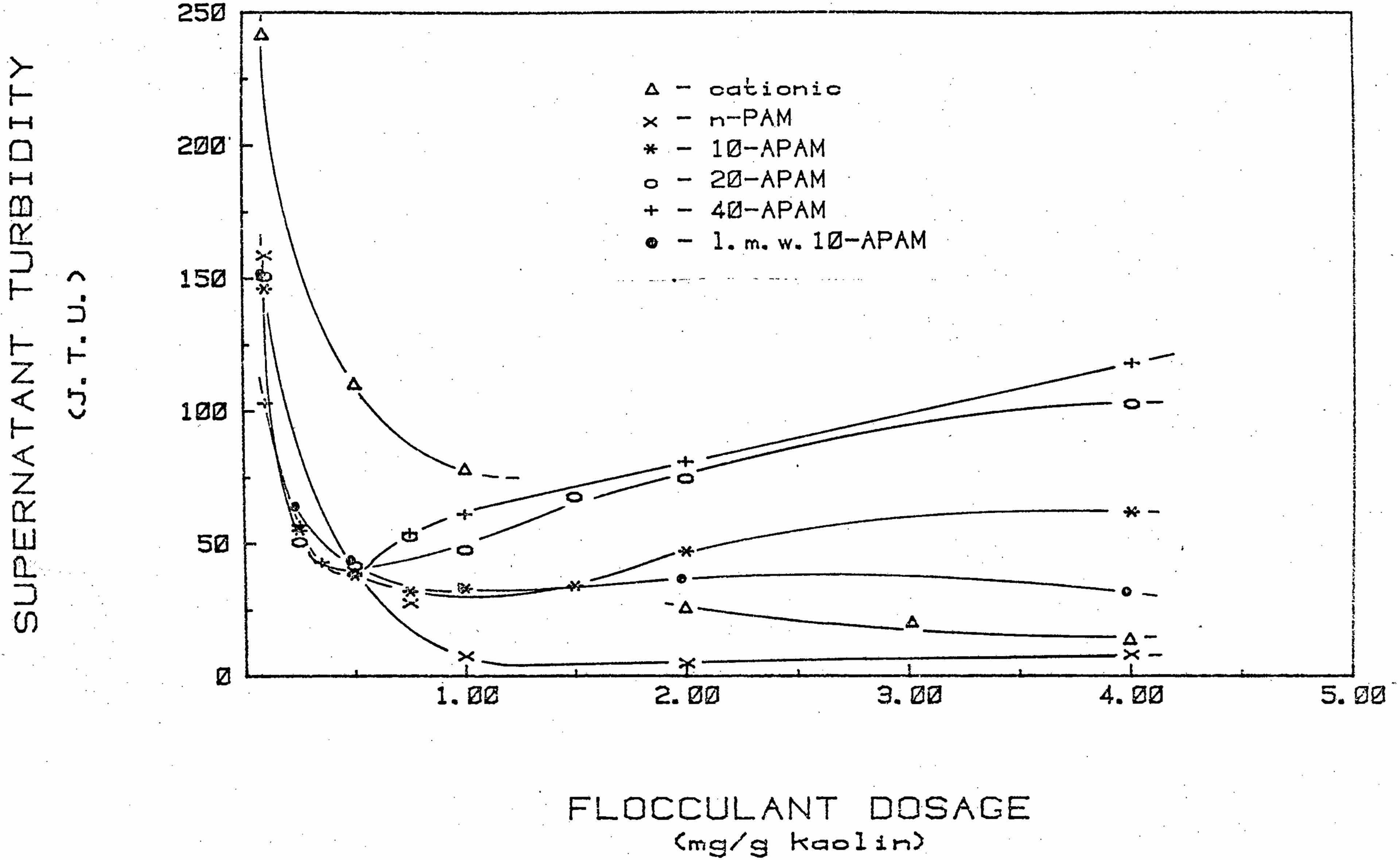


FIGURE 3.16

SUPERNATANT TURBIDITY vs. DOSAGE for Ca^{2+} KAOLIN

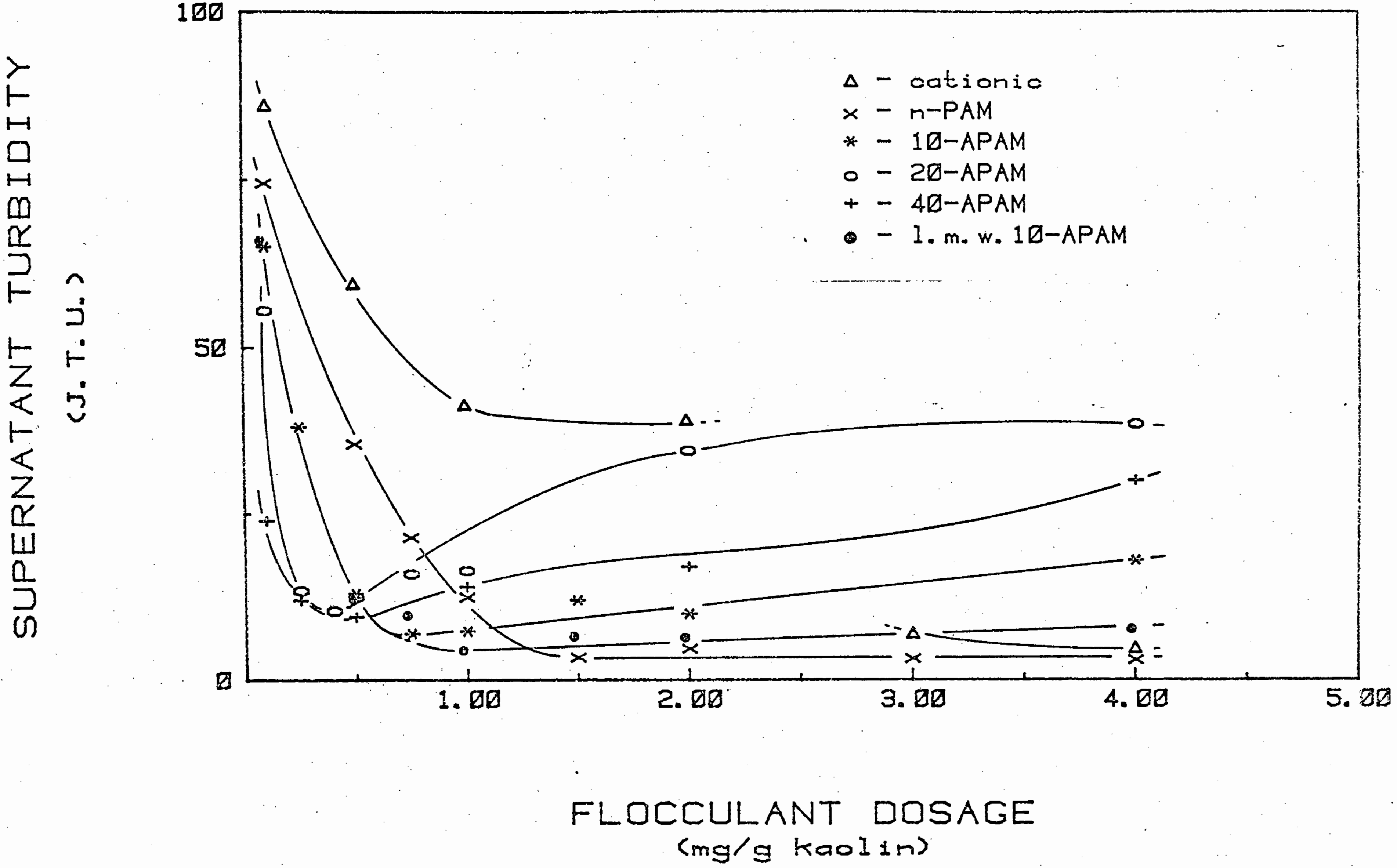


FIGURE 3.17

SUPERNATANT TURBIDITY vs. DOSAGE for H+ KAOLIN

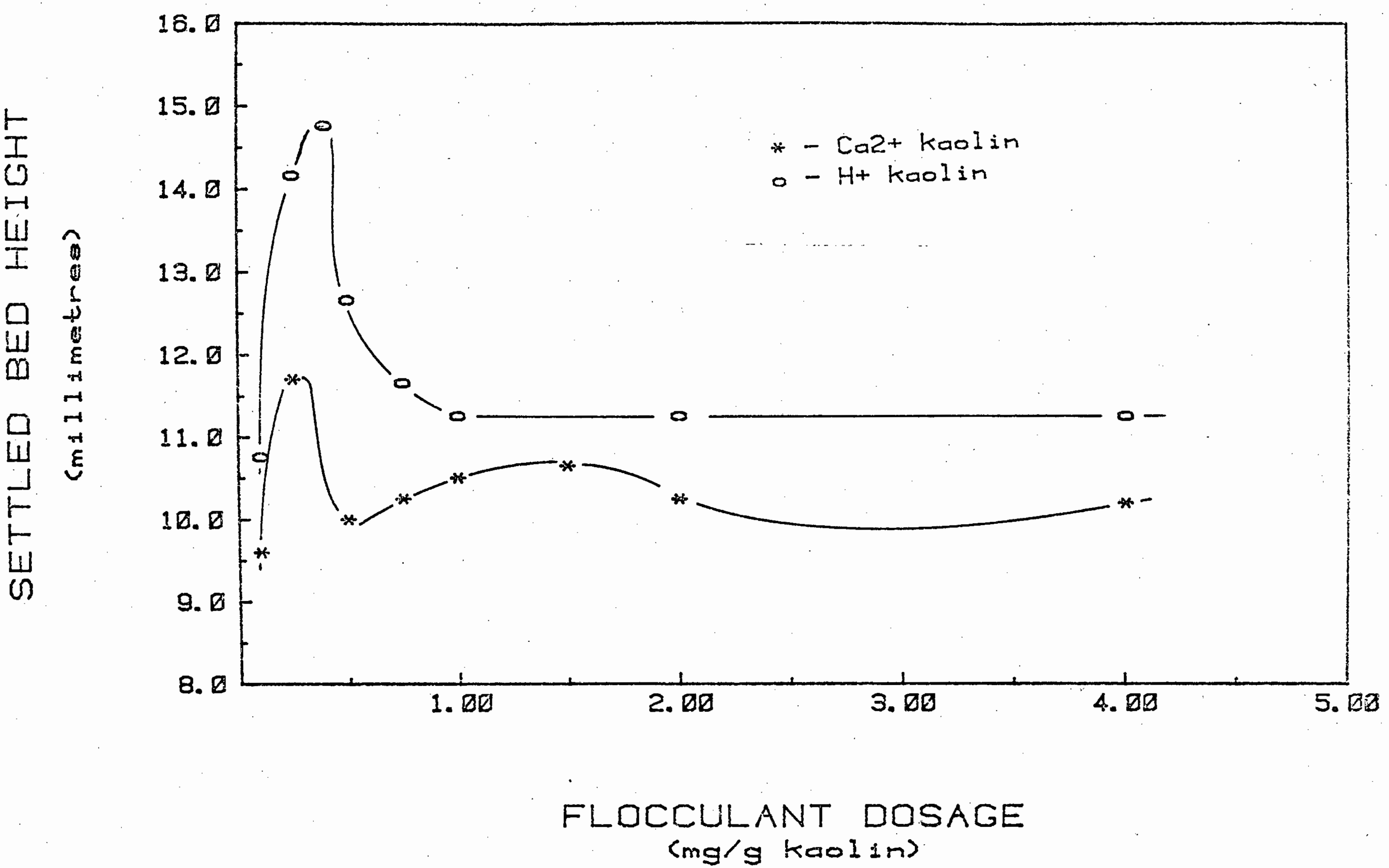


FIGURE 3.18

SETTLED BED HEIGHT vs. DOSAGE for 20-APAM

Figure 3.19 is the settled bed height vs dosage for the Na^+ kaolin for the cationic flocculant and n-PAM. The characteristics of the curve for the n-PAM are essentially the same as for the example given above. It will be noted that the peak is broader (the cationic peak appears even broader still) and there also appears to be an increase in bed height at the highest dosage. This may be partly due to packing of the flocs being less efficient with increase in floc size (Dollimore and Horridge 1971/1972).

Figure 3.20 is of the settled bed height vs flocculant dosage for the Ca^{2+} kaolin. The initial maximum with the decrease to a plateau is present, though for the cationic flocculant the decrease is not complete. The dosage at which the maximum is achieved decreases in the order cationic > n-PAM > low m.w. 10-APAM > 10-APAM > 20-APAM > 40-APAM. A minor secondary maximum is apparent for 20-APAM and may be present for the kaolin treated with 40-APAM and 10-APAM. The lowest minima are the 40-APAM and the n-PAM with 20-APAM, 10-APAM and low m.w. 10-APAM being higher and very similar. The maxima for the 10-APAM and low m.w. 10-APAM are the broadest and it appears that higher anionic strengths result in sharper peaks.

Figure 3.21 shows the settled bed height vs flocculant dosage for the H^+ kaolin. Again there are pronounced initial maxima followed by decrease in settled bed height to a minimum value. The dosage at which the settled bed height is a maximum is essentially the same as for the Ca^{2+} kaolin except that the differences seem more pronounced so again cationic > n-PAM > low m.w. 10-APAM > 10-APAM > 20-APAM > 40-APAM. The minima in bed height increase in the order 40-APAM < 20-APAM < 10-APAM < n-PAM. Again the narrowing of the peak for the settled bed maximum is apparent with increase in anionic character.

There is a very distinct relationship between the reduction in supernatant turbidity and the increase in settled bed height to a maximum. In particular this trend can be noted in the reduction in dosages required to achieve the settled bed maxima and the turbidity minima with increasing anionic character of the flocculant. The relationship of the flocculation parameters to flocculant adsorption is less clear. At higher dosages it seems that the fractional adsorption of flocculant is reduced and that this

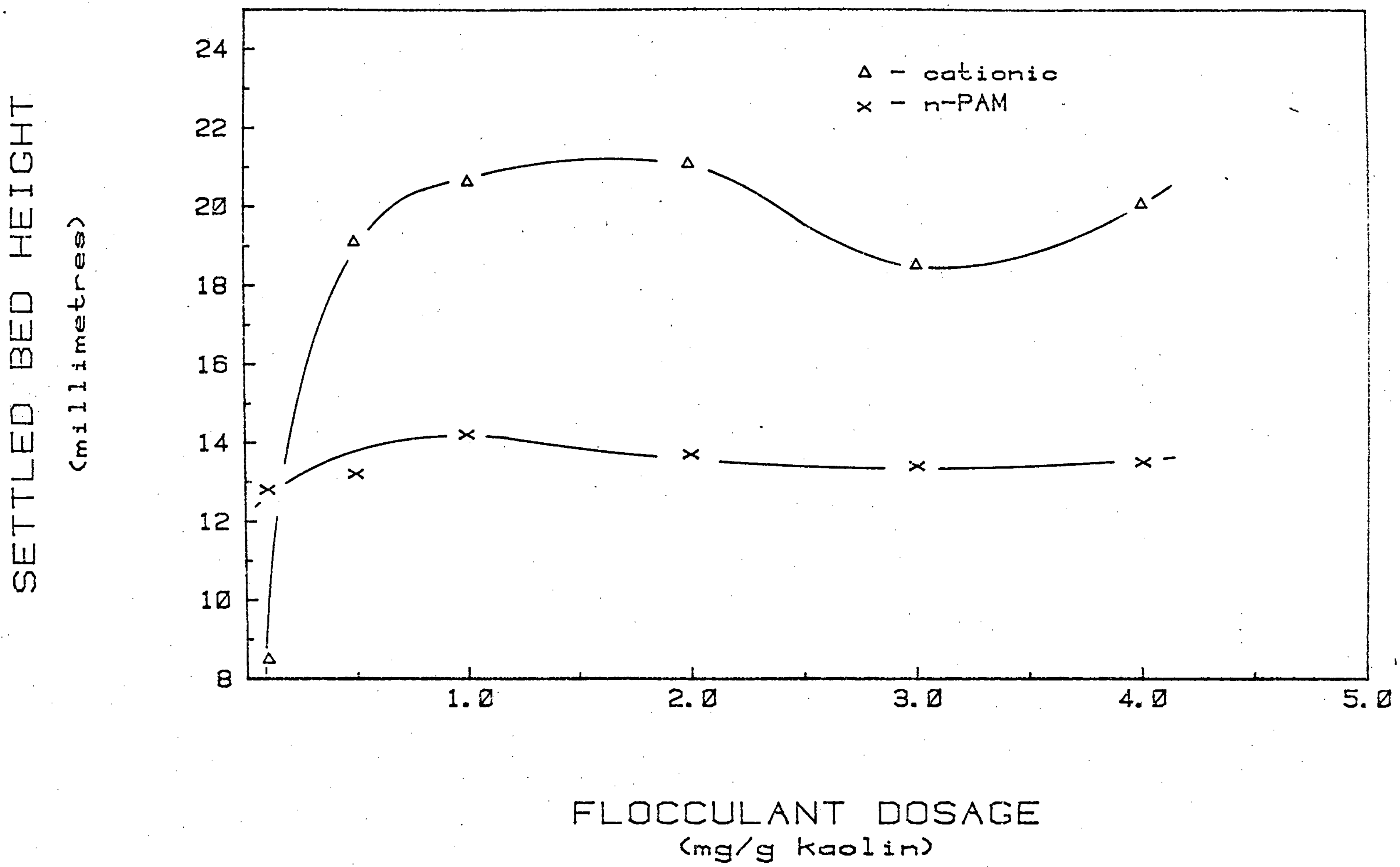


FIGURE 3.19

SETTLED BED HEIGHT vs. DOSAGE for Na+ KAOLIN

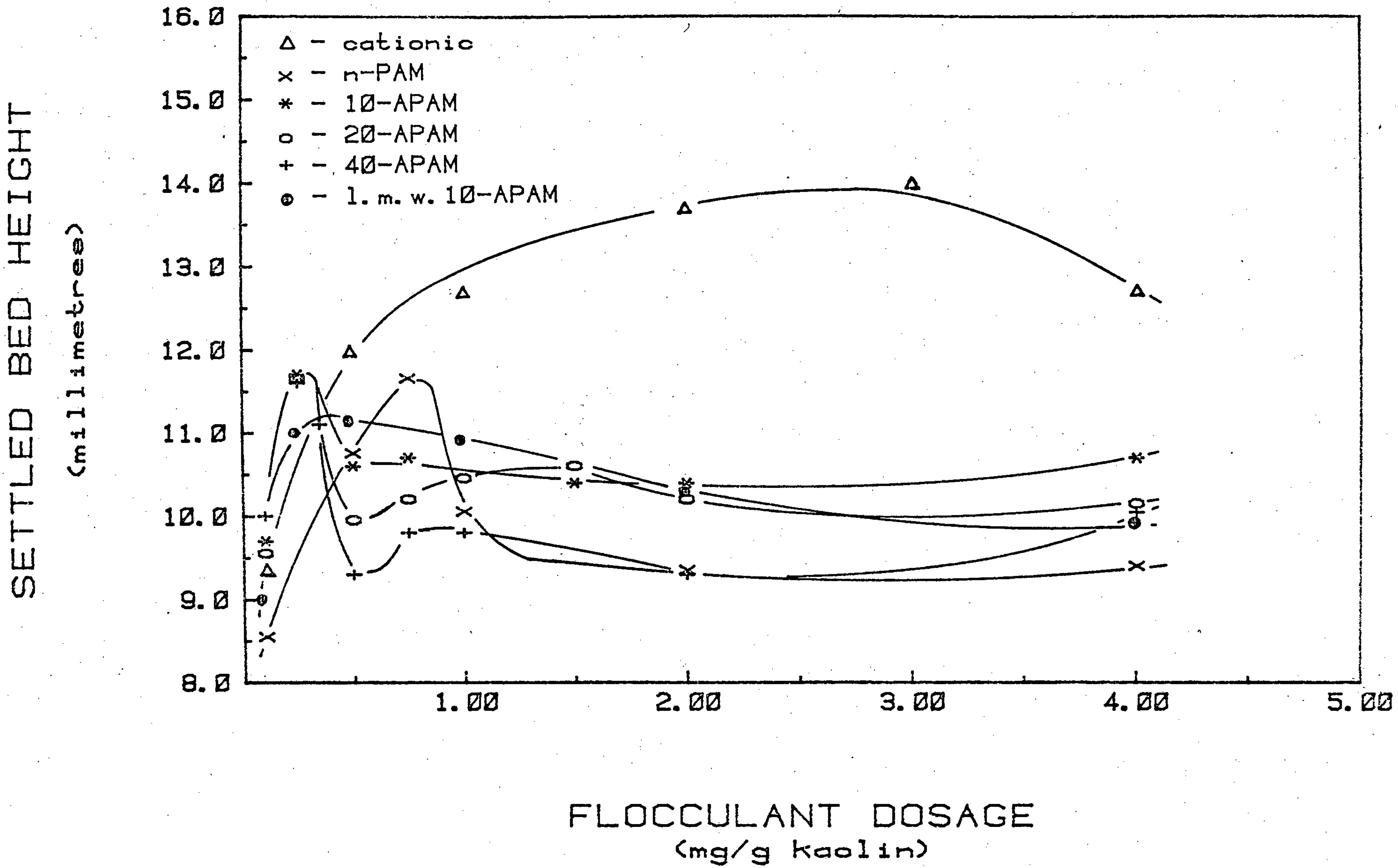


FIGURE 3.20

SETTLED BED HEIGHT vs. DOSAGE for Ca2+ KAOLIN

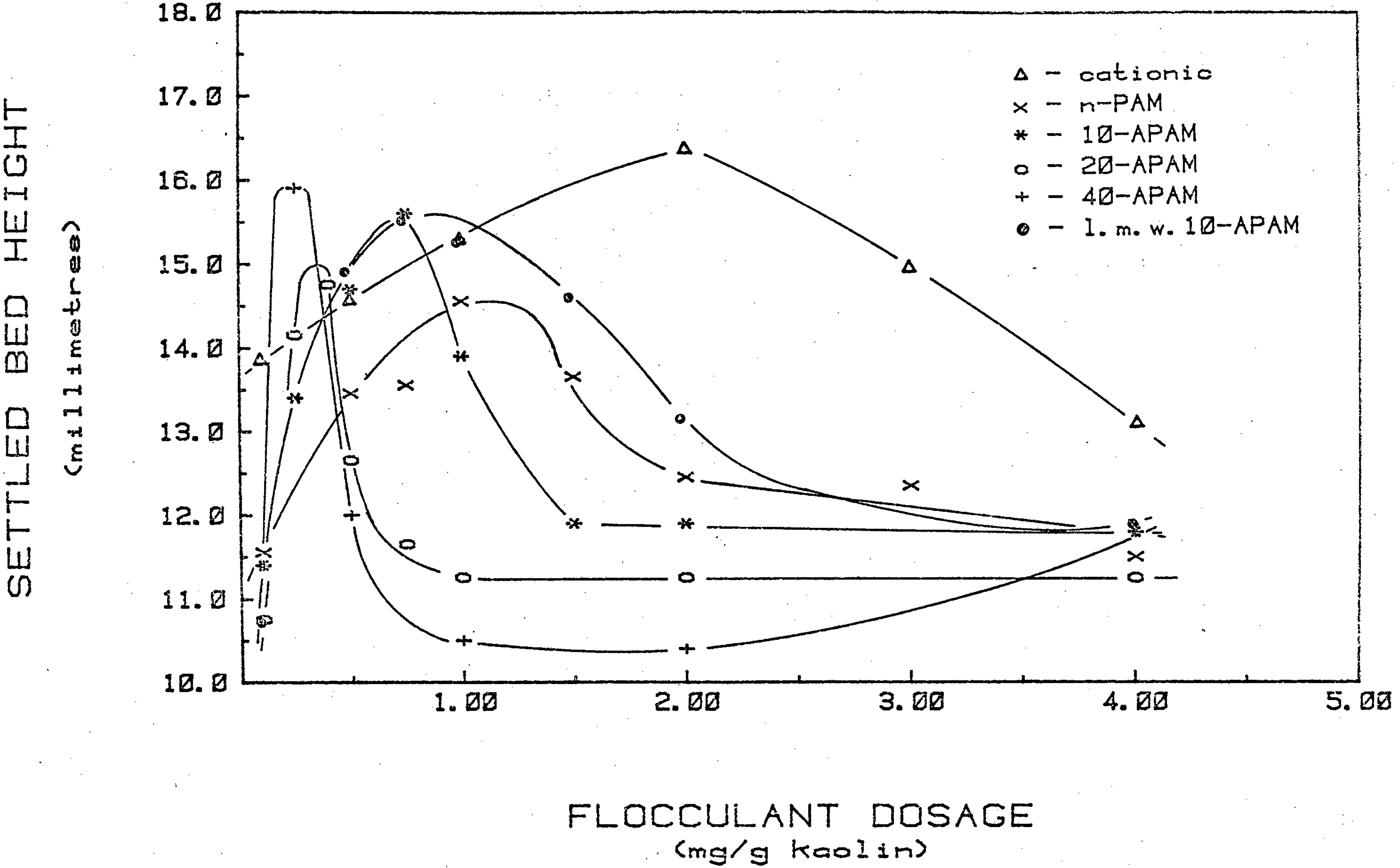


FIGURE 3.21

SETTLED BED HEIGHT vs. DOSAGE for H+ KAOLIN reduction in fraction of adsorbed flocculant is coincident with the minimum in supernatant turbidity (i.e. at the knee in the adsorption-dosage curves).

3.2.4 Single Floc Settling - Floc Size/Density Relationships

The rate of settling at a solids concentration of 1% w/w was either extremely high or, in the case of Na^+ kaolin treated with anionic flocculants, so low as not to merit measurement. However it was felt that some method should be applied to gain an impression of the settling rate and density of the flocs. This was achieved by timing single flocs across a graticule in a stereo-optical microscope and simultaneously estimating the floc diameter. The full method is described in Appendix 6. The results generated consisted of distributions of particle densities (calculated from Stokes law) at various estimated particle sizes. These distributions could be quite broad though on occasion (particularly for larger flocs) they were not (Figure 3.22). In order to reduce the volume of data and in order to get an indication of the trends, the mean value of the floc density was calculated at each estimated floc diameter. Thus it was possible to plot the floc size (diameter) against the mean density difference for each floc size (ie. the difference between the density of the floc and the density of water at the temperature at which the experiment was conducted).

It was shown that for the vast majority of results the type of curve that best fitted the results was a power expression. In this example (Figure 3.22) the r^2 correlation coefficient for the linearized least squares regression was 0.995. Similarly all curves with regression coefficients better than 0.94 were regarded as acceptable in view of the type of assumptions made about the data.

The set of curves for the Na^+, H^+ and Ca^{2+} kaolin treated with n-PAM are presented in Figures 3.23, 3.24 and 3.25. The general trend that can be observed is increasing density of the flocs with increase in flocculant concentration. This is observed across the range of floc sizes measured. An assessment of the accuracy of the observations can be deduced from the lack of overlap between the curves and the data points that give rise to

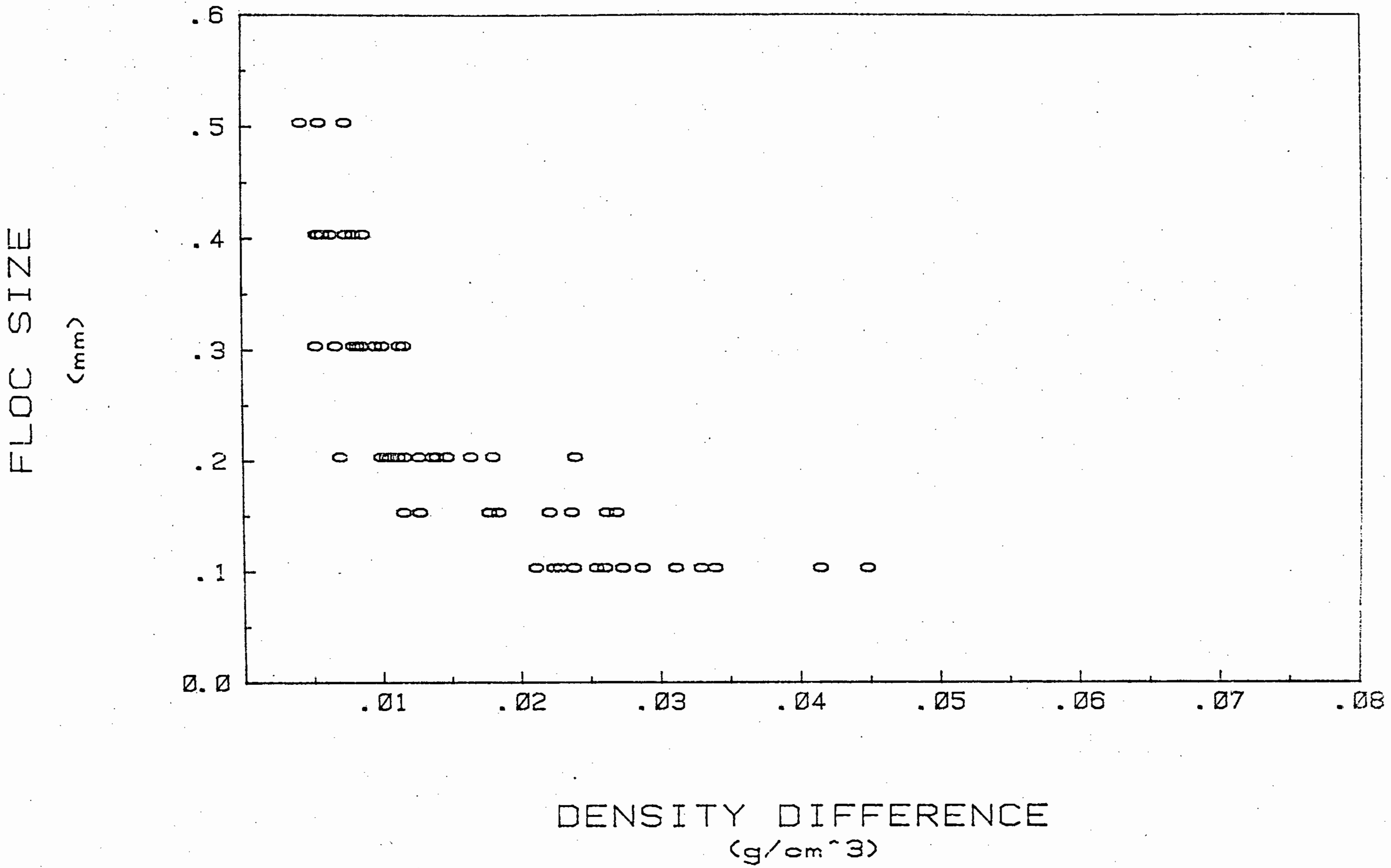


FIGURE 3.22

FLOC SIZE vs. DENSITY DIFFERENCE: Na KAOLIN - 20-APAM 0.5mg/g.

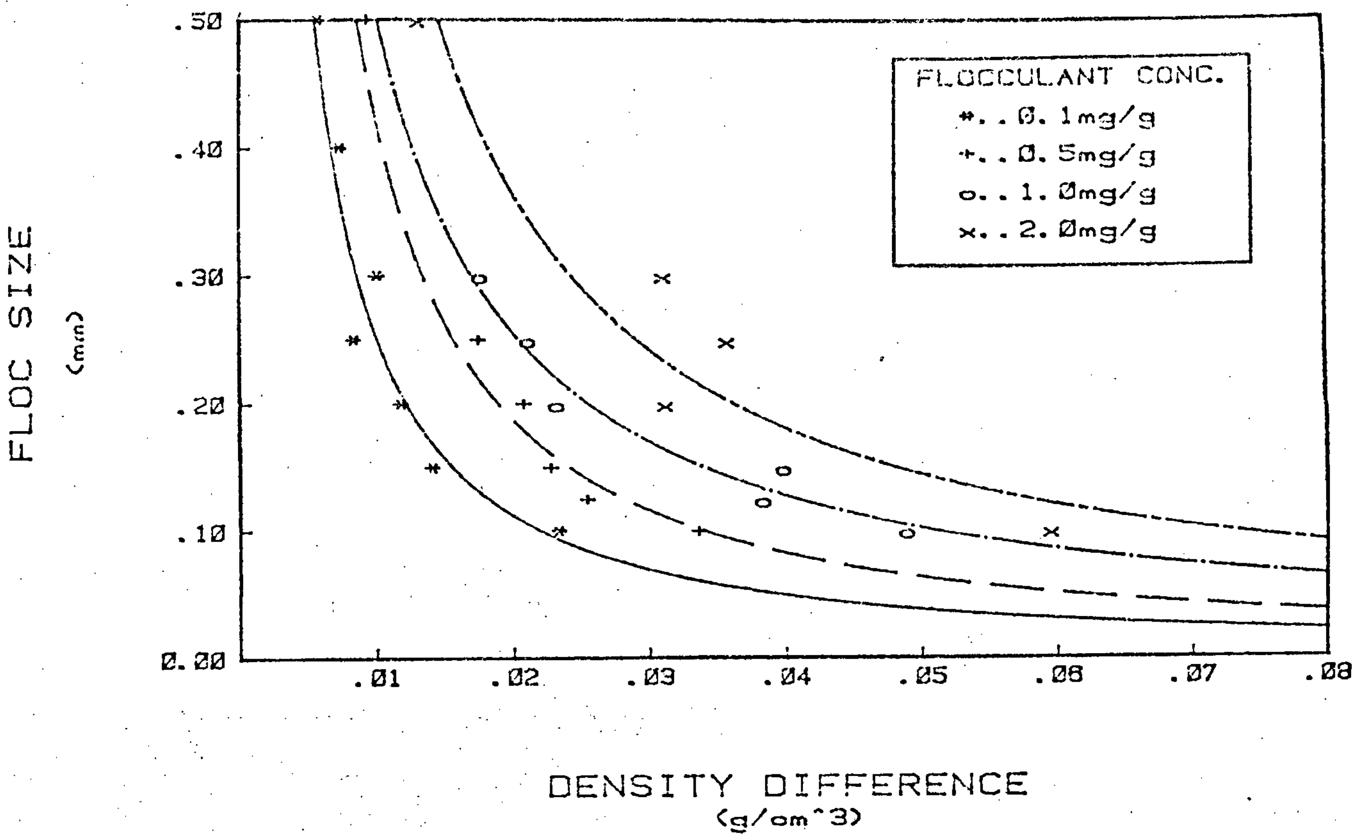


FIGURE 3.23

FLOC SIZE vs. DENSITY DIFFERENCE [Na-Kaolin / N-Polyacrylamide]

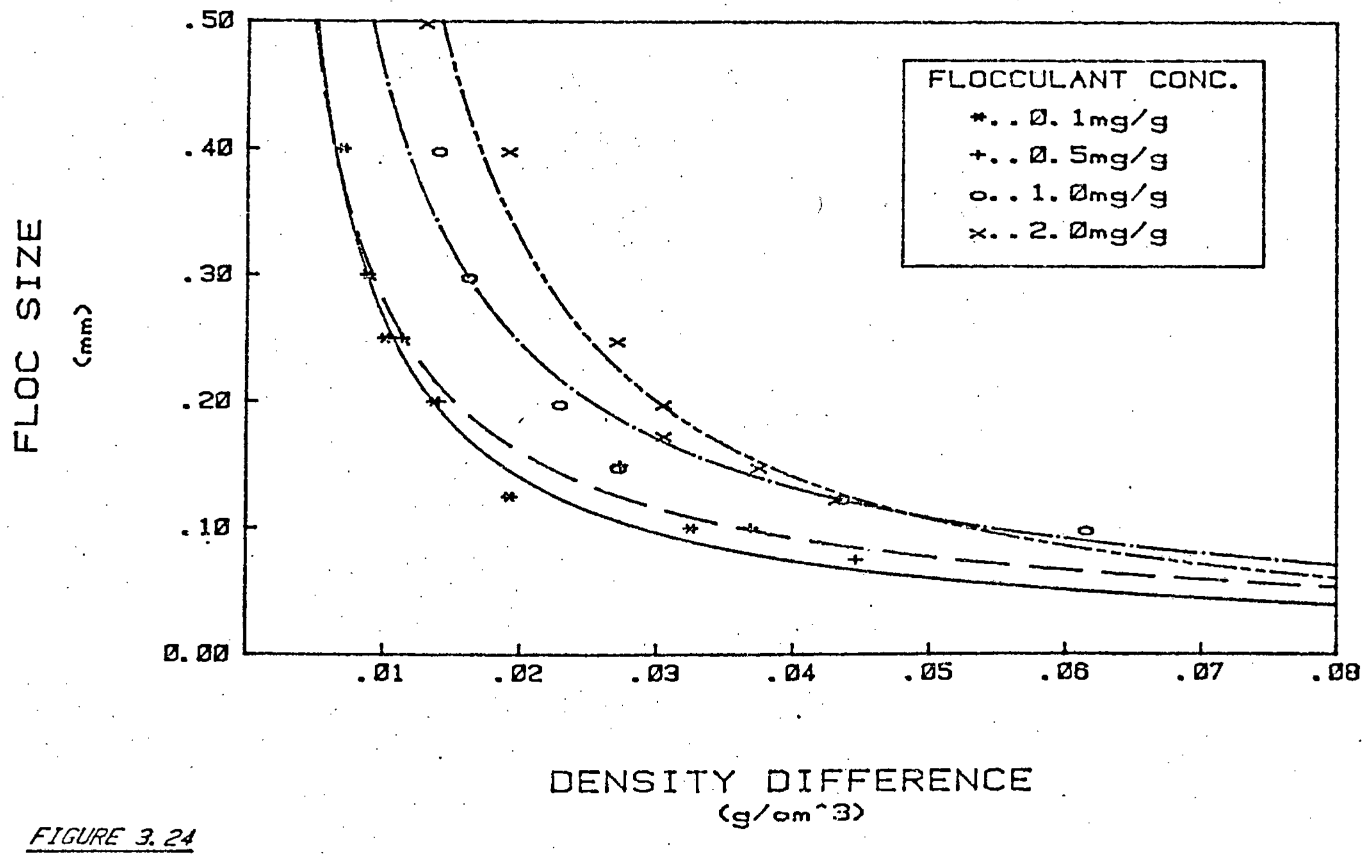


FIGURE 3.24

FLOC SIZE vs. DENSITY DIFFERENCE [H-Kaolin / N-Polyacrylamide]

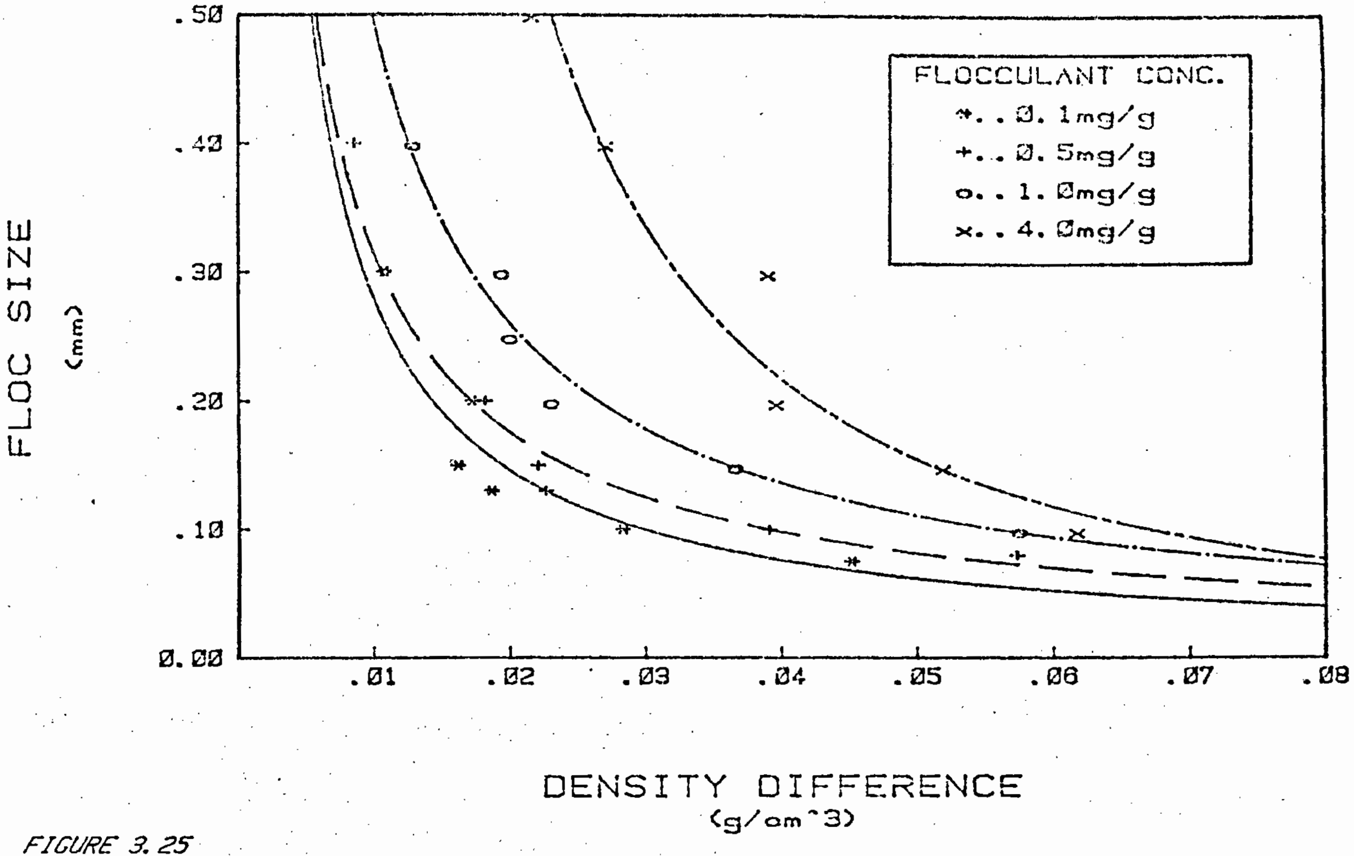


FIGURE 3.25

FLOC SIZE vs. DENSITY DIFFERENCE [Ca-Kaolin / N-Polyacrylamide]

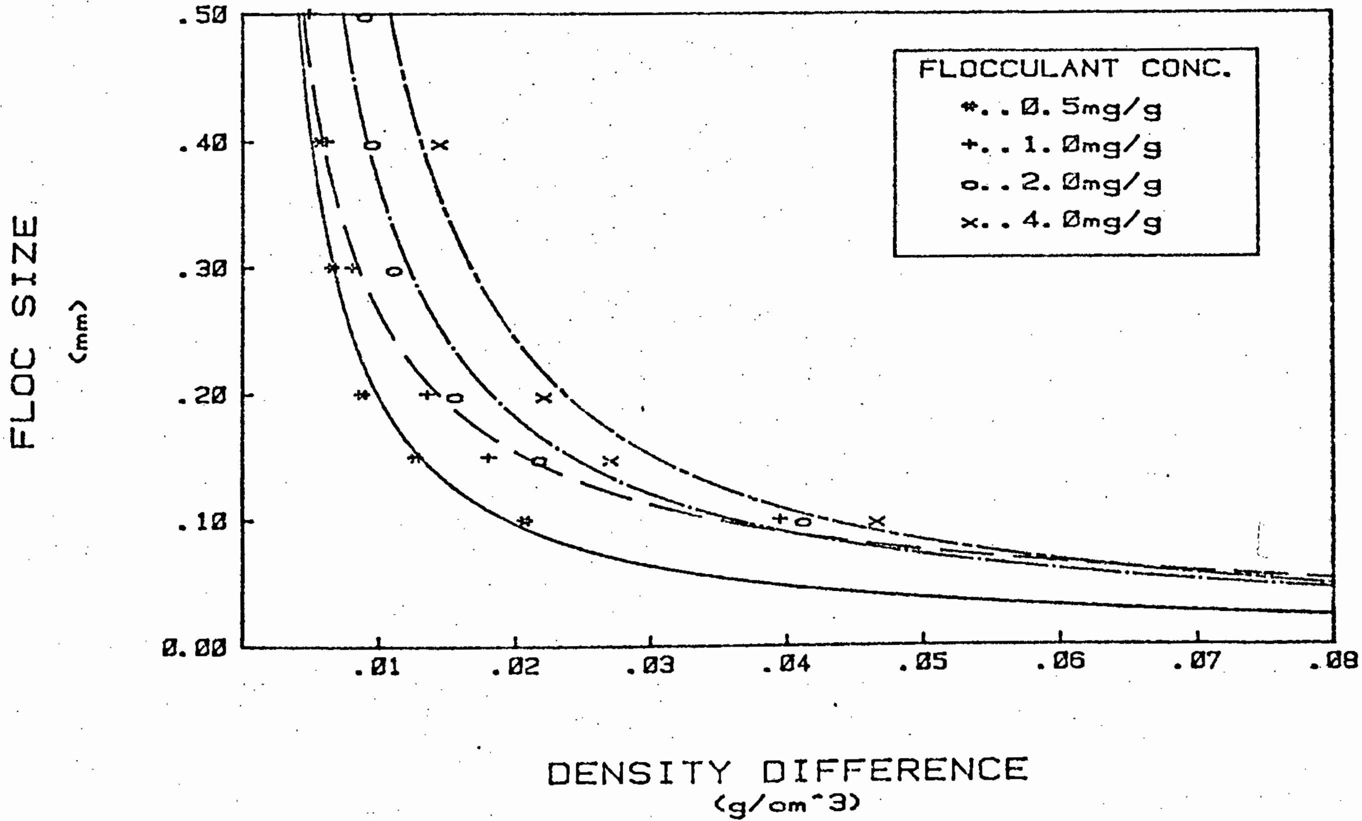


FIGURE 3.26

FLOC SIZE vs DENSITY DIFFERENCE [Na-Kaolin/low m. w. 10%Cat-Flocculant them. These results indicated that an increase in the amount of flocculant adsorbed tends to increase the density of the flocs irrespective of the nature of the exchangeable cation for the n-PAM.

Figures 3.26, 3.27 and 3.28 show the floc size-density difference curves for the Na^+, Ca^{2+} and H^+ kaolin treated with 10% cationic flocculant. The Na^+ kaolin showed no flocculation at a dosage of 0.1 mg/g and thus the density of the flocs could not be computed. The same trend of increasing floc density with flocculant dosage is observed. The same pattern of increasing floc density with diminishing floc size is observed. These trends become less distinct in the anionic flocculants, and they are perhaps best treated as functions of the different homoionic types as distinctive behaviours appear for each type. Figures 3.29, 3.30, 3.31 and 3.32 are the floc size density difference data for the low m.w. 10-APAM, 10-APAM, 20-APAM and the 40-APAM respectively for the Na^+ kaolin.

Figure 3.29 shows that at the dosage of 0.1 mg/g there exists a low floc density particularly at the larger floc radii. However the trend of increasing density with increasing flocculation dosage is not followed, the density being very similar at the higher floc diameters for the 0.5 mg/g, 1 mg/g and 2 mg/g, dosages. At the higher dosages the smaller flocs seem to be less dense than the flocs at the 0.5mg/g dosage. Figure 3.30 (10-APAM) shows the development of density with dosage from 0.1 mg/g to 1.0 mg/g with a decrease in density at higher dosages. Figure 3.31 shows for the 20-APAM a very similar density for all three dosages. The 40-APAM (Figure 3.32) shows an increase in density from 0.1 to 0.5 mg/g with a drop in density at the highest dosage (2 mg/g) in the larger floc sizes.

These four graphs indicate that for Na^+ kaolin there is with each type of anionic flocculant a limiting density (for larger floc diameters) which appears to be most pronounced with the 20-APAM. This limiting density may or may not be maintained at higher dosages of flocculant.

Figures 3.33, 3.34, 3.35 and 3.36 show the floc size-density behaviour for the low m.w. 10-APAM, 10-APAM, 20-APAM and 40-APAM respectively for the H^+ kaolin. For the low m.w. 10-APAM, 10-APAM and the 20-APAM the general trend of the results is increasing density with increasing flocculant dos-

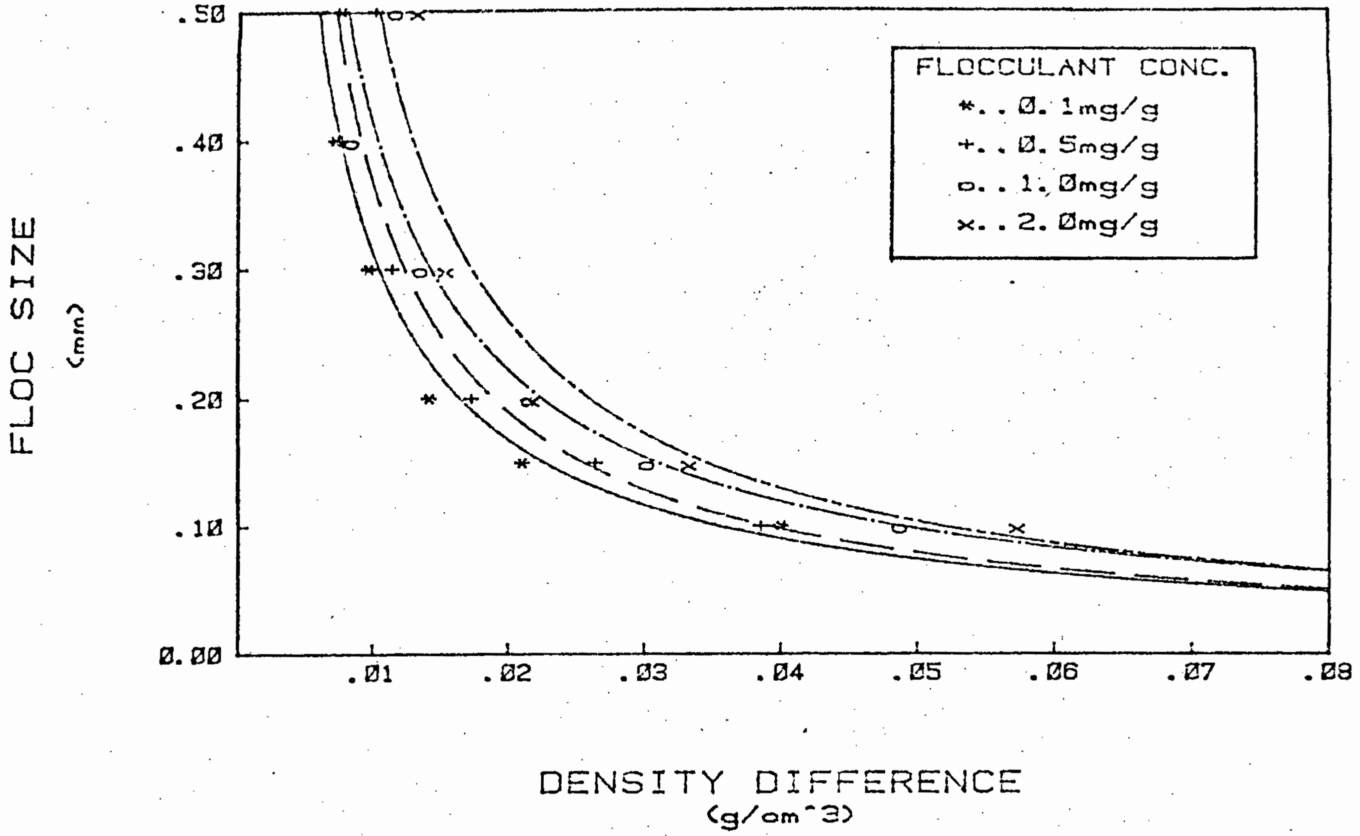


FIGURE 3.27

FLOC SIZE vs DENSITY DIFFERENCE [Ca-Kaolin/low m. w. 10%Cat Flocculant]

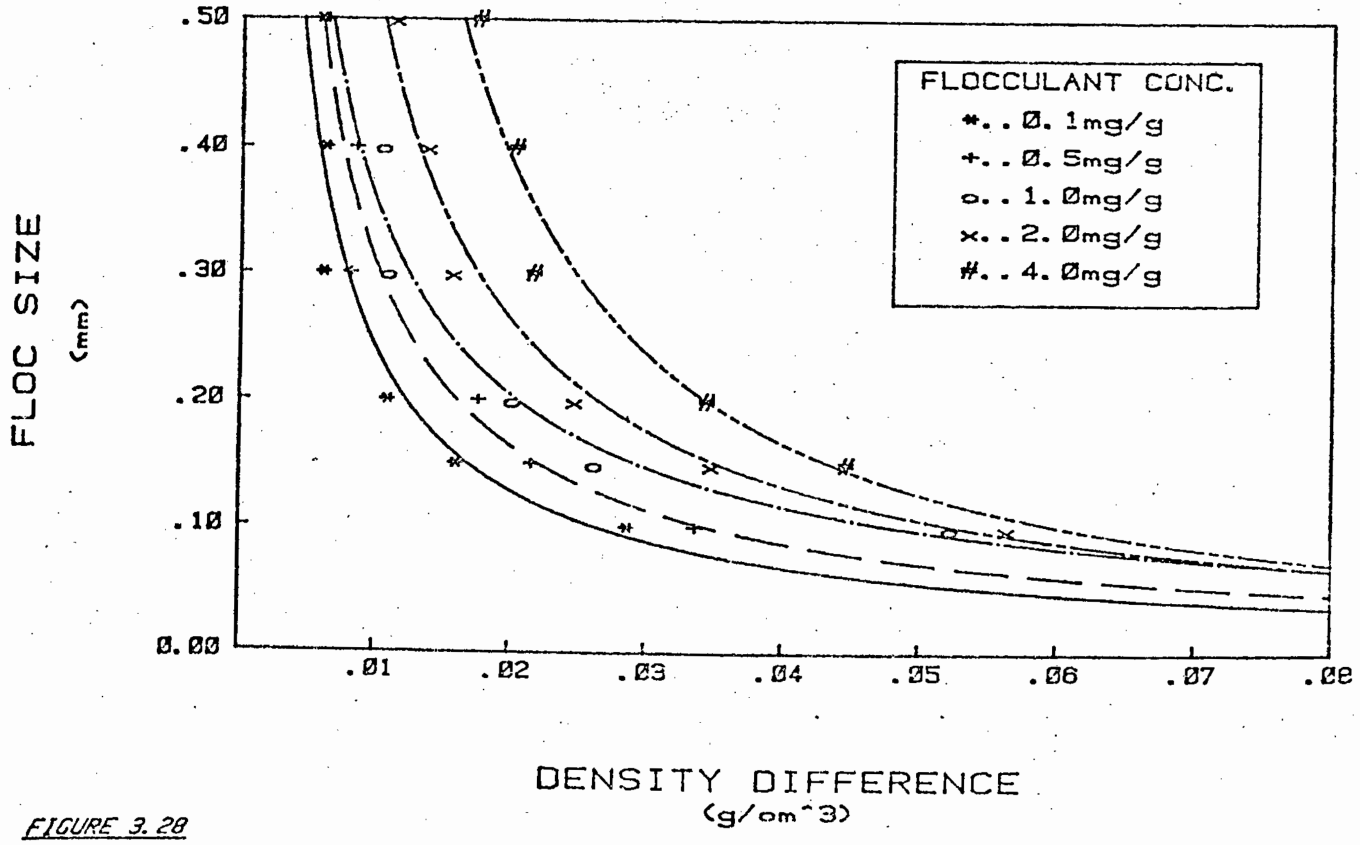


FIGURE 3.28

FLOC SIZE vs DENSITY DIFFERENCE [H-Kaolin/low m. w. 10%Cat Flocculant]

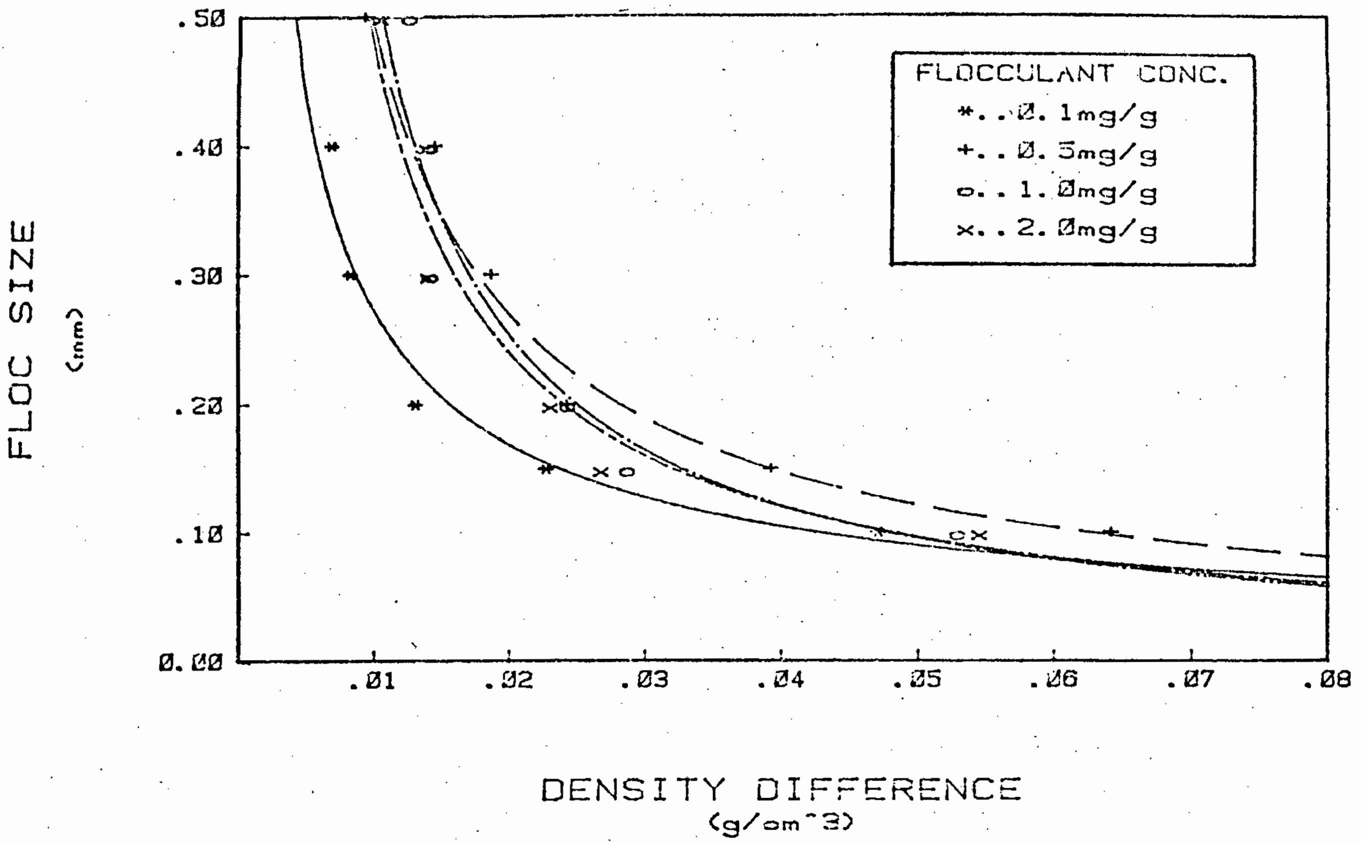


FIGURE 3.29

FLOC SIZE vs DENSITY DIFFERENCE Na-Kaolin/low m.w. 10%An-Polyacrylamide.

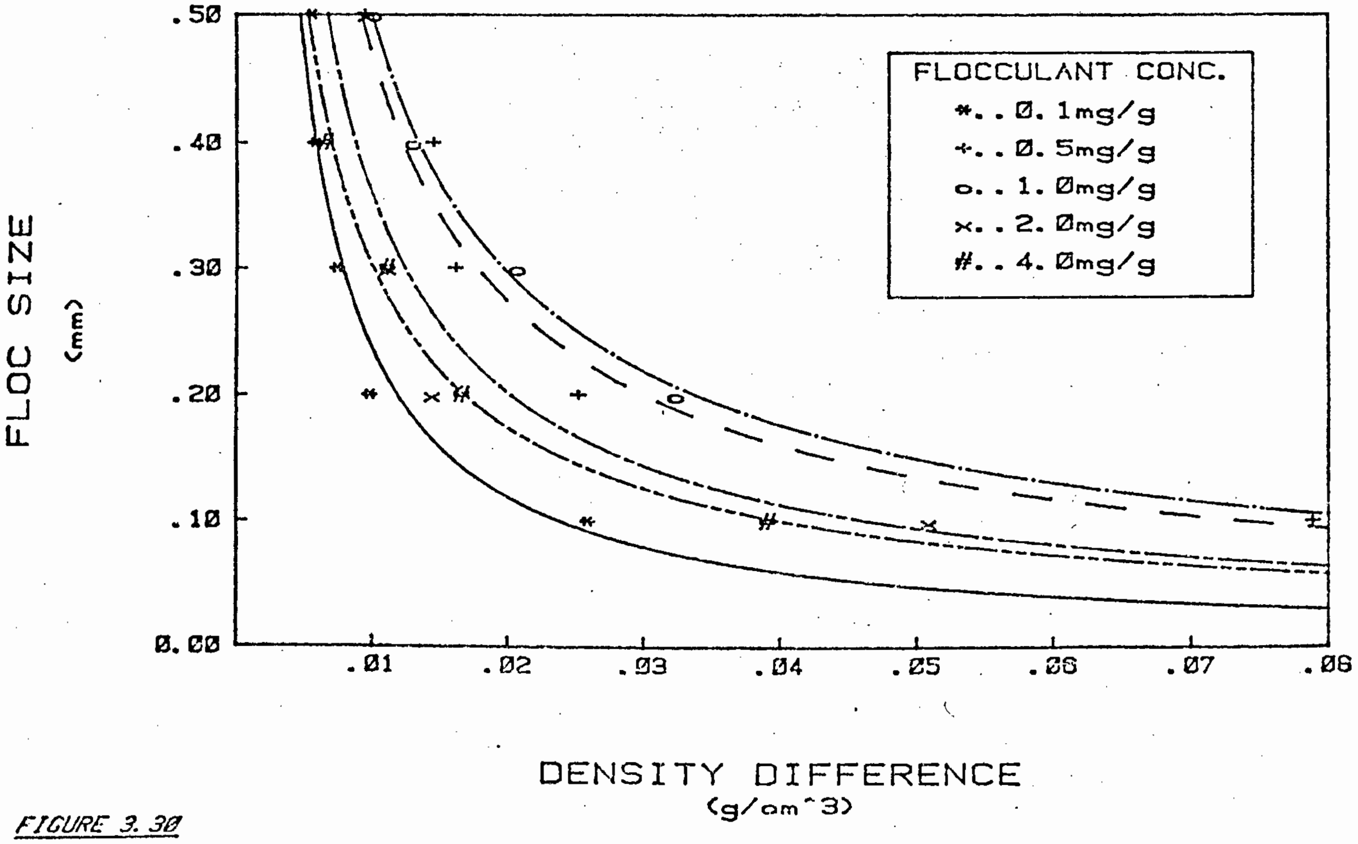


FIGURE 3.30

FLOC SIZE vs. DENSITY DIFFERENCE [Na+-Kaolin / 10%An-Polyacrylamide]

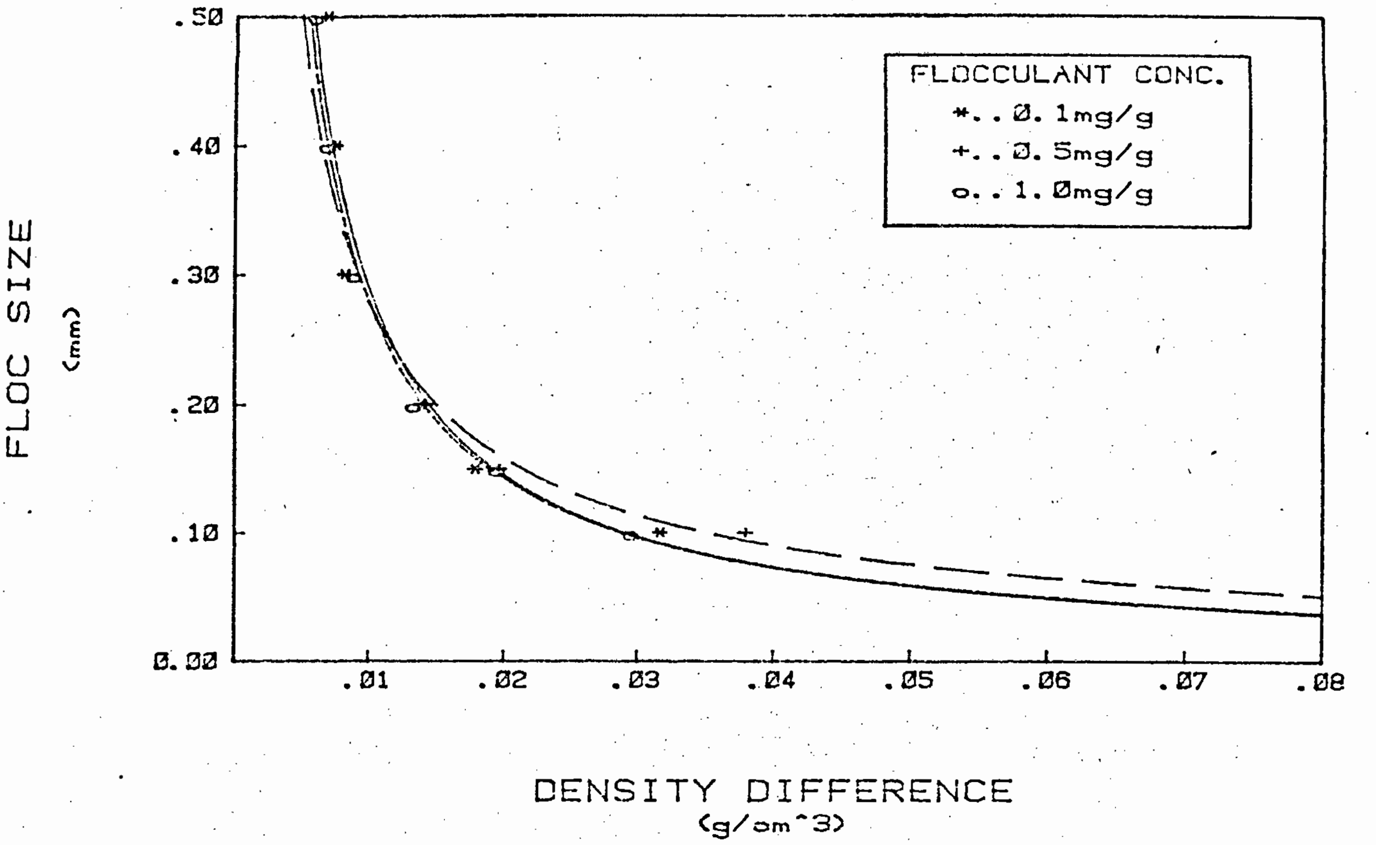


FIGURE 3.31

FLOC SIZE vs. DENSITY DIFFERENCE [Na-Kaolin / 20%An-Polyacrylamide]

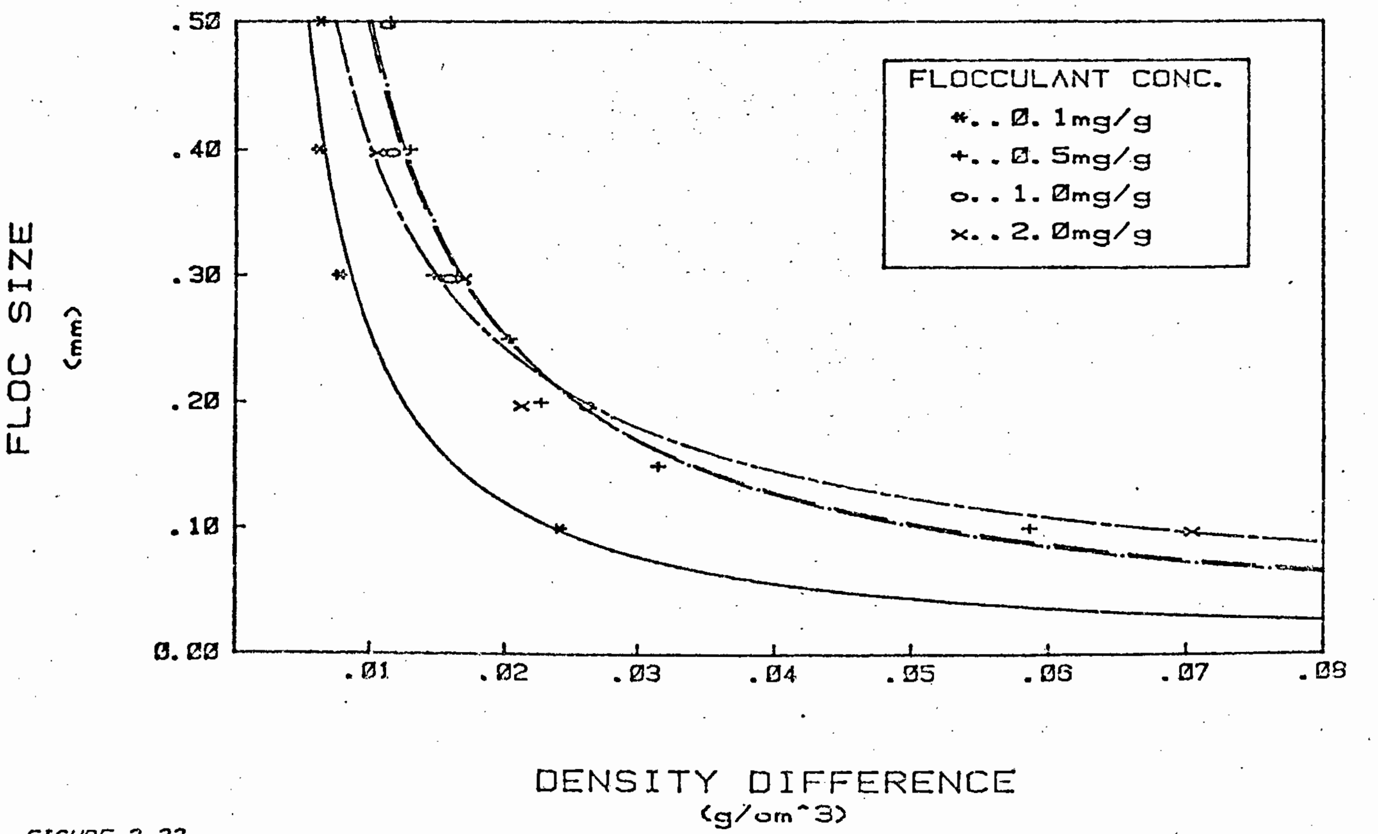


FIGURE 3.32

FLOC SIZE vs. DENSITY DIFFERENCE [Na+-Kaolin / 40%An-Polyacrylamide]

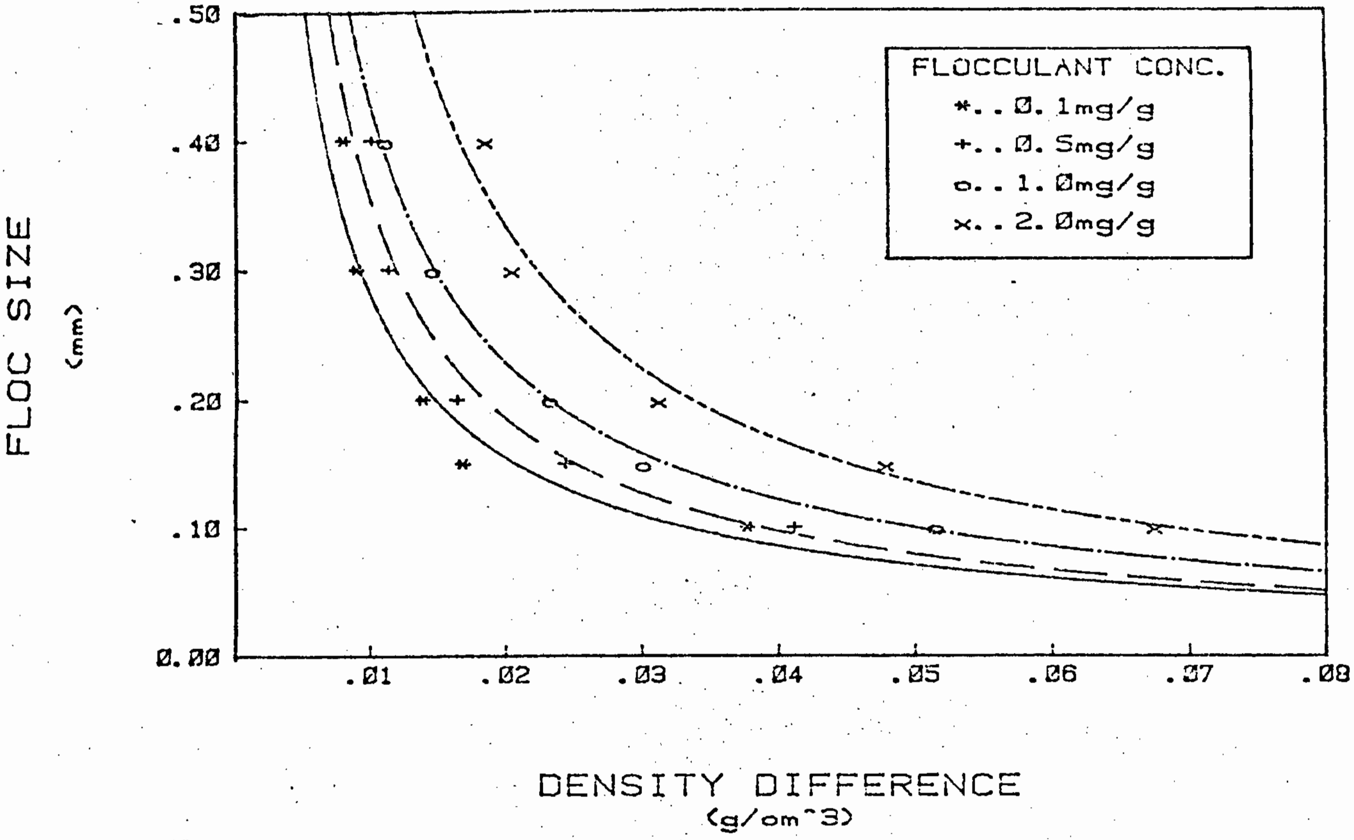


FIGURE 3.33

FLOC SIZE vs DENSITY DIFFERENCE H-Kaolin/low m. w. 10%An-Polyacrylamide

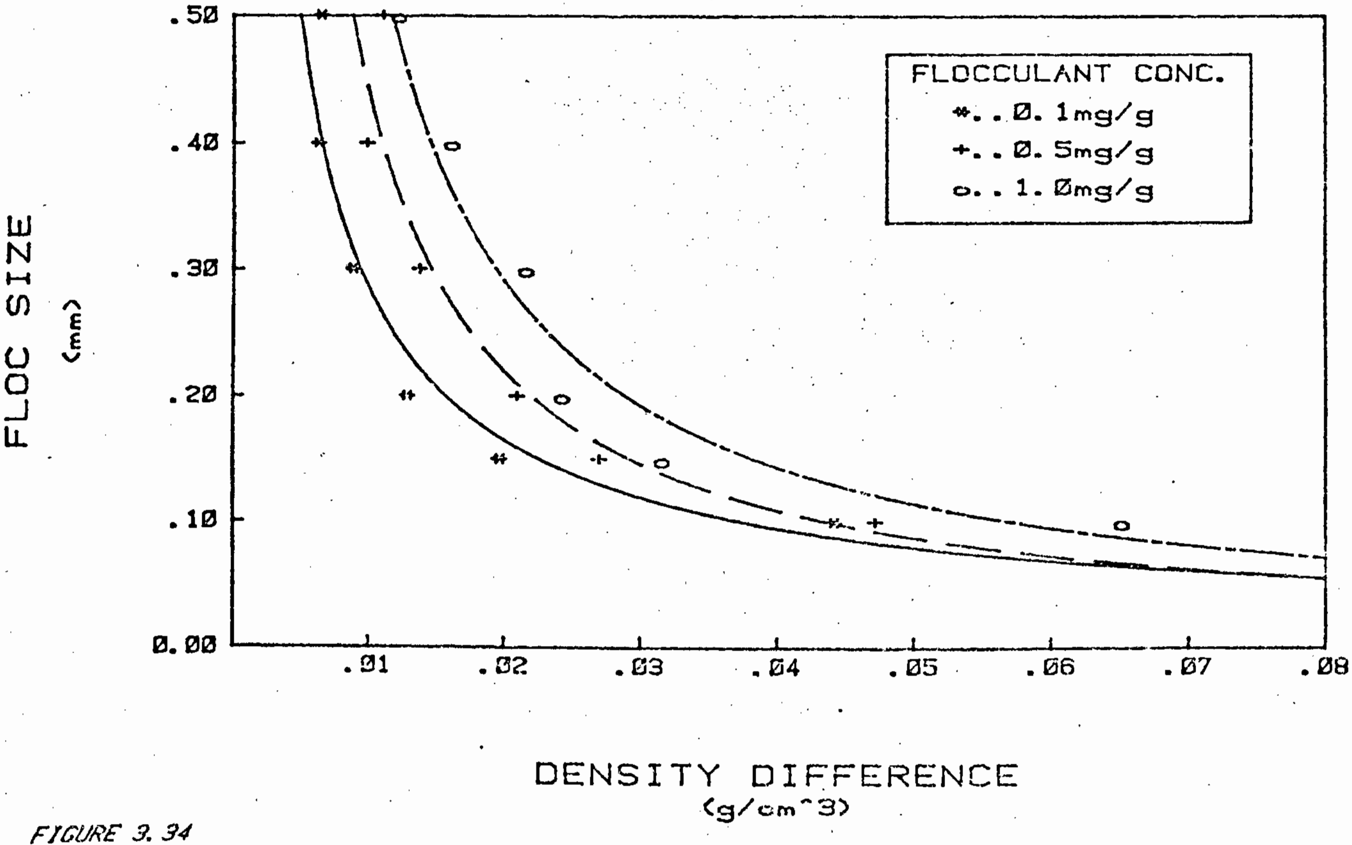


FIGURE 3.34

FLOC SIZE vs. DENSITY DIFFERENCE [H-Kaolin / 10%An-Polyacrylamide]

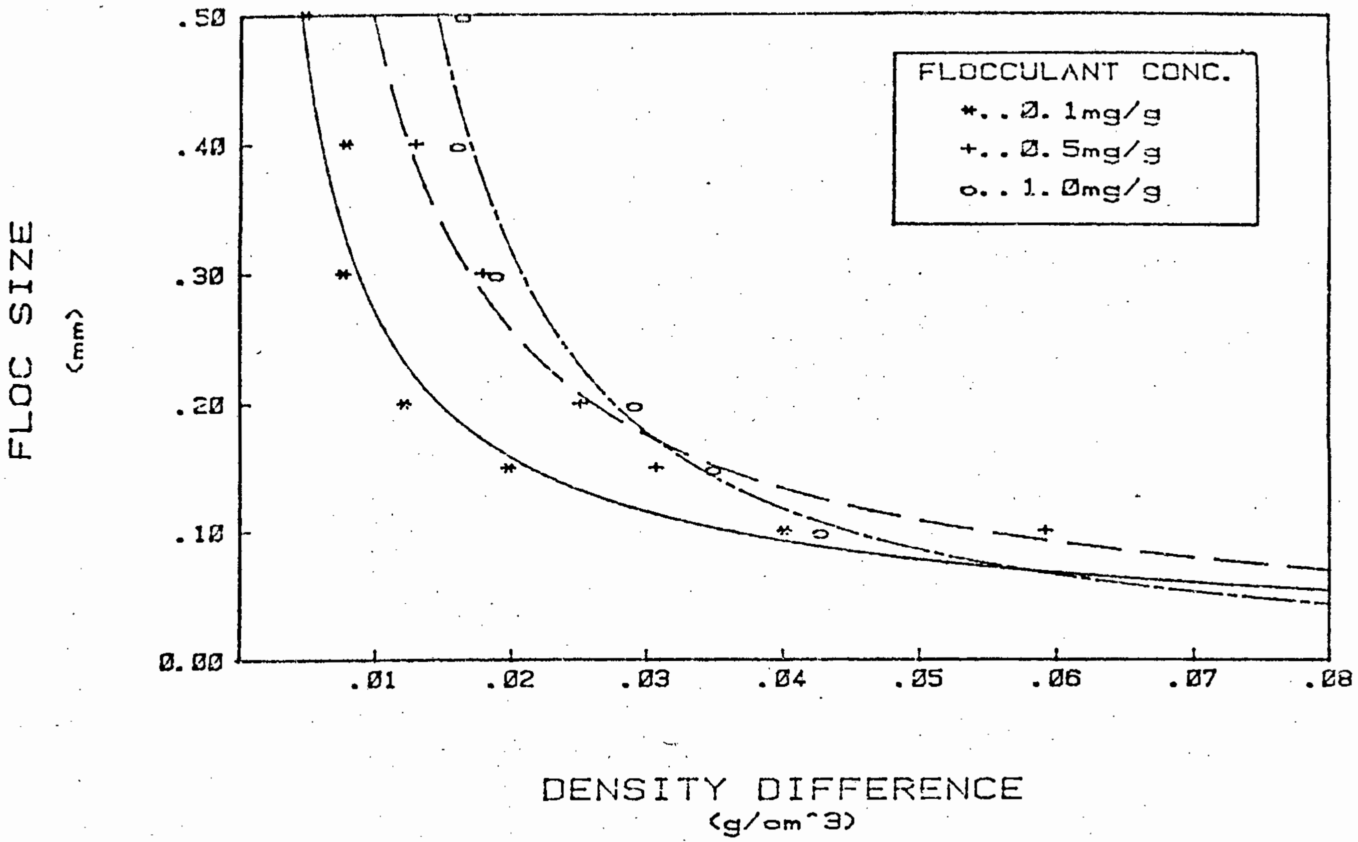


FIGURE 3.35

FLOC SIZE vs. DENSITY DIFFERENCE [H-Kaolin / 20%An-Polyacrylamide]

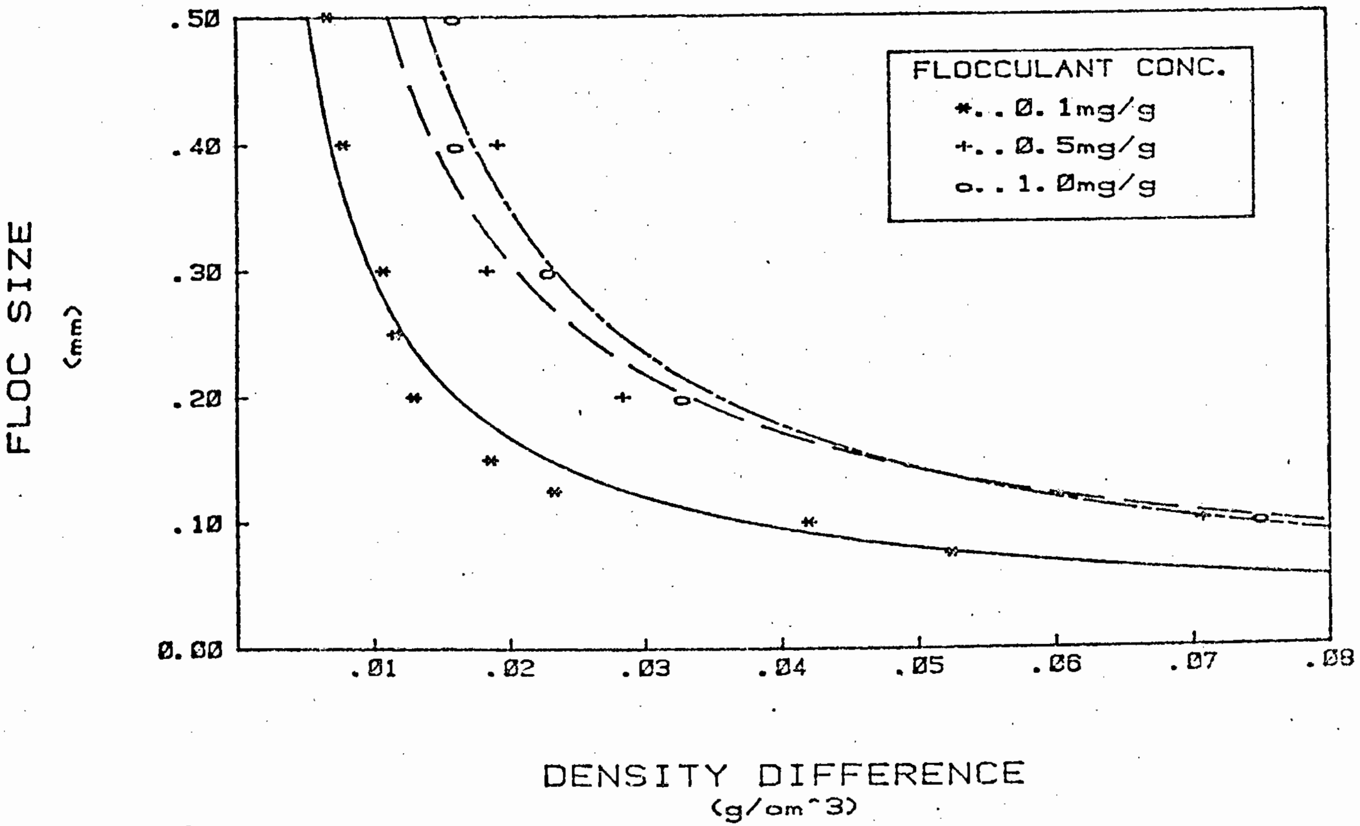


FIGURE 3.36

FLOC SIZE vs. DENSITY DIFFERENCE [H-Kaolin / 40%An-Polyacrylamide] age, as was noted for the n-PAM for all three homoionic forms of the kaolin. This consistent relationship breaks down with the 40-APAM which appears to reach a limiting density for the 0.5 mg/g and 1.0 mg/g dosages. The same may be said for smaller floc sizes for the 20-APAM. The same basic trend is followed for the Ca^{2+} kaolin (Figures 3.37, 3.38, 3.39 and 3.40) for the low m.w. 10-APAM, 10-APAM, 20-APAM and 40-APAM though the highest dosage (4 mg/g) for the 10-APAM shows a decrease in density. Thus the limit in floc density with dosage seems to be restricted, for the flocculant concentrations measured, to Na^+ kaolin treated with anionic flocculants and H^+ and Ca^{2+} kaolin treated with highly anionic flocculants. There is always, except in the case of the Na^+ kaolin treated with 20-APAM, some increase in floc density with increase in flocculant dosage.

A number of other interesting phenomena may be observed from the floc size density difference relationships. One of the most striking is the coincidence in the floc size density data for the lowest dosage of flocculant (0.1 mg/g). There is no similar relationship for the maximum densities achieved. The highest density differences recorded are for the smaller flocs but none of them approaches the density difference between kaolin and water (1.65 g/cm^3) the highest being about 0.25 g/cm^3. This corresponds to a particle mass concentration of about 16%. The lowest densities (large flocs/low dosages) correspond to density differences of about 0.004 g/cm^3, or a solids concentration of about 0.24%. This represents a density change of nearly two orders of magnitude. However for the same floc size (say flocs of 0.3 mm diameter) the density slightly more than doubles in the most extreme cases of density difference increase (that is to say the solids concentration doubles).

3.2.5 Floc Photography.

Floc photography was used to examine the visual characteristics of flocs. That information in conjunction with the flocculation-adsorption measurements and the floc density determinations can provide an assessment of the flocculation process. The photographs presented here are intended to provide a basis for the interpretation of photographic records of flocculated slurries.

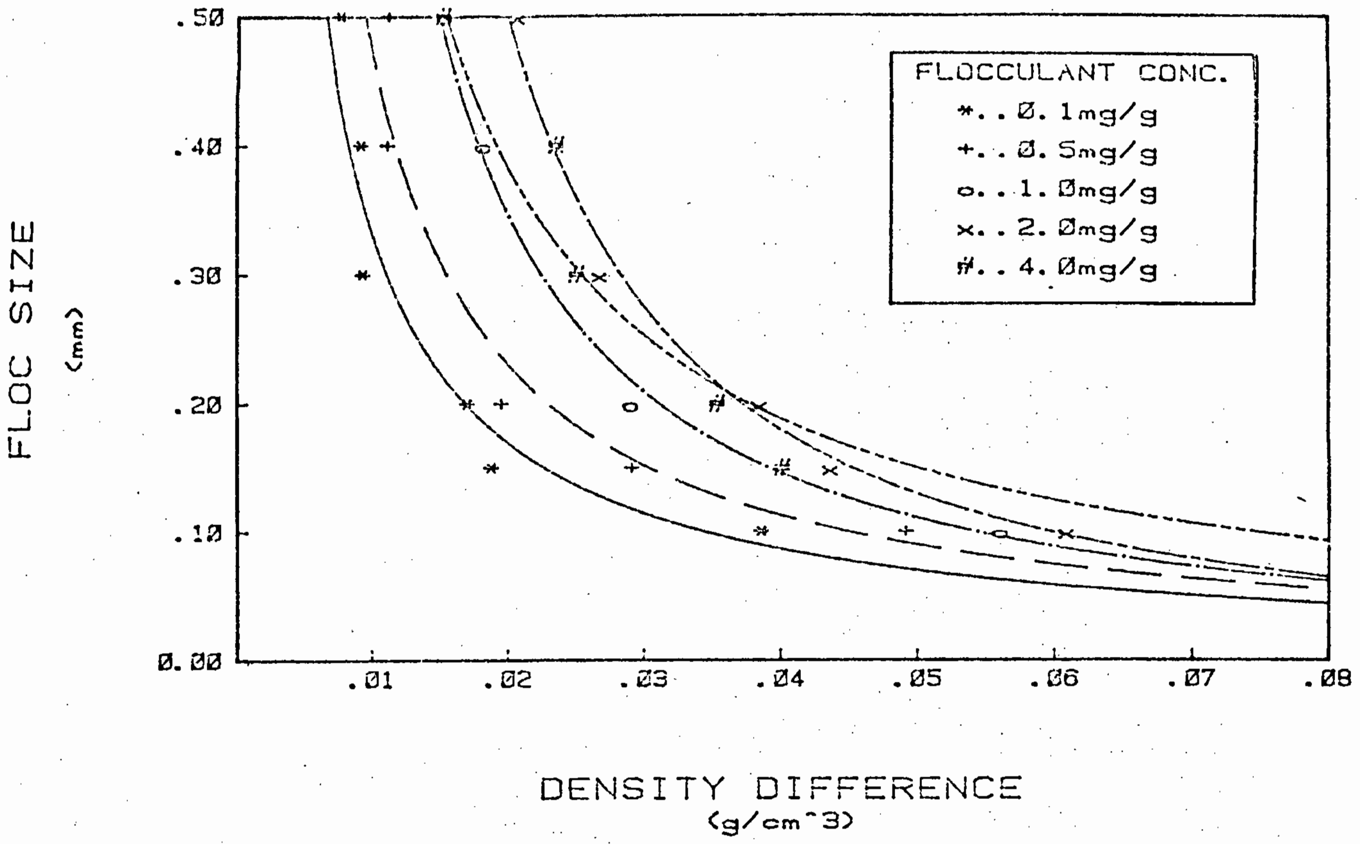


FIGURE 3.37

FLOC SIZE vs DENSITY DIFFERENCE Ca-Kaolin/low m. w. 10%An-Polyacrylamide

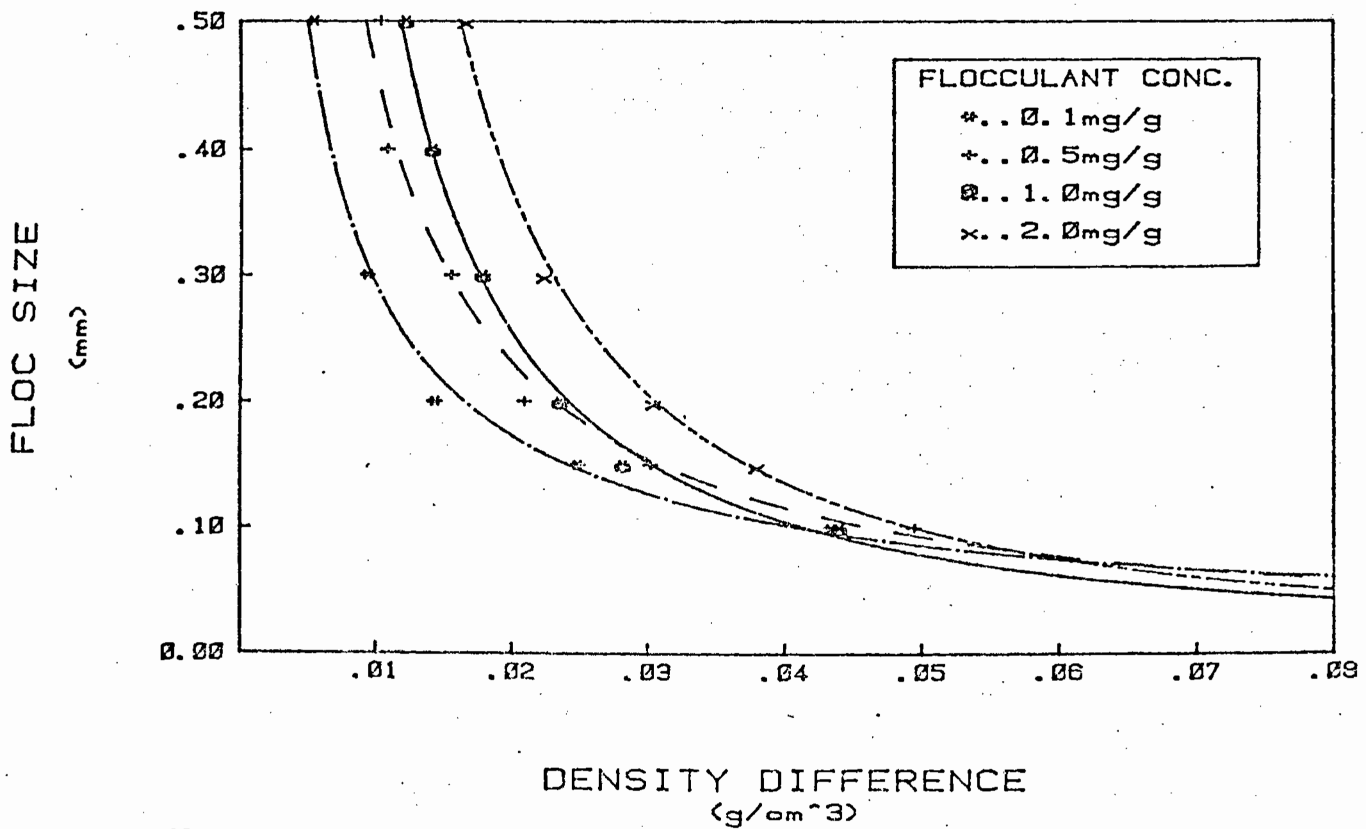


FIGURE 3.38

FLOC SIZE vs. DENSITY DIFFERENCE [Ca-Kaolin / 10%An-Polyacrylamide]

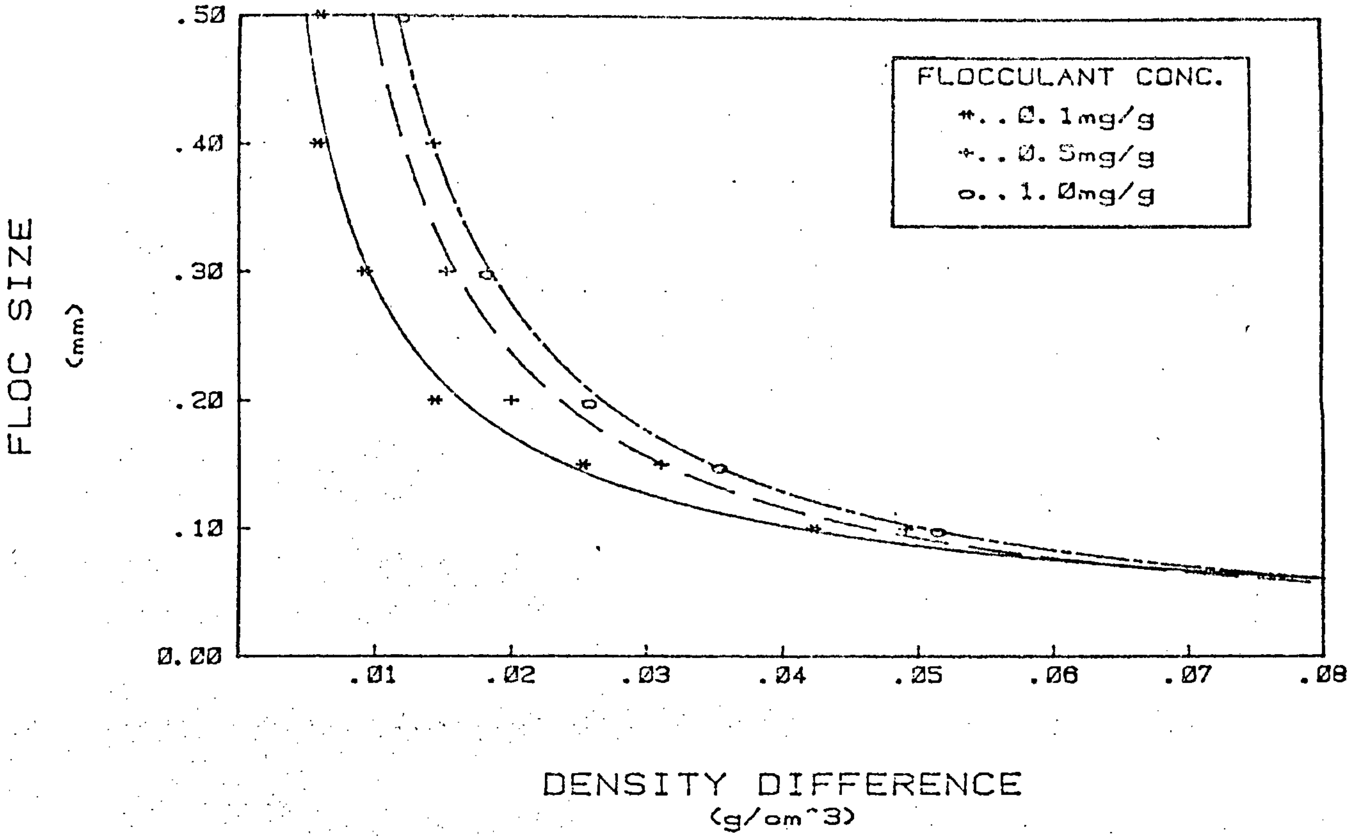


FIGURE 3.39

FLOC SIZE vs. DENSITY DIFFERENCE [Ca-Kaolin / 20%An-Polyacrylamide]

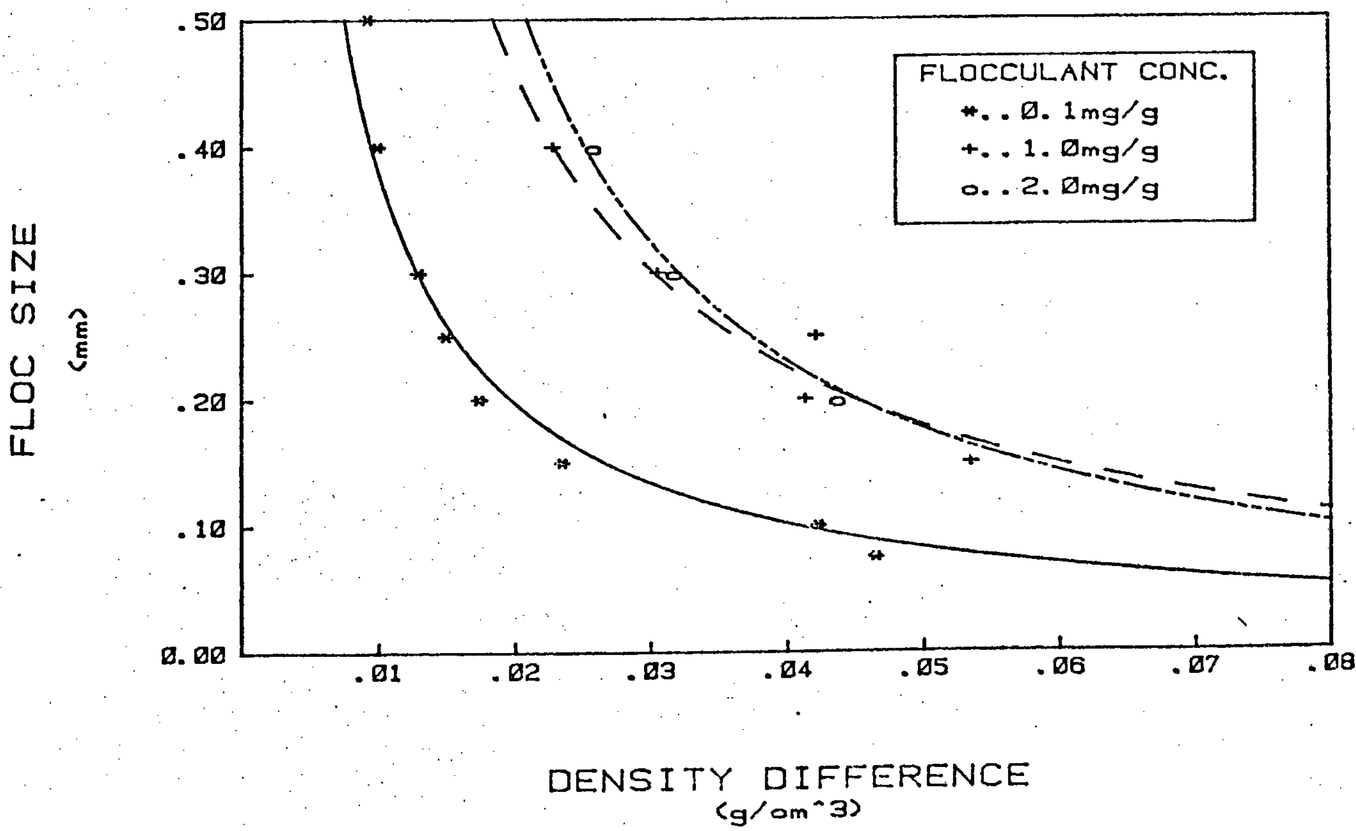


FIGURE 3.40

FLOC SIZE vs. DENSITY DIFFERENCE [Ca-Kaolin / 40%An-Polyacrylamide]

One of the primary assessments that can be made from the photographic record is that of floc size. The change in floc size with the following variables can be observed :-

(i) flocculant dosage
(ii) different flocculants at a single dosage and
(iii) different homoionic forms of the kaolin with a single flocculant at a single dosage.

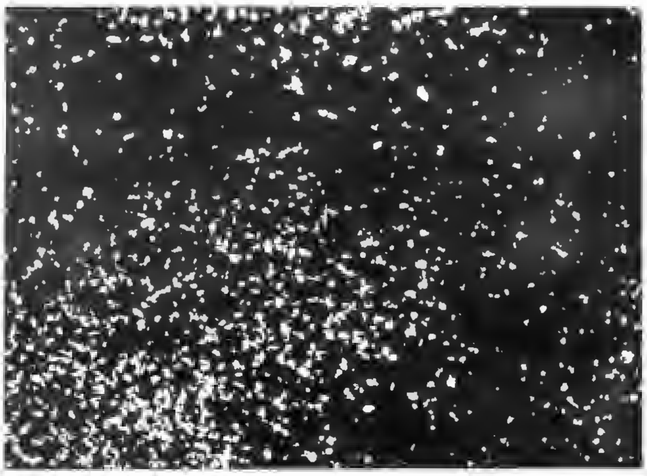
An example of the first instance is the series of photographs of the Na^+ kaolin treated with n-PAM (0.25 mg/g, 1 mg/g, 2 mg/g and 4 mg/g) that were used for evaluating floc size by image analysis (see Section 3.6). The rapid increase in floc size with flocculant dosage is obvious (Figure 3.41). By contast the H^+ kaolin treated with 40-APAM shows the ultimate floc size is already achieved at a concentration of 1 mg/g with no apparent increase at higher dosages (Figure 3.42).

The second type of assessment that can be made is of the different floc sizes at a single dosage for different flocculants. This can already be noted by cross comparison of Figures 3.41 and 3.42. Figure 3.43 is the photographs of the Ca^{2+} kaolin treated by a range of flocculants at a dosage of 1 mg/g. It is apparent from these photographs that the cationic flocculant has the smallest floc size (the flocs are of the "woolly" type). The 20-APAM and 10-APAM have the largest flocs with the low m.w. 10-APAM and 40-APAM perhaps somewhat smaller and the n-PAM smaller though considerably more discrete than is the case for the cationic flocculant.

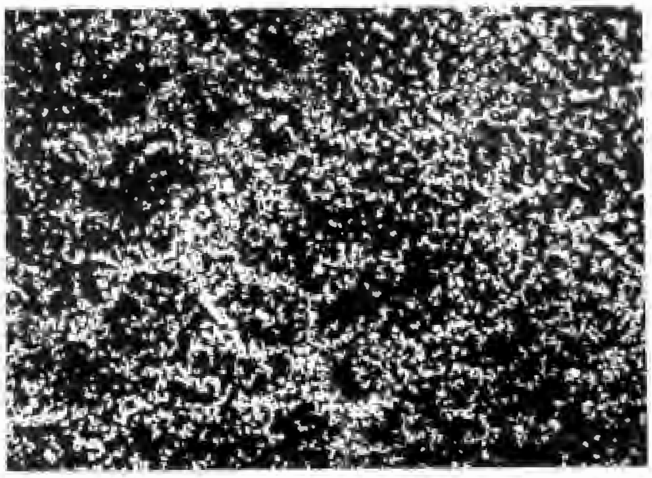
The situation for the H^+ kaolin is somewhat different (Figure 3.44). At the 1 mg/g dosage the largest flocs are generated by the 20-APAM with the sizes decreasing in the order of 20-APAM >> 40-APAM > 10-APAM $\sim$ n-PAM > low m.w. 10-APAM $\sim$ cationic. A similar examination of the Na^+ kaolin at the same dosage of flocculant (Figure 3.45) reveals the order n-PAM >> 40-APAM $\sim$ 20-APAM > low m.w. 10-APAM > cationic, the result for the 10-APAM being similar to the low m.w. 10 APAM, but no photograph is available.

cationic

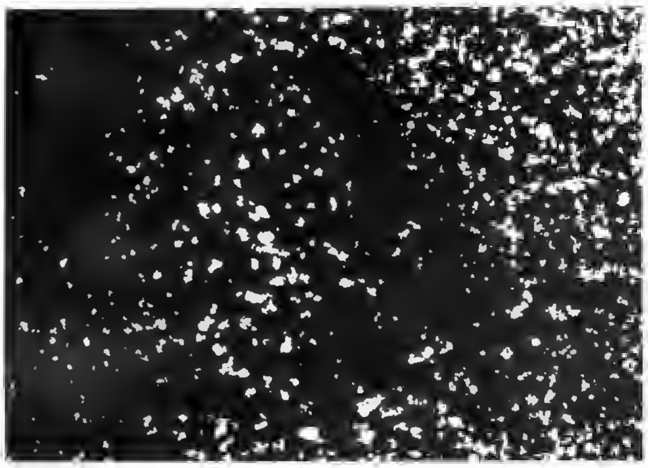
n-PAM



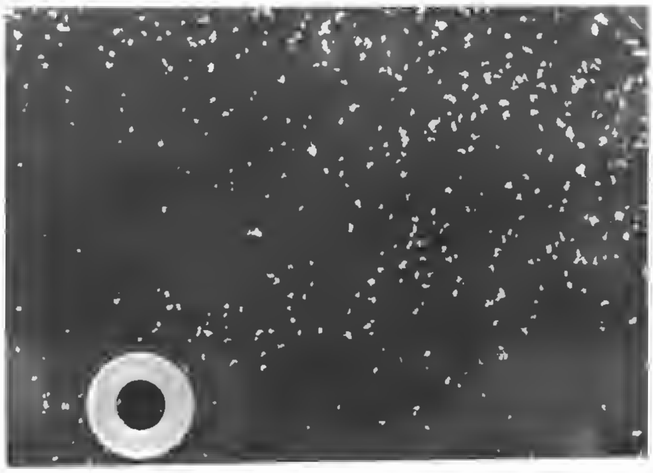
10-APAM



low m.w. 10-APAM



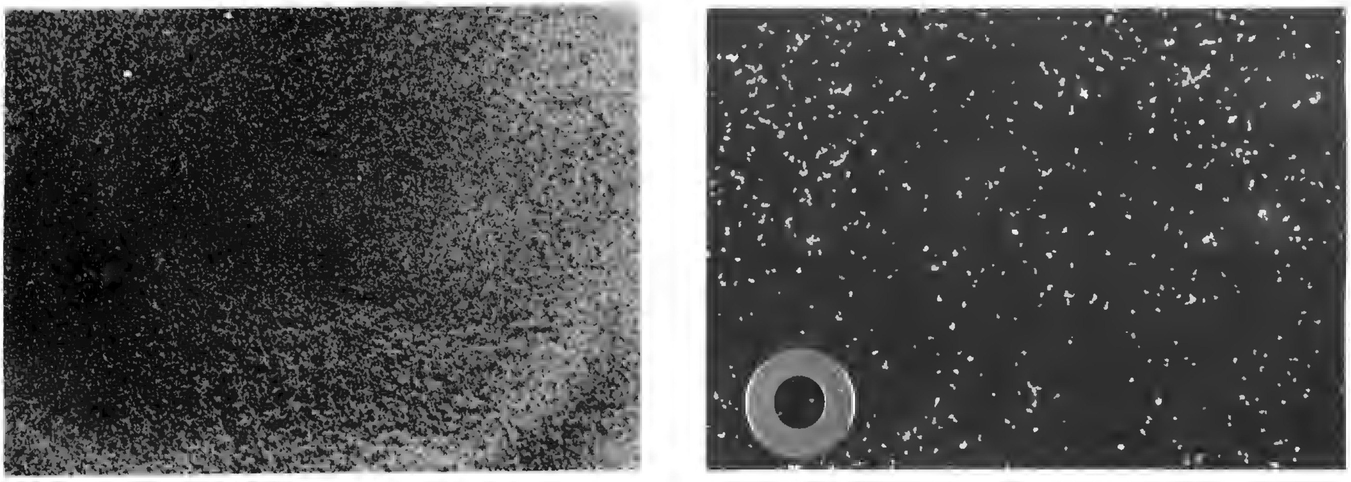
20-APAM



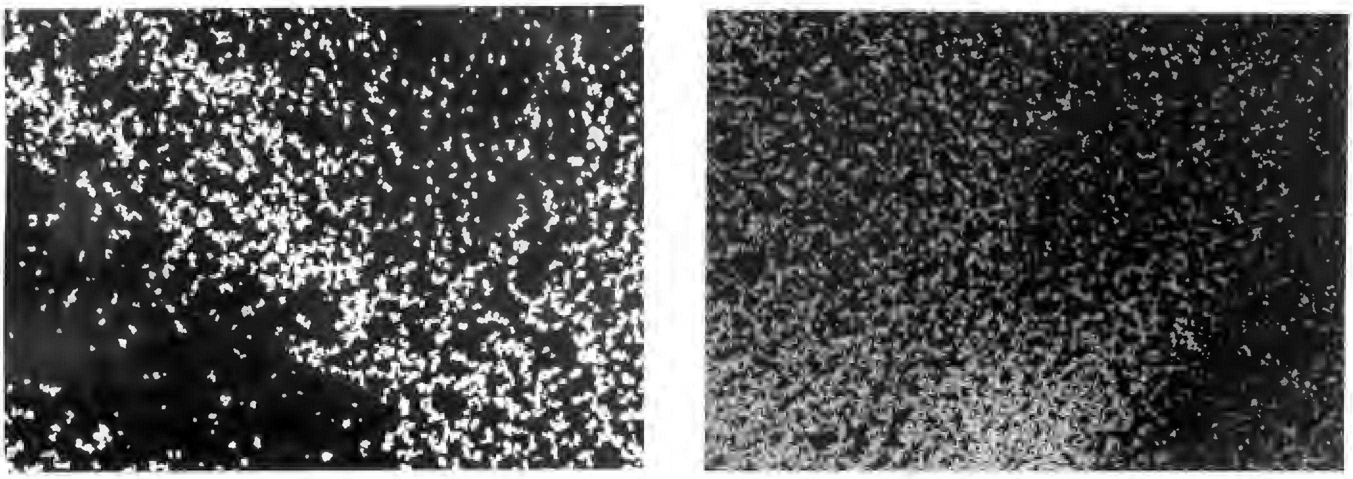
40-APAM

2.0cm

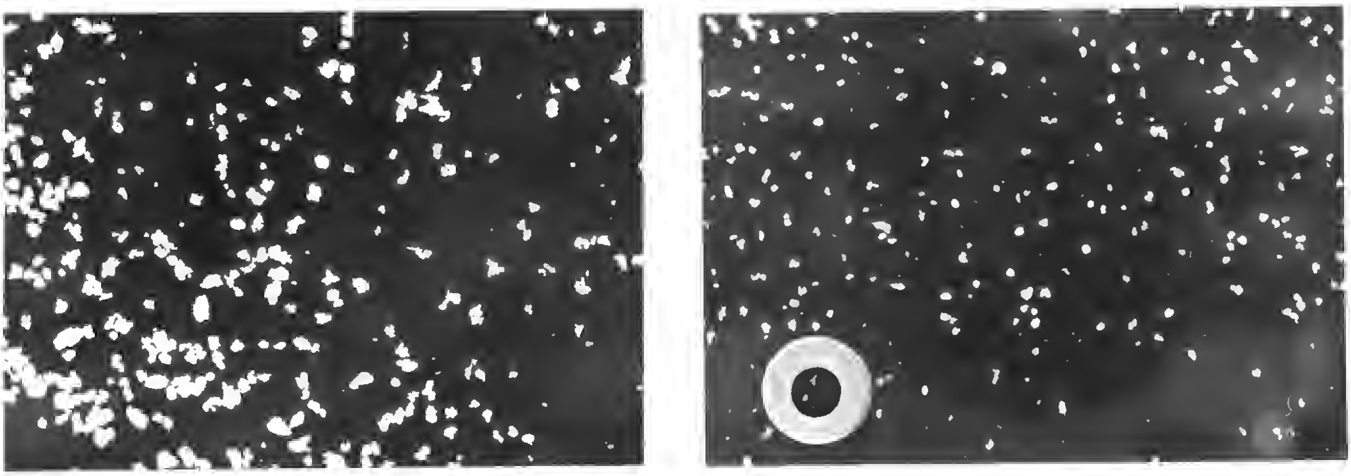
Figure 3.43: Ca^{2+} kaolin treated with various flocculants. Dosage 1mg/g kaolin.



cationic n-PAM



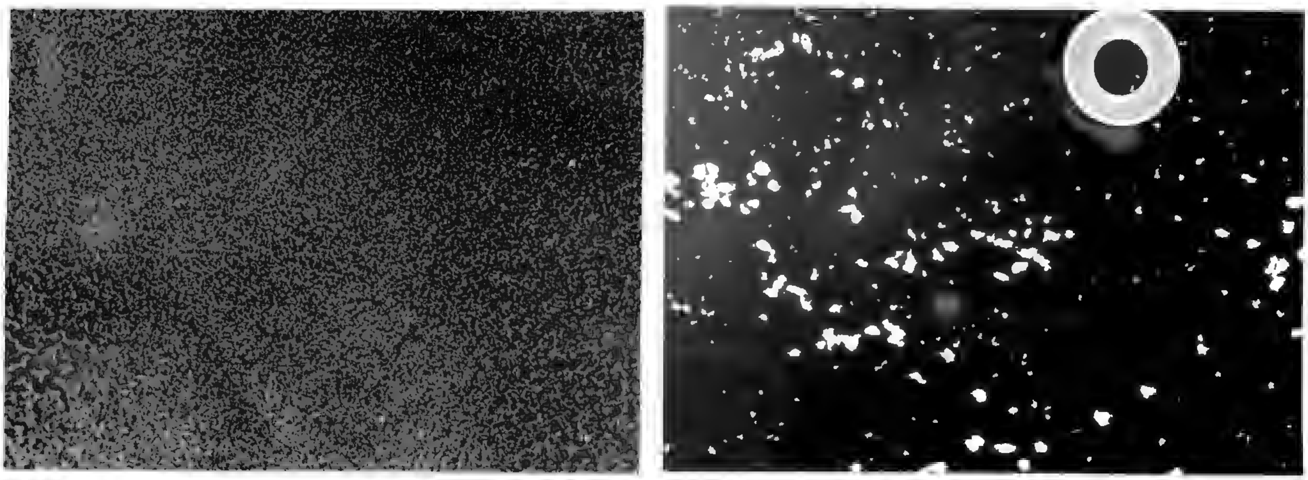
10-APAM low m.w. 10-APAM



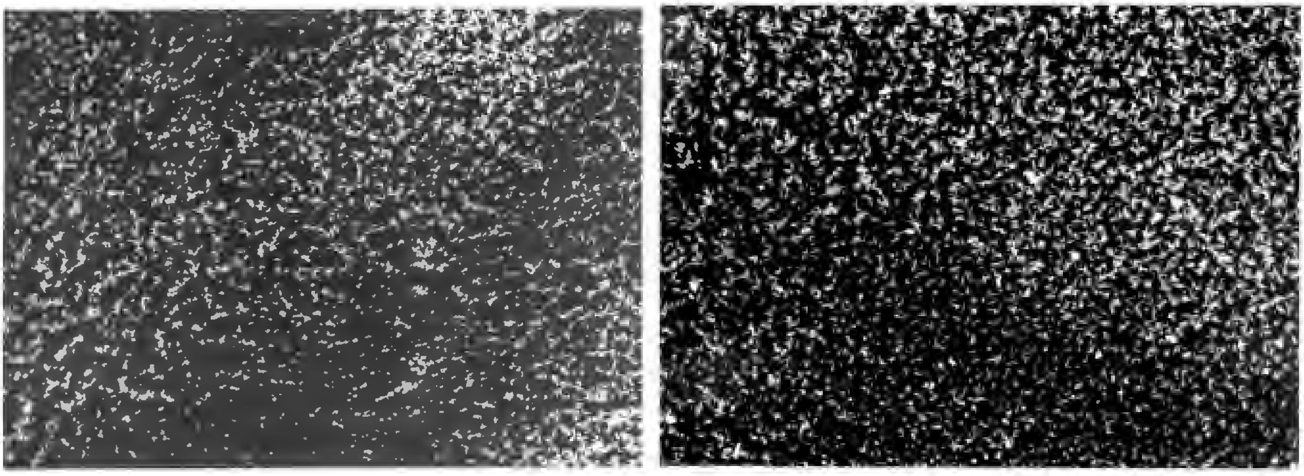
20-APAM 40-APAM

2.0cm

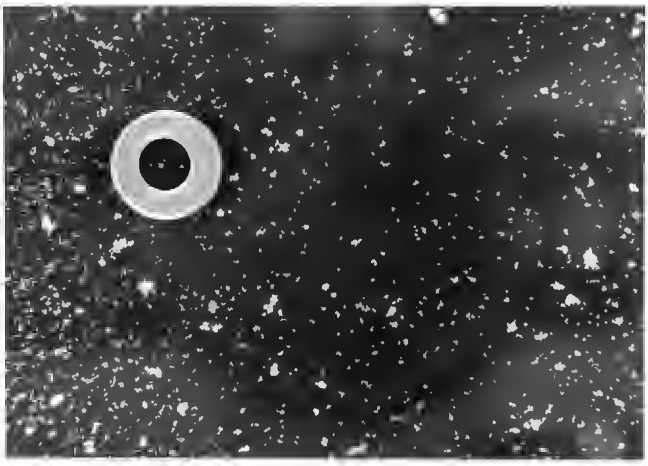
Figure 3.44: H$^+$ kaolin treated with various flocculants. Dosage 1mg/g kaolin.



cationic n-PAM



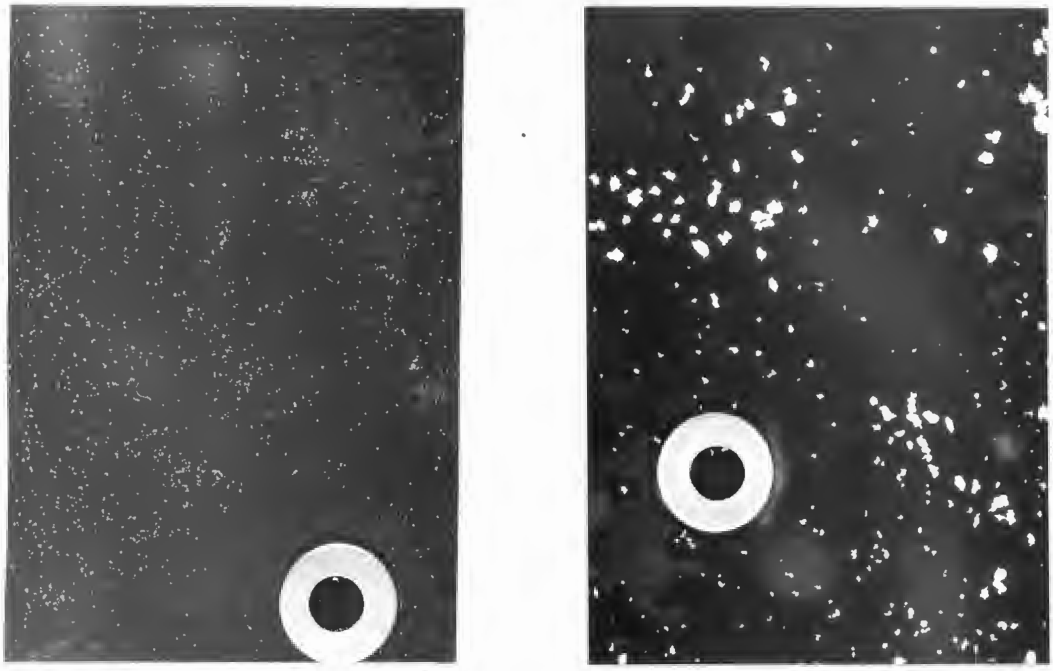
low m. w. 10-APAM 20-APAM



40-APAM

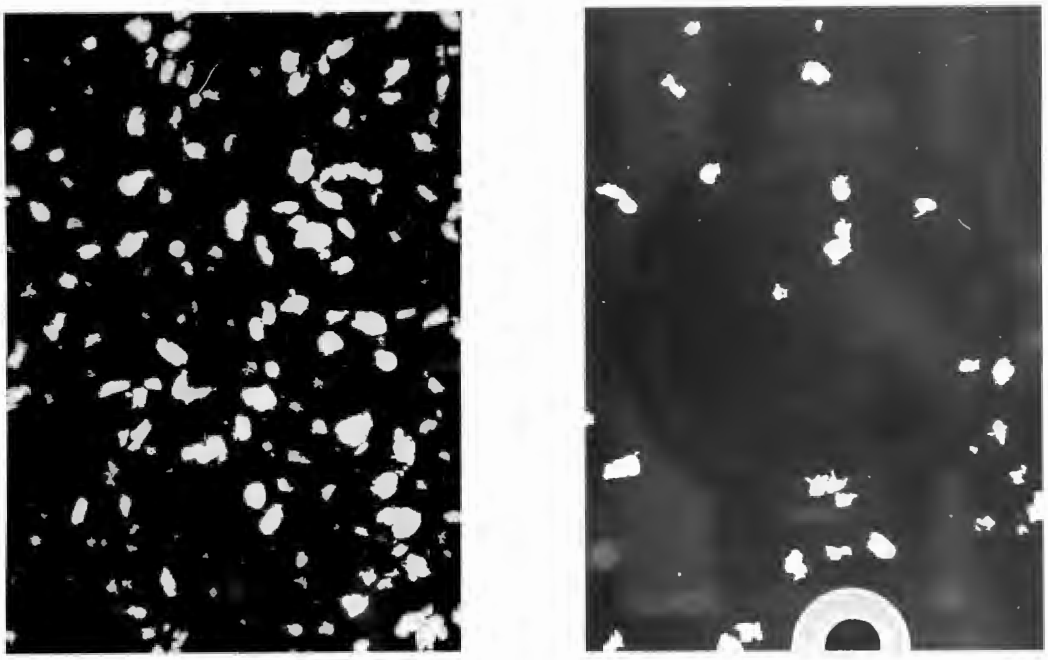
2.0cm

Figure 3.45: Na$^+$ kaolin treated with various flocculants. Dosage 1mg/g.



0.25mg/g kaolin

1mg/g kaolin

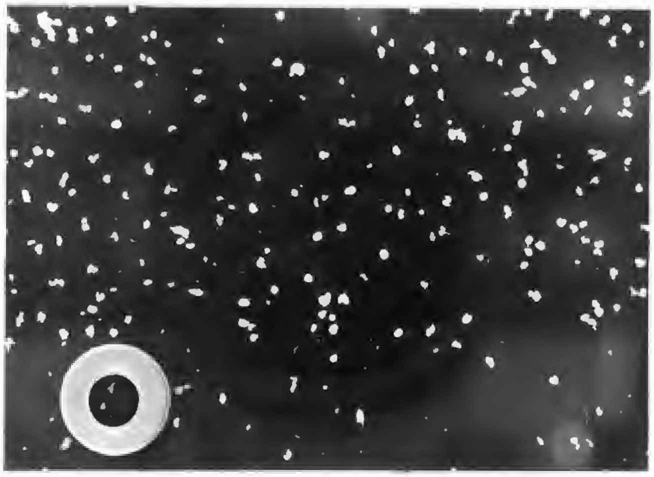


2mg/g kaolin

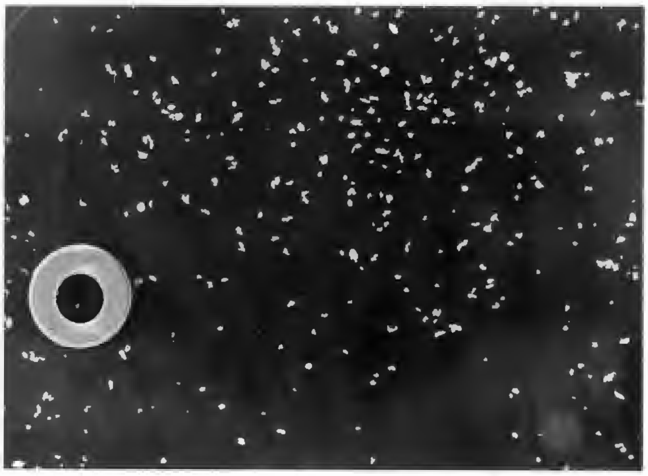
4mg/g kaolin

2.0cm

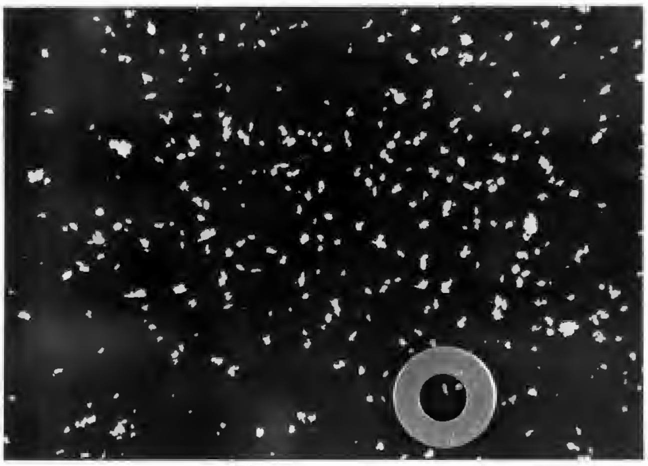
Figure 3.41: Increase in floc size with dosage for Na^+ kaolin treated with n-PAM.



Dosage: 1mg/g kaolin



Dosage: 2mg/g kaolin



Dosage: 4mg/g kaolin

2.0cm

Figure 3.42: H^+ kaolin treated with 40-APAM. The floc sizes in these photographs were shown to be nearly identical by image analysis.

From the appearance of the flocs it is clear that at the natural pH of the Na^+ kaolin only the n-PAM generates stable coherent flocs. All the other flocs appear to be more or less disrupted, with extremely small flocs contributing to larger weak aggregates. This is most easily observed for the 40-APAM.

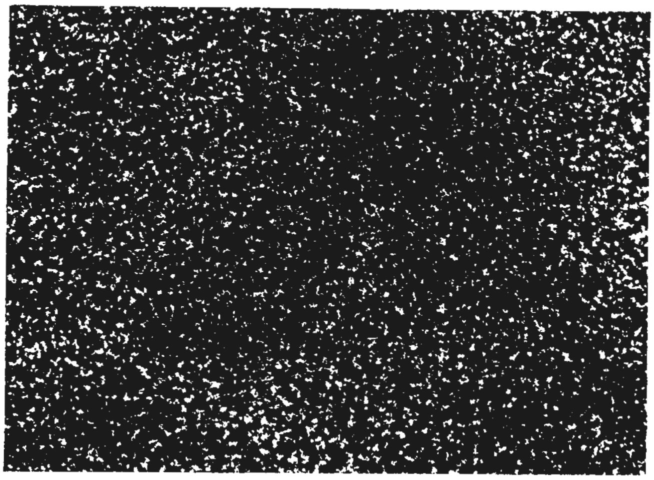
Thus floc sizes appear to be a function of the homoionic form of the kaolin (under natural pH conditions) rather than the flocculant used. Another element of this study is the comparison of the performance of the low m.w. 10-APAM and the 10-APAM. Comparison using Figures 3.43 and 3.44 shows that there is a difference in behaviour between the H^+ and Ca^{2+} kaolins, in that the floc size of the H^+ kaolin treated with 10-APAM is much larger than with the low m.w. 10-APAM, while the difference, though notable, is not nearly as large as for the Ca^{2+}. This distinction is maintained at higher dosages.

The following additional general assessments have been made:

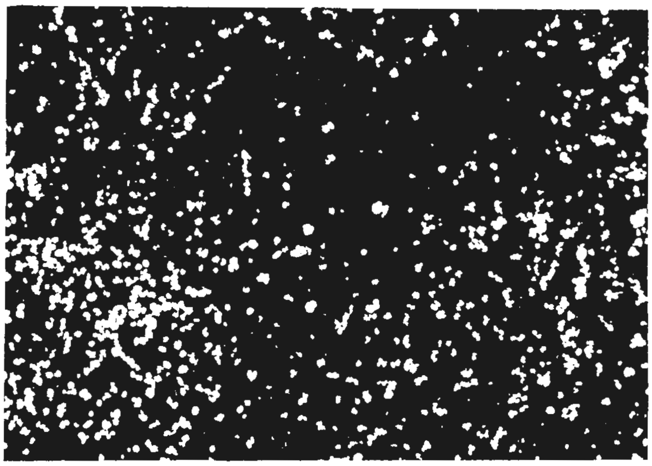
1) The cationic flocculant generates small woolly flocs at all dosages up to 4 mg/g.
2) The general pattern of the floc size development is small "woolly" flocs that undergo the association process described earlier (Chapter 2.1) at low dosages. At higher dosages discrete larger flocs form which associate to a lesser degree.
3) The more pronounced the anionic character of the flocculant the lower the dosage required to form discrete flocs for the Ca^{2+} and H^+ clay. This is clearly demonstrated for the H^+ kaolin (0.5 mg/g dosage) for three flocculants in Figure 3.46. There does also seem to be a general reduction in floc size for the 40-APAM flocculant for these two materials.

Microscopic examination of floc structures also allows useful comparisons to be made. Moreover the type of information, although useful in assessing floc size, also allows a more detailed view of the individual flocs or aggregates of small flocs.

cationic



10-APAM



20-APAM

2.0cm

Figure 3.46: Dosage required to form stable flocs drops with increase in anionic character of the flocculant. H^+ kaolin treated with three flocculants. 20-APAM flocs large at dosage of 0.5mg/g.

The focusing of the microscope proved to be an extremely sensitive variable and optical microscopy therefore was not always as productive as anticipated. In addition the comparatively simple copy board technique resulted in the microscope being used less frequently. The results presented below are intended to show the possibilities of the method rather than provide a basis for exhaustive analysis of results. Figure 3.47 is a series of four micrographs of Na^+ kaolin treated with increasing dosages of n-PAM. The increase in floc size is the most obvious characteristic of these micrographs with the flocs initially being woolly and associative and ultimately being very large discrete entities. It is useful to note that the flocs do not always assume spherical shape.

Figure 3.48 shows Na^+ kaolin treated with 40-APAM at two different flocculant concentrations. At the low concentration the flocs are larger than is the case for the n-PAM treated material but they are still small woolly and associative. The higher dosage results in larger flocs. When compared to the n-PAM 2 mg/g dosage the flocs appear less "dense" and more small flocs appear to be present and not associated with other larger flocs.

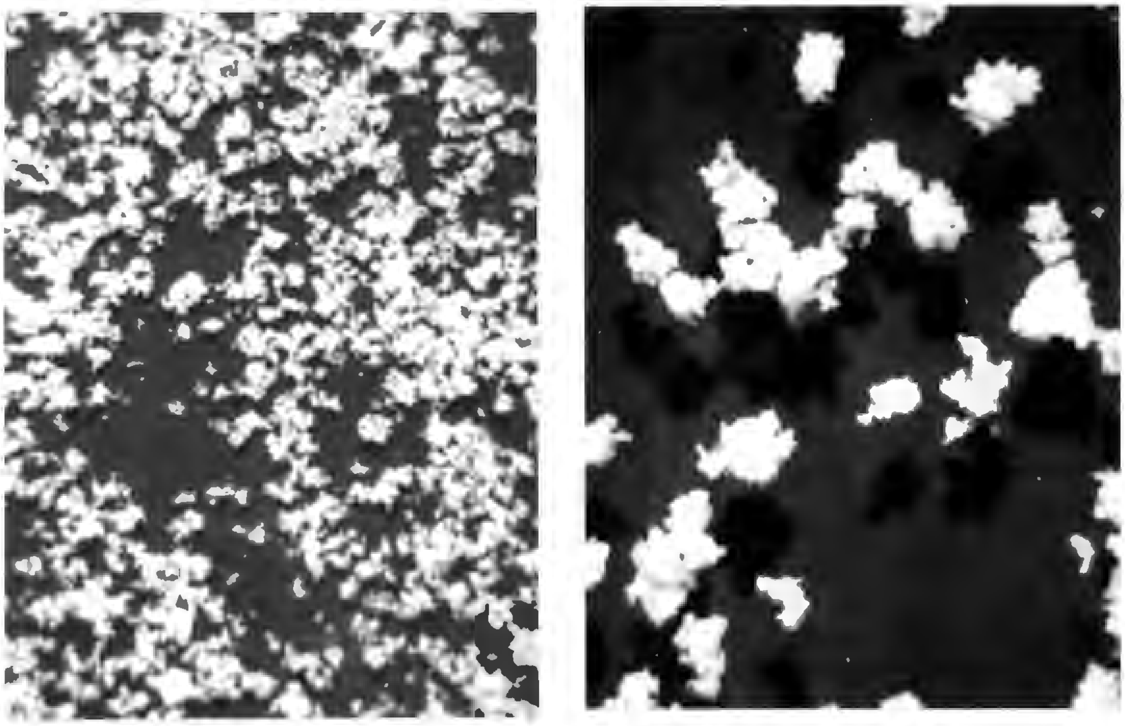
This is a characteristic of Na^+ kaolin treated with 40-APAM and it appears that the flocs are in reality disrupted larger flocs degraded, perhaps, by the process of agitation.

3.3 The Effect of pH Variation on Flocculation

All the previous experiments were conducted at the natural pH of the various homoionic forms of the kaolin. In order to examine the effect of pH on the flocculation parameters and on adsorption it was decided to use the n-PAM and the 40-APAM as flocculants. The pH was varied by the addition of NaOH or HCl one minute before the addition of the flocculant.

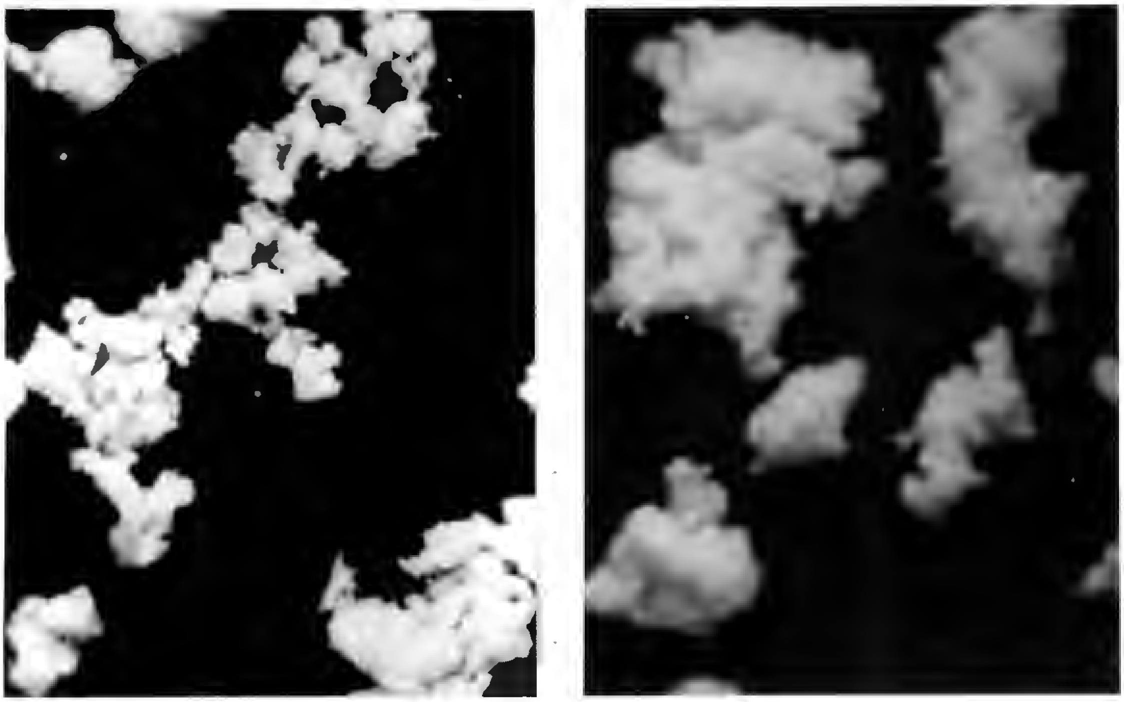
3.3.1 Control Samples

In order to keep a control on the effect of pH on the clay a 50 ml sample was decanted immediately prior to the addition of flocculant and the supernatant turbidity and the settled bed height after 15 minutes were recorded. The flocculated suspension was then treated in exactly the same manner as in the previous experimental procedure. The pH of the untreated control



0.5mg/g kaolin

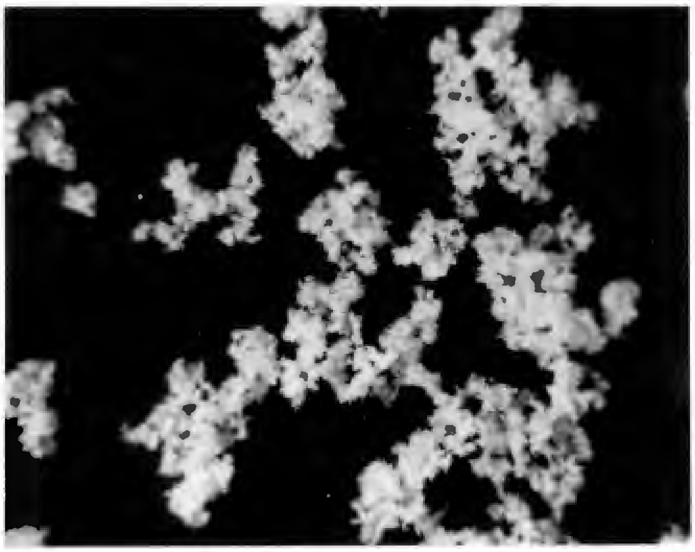
1mg/g kaolin



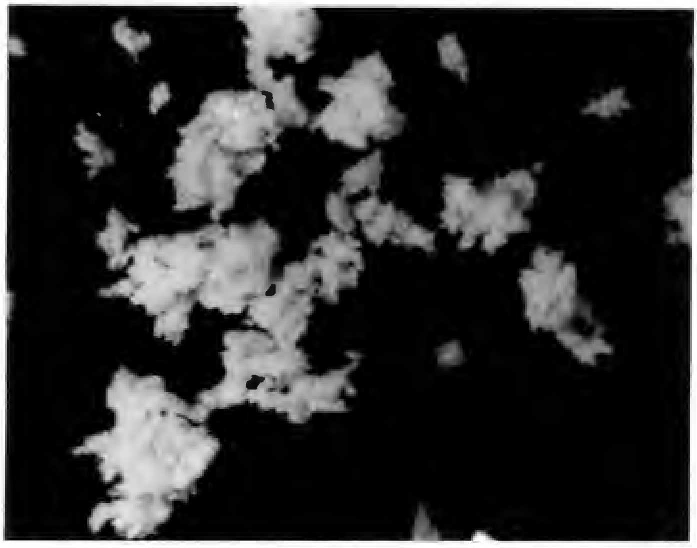
2mg/g kaolin

4mg/g kaolin

Figure 3.47: Micrographs showing increase in floc size of Na^+ kaolin treated with n-PAM with increase in dosage of flocculant.



Dosage: 0.5mg/g kaolin



Dosage: 2mg/g kaolin

2.0mm

Figure 3.48: Na$^+$ kaolin treated with 40-APAM at two different dosages.

and the pH of the treated suspension was measured after 15 minutes. The pH range 3 - 8 was most closely investigated since the addition of acid and alkali in this range did not alter the ionic strength too significantly. Beyond this range the contribution of the change in ionic strength could not be ignored. However with the neutral flocculant and the singly valent homoionic clays this range was extended for higher pH studies. Figure 3.3.1 is the settled bed heights of the untreated kaolins as a function of pH. It will be obvious that the adsorbed cation plays a considerable role (in the case of the Na^+ kaolin) in producing an extremely high settled bed volume at low pH. This exceeds the settled bed volumes of most of the flocculated suspensions generated in this study. The H^+ and Ca^{2+} kaolin, while the bed height is increased at low pH do not have the same marked change as the Na^+ kaolin. At high pH the settled bed volumes are low and similar for the three kaolins. Figure 3.3.2 shows the change in supernatant turbidity for the untreated kaolins as a function of pH. Above pH 7 the H^+ kaolin has a turbidity of >500 JTU after settling for 15 minutes. Above a pH of 6.5 the same is true for the Na^+ kaolin. The supernatant turbidity for the Ca^{2+} kaolin initially increases rapidly and then drops at higher pH to a value of about 170 JTU. This does not occur for the singly valent homoionic kaolins. It is again worth noting the differences in behaviour which can be attributed to the different exchangeable cation on the clay surface. However all the kaolins have a minimum in supernatant turbidity in the range pH 3 - 4.

3.3.2 Flocculant Adsorption

Figures 3.3.3, 3.3.4 and 3.3.5 show the adsorption of flocculant as a function of pH for a flocculant dosage of 2 mg/g of kaolin for the Na^+, H^+ and Ca^{2+} kaolins respectively.

The Na^+ kaolin shows distinctively different adsorption characteristics for the 40-APAM and n-PAM flocculants as a function of pH. The n-PAM is distinguished by a linear portion of decreasing adsorption over the range pH 3 - 8 with an increasing adsorption at higher pH and a decreasing adsorption at lower pH. The 40-APAM is adsorbed least at about pH 5.2 and adsorption increases steeply on both sides of the minimum. The H^+ kaolin exhibits similar adsorption characteristics to the Na^+ kaolin, except that there is

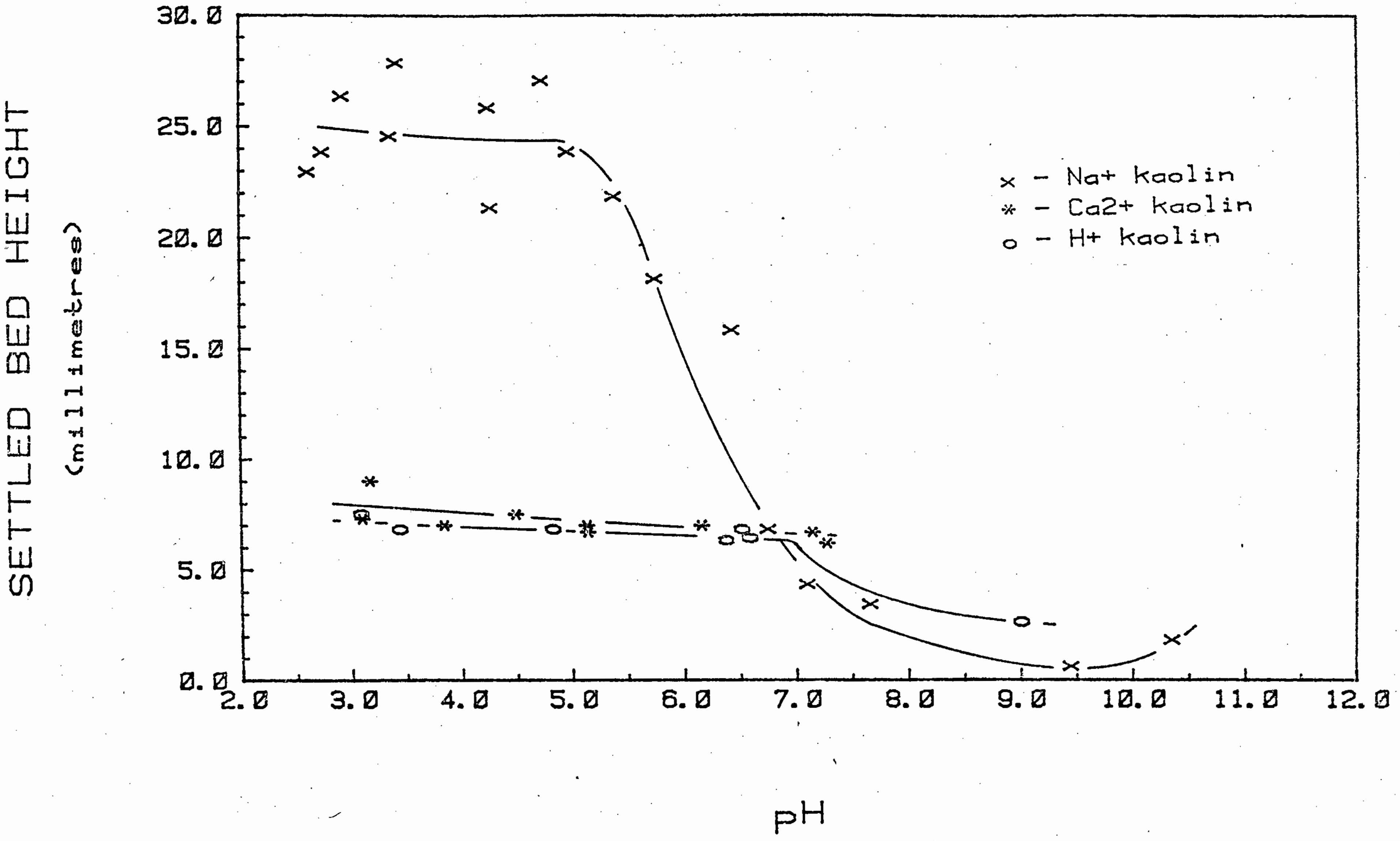


FIGURE 3.3.1

SETTLED BED HEIGHT vs pH for UNTREATED CONTROL SAMPLES

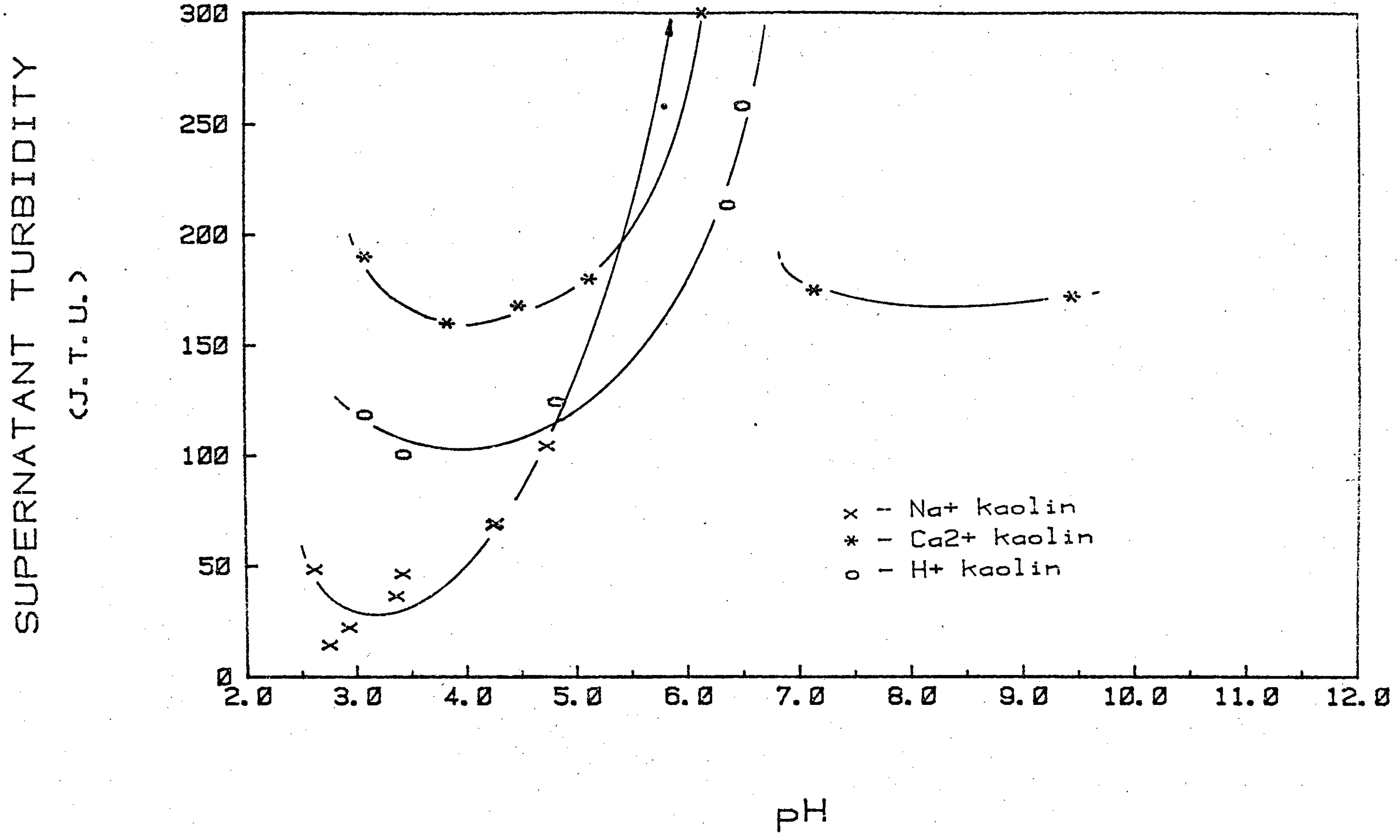


FIGURE 3.3.2

SUPERNATANT TURBIDITY vs pH for UNTREATED CONTROL SAMPLES

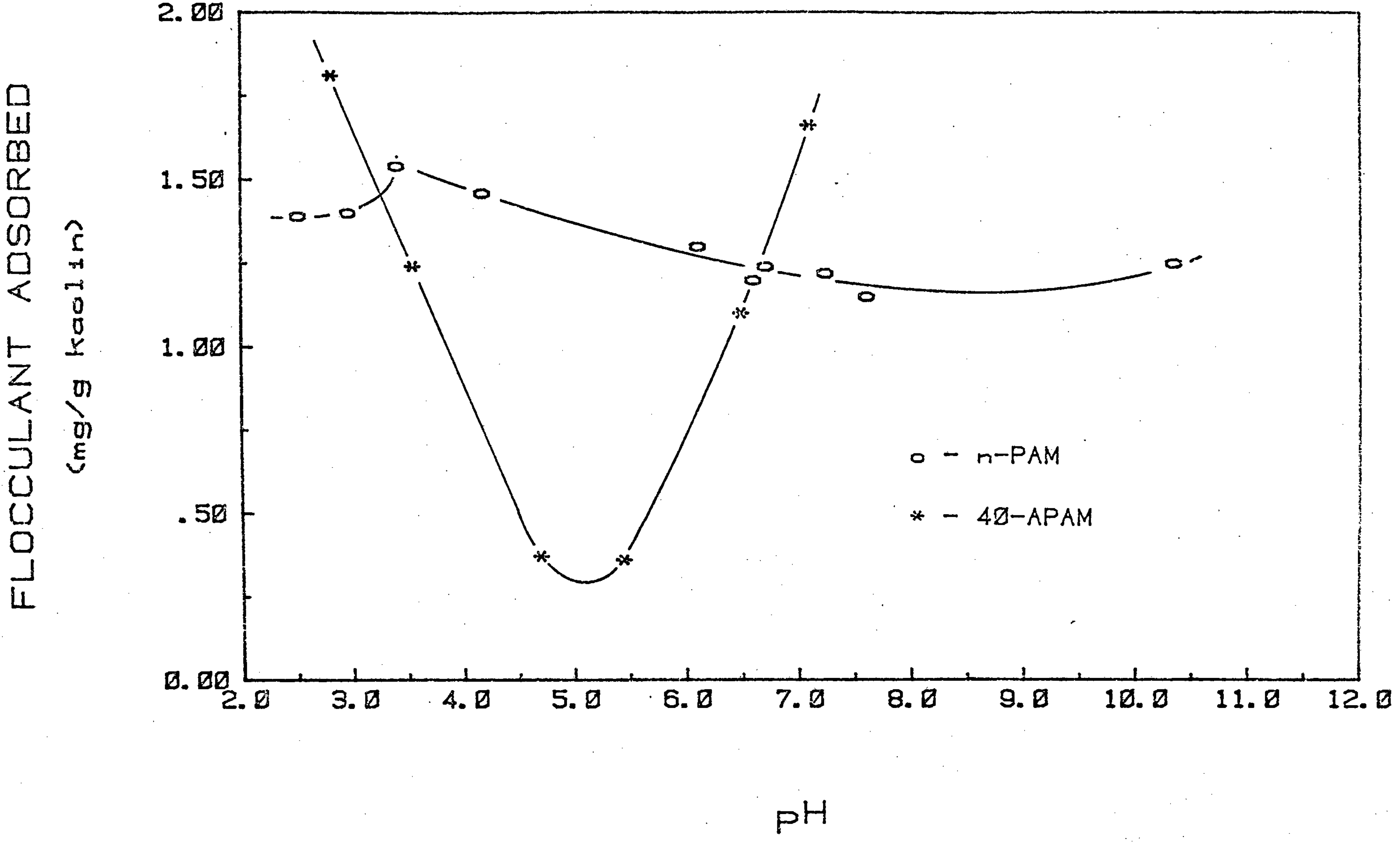


FIGURE 3.3.3

FLOCCULANT ADSORBED vs pH for Na+ KAOLIN

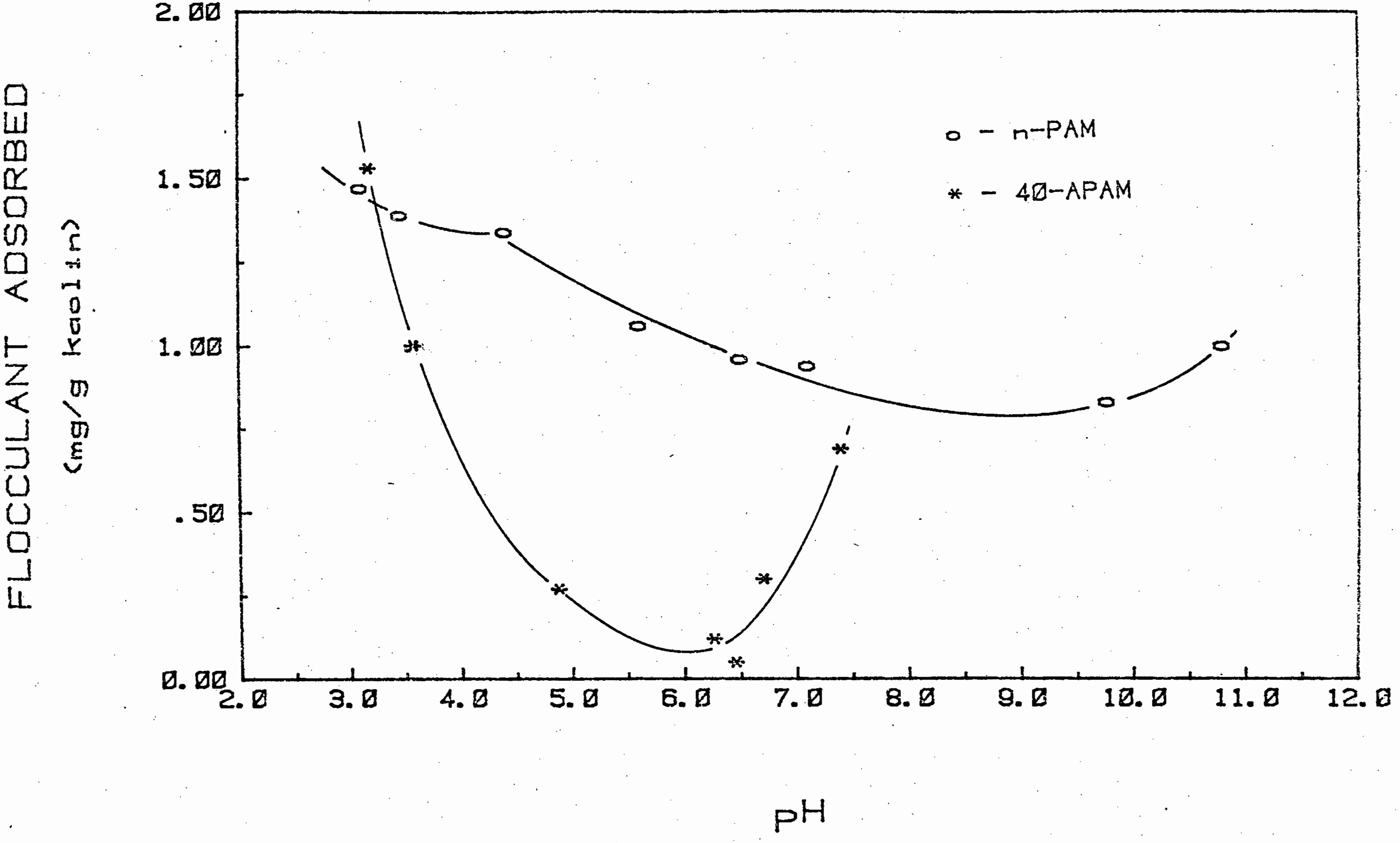


FIGURE 3.3.4

FLOCCULANT ADSORBED vs pH for H+ KAOLIN

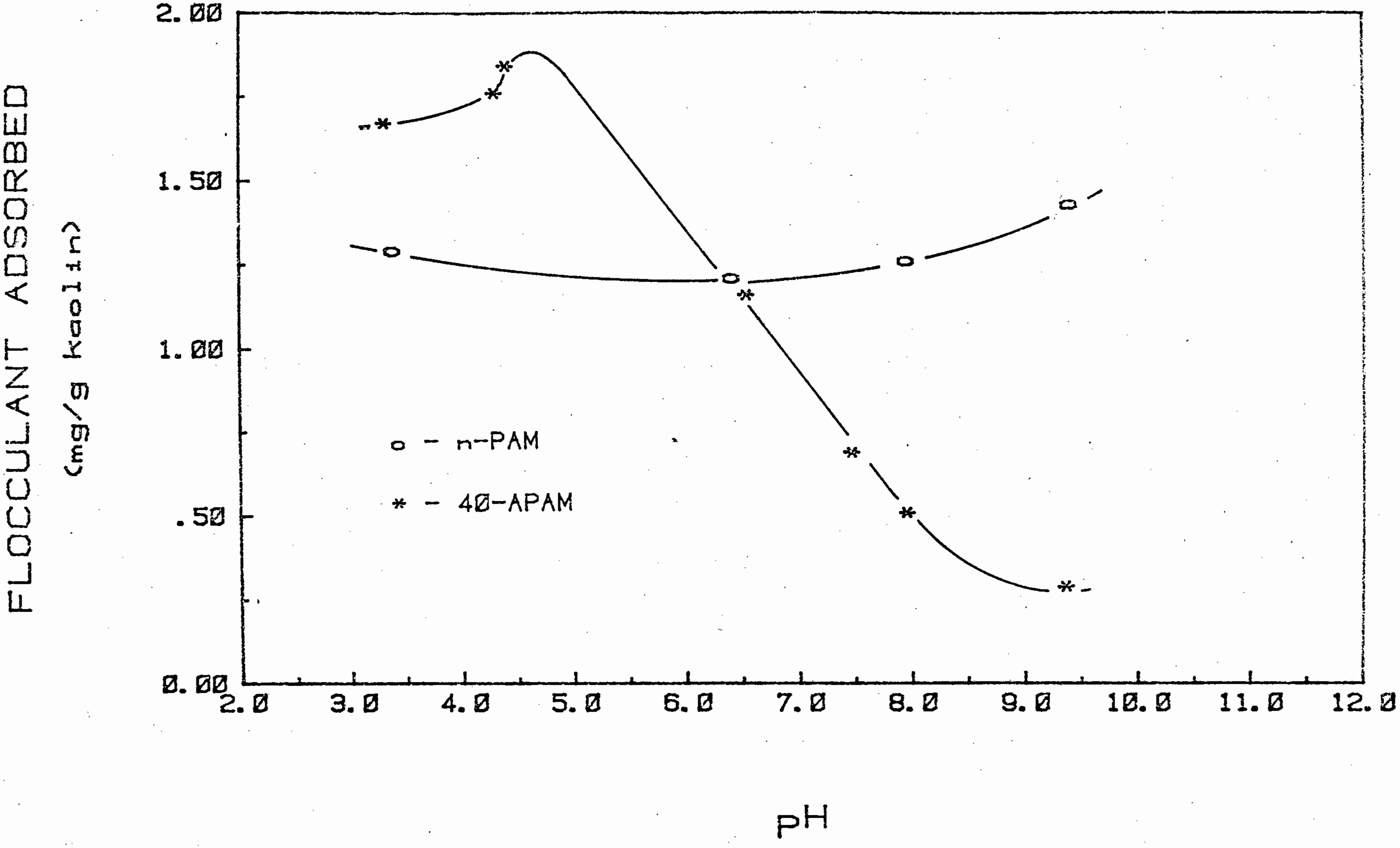


FIGURE 3.3.5

FLOCCULANT ADSORBED vs pH for Ca2+ KAOLIN no drop off in adsorption below pH 3.5 as with the Na^+ kaolin treated with n-PAM. The minimum of the 40-APAM adsorption curve is somewhat lower and at a pH of 6.1. The Ca^{2+} kaolin shows a distinctively different behaviour. The n-PAM does not decrease in adsorption as significantly as with the Na^+ and H^+ kaolins. The 40-APAM adsorption increases initially and then falls off linearly to a low level and then begins to flatten out. No minimum is reached in the region studied. Superposition of figures 3.3.3 and 3.3.4 (Figure 3.3.6) shows the intersection of all four adsorption pH curves for the singly valent homoionic clays at a pH of 3.1. The Ca^{2+} kaolin does not follow this pattern.

3.3.3 Supernatant Turbidity

Figures 3.3.7, 3.3.8 and 3.3.9 show the variation in supernatant turbidity for the Na^+, H^+ and Ca^{2+} kaolin respectively treated with n-PAM and 40-APAM.

There is a small increase in supernatant turbidity with increasing pH for the Na^+ material treated with n-PAM. The 40-APAM however shows a low turbidity at low pH which increases rapidly and is in excess of 500 JTU at pH 6.5. The H^+ kaolin (Figure 3.3.8) follows a practically identical pattern with the increase in turbidity with the 40-APAM being shifted slightly to the right (higher pH). The n-PAM treated Ca^{2+} kaolin (Fig. 3.3.9) is very similar to the H^+ and Na^+ kaolins when the turbidities are compared.

However the Ca^{2+} kaolin when treated with 40-APAM exhibits a region of high turbidity from pH 4 to 6.5 with regions of low turbidity at higher and lower pH's and at pH 9 there is again an increased turbidity.

3.3.4 Settled Bed Height

The settled bed heights vs pH of the kaolins flocculated by n-PAM are presented in Figure 3.3.10. As can be seen there is in each case a decrease in bed height with increase in pH (almost not evident for Ca^{2+}). The bed heights decrease in the order $Na^+ > H^+ > Ca^{2+}$ which is the same as the results in the natural pH studies. The bed heights for the kaolins treated with 40-APAM as a function of pH are presented in Figure 3.3.11. In this

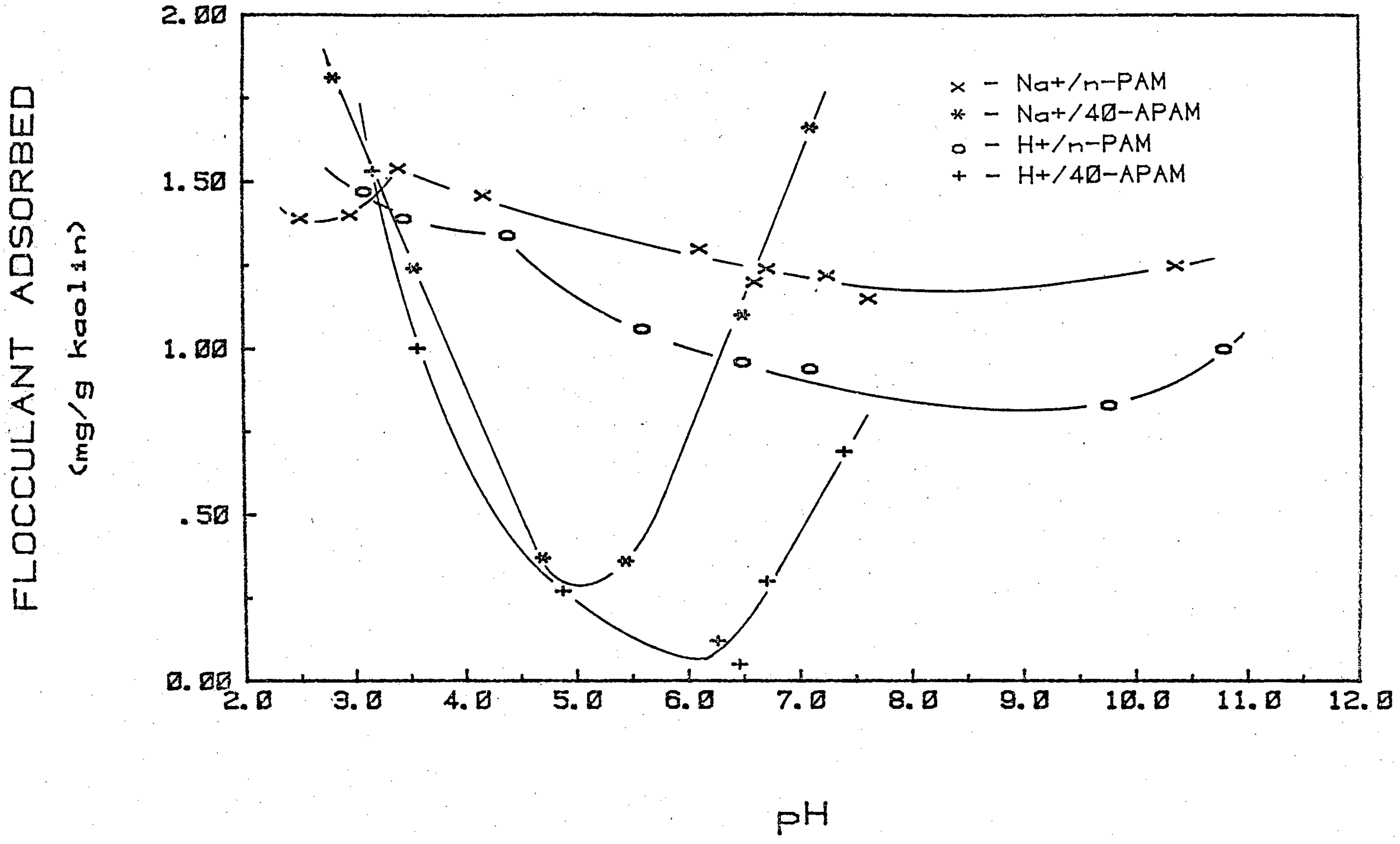


FIGURE 3.3.6

FLOCCULANT ADSORBED vs pH for Na+ and H+ KAOLIN

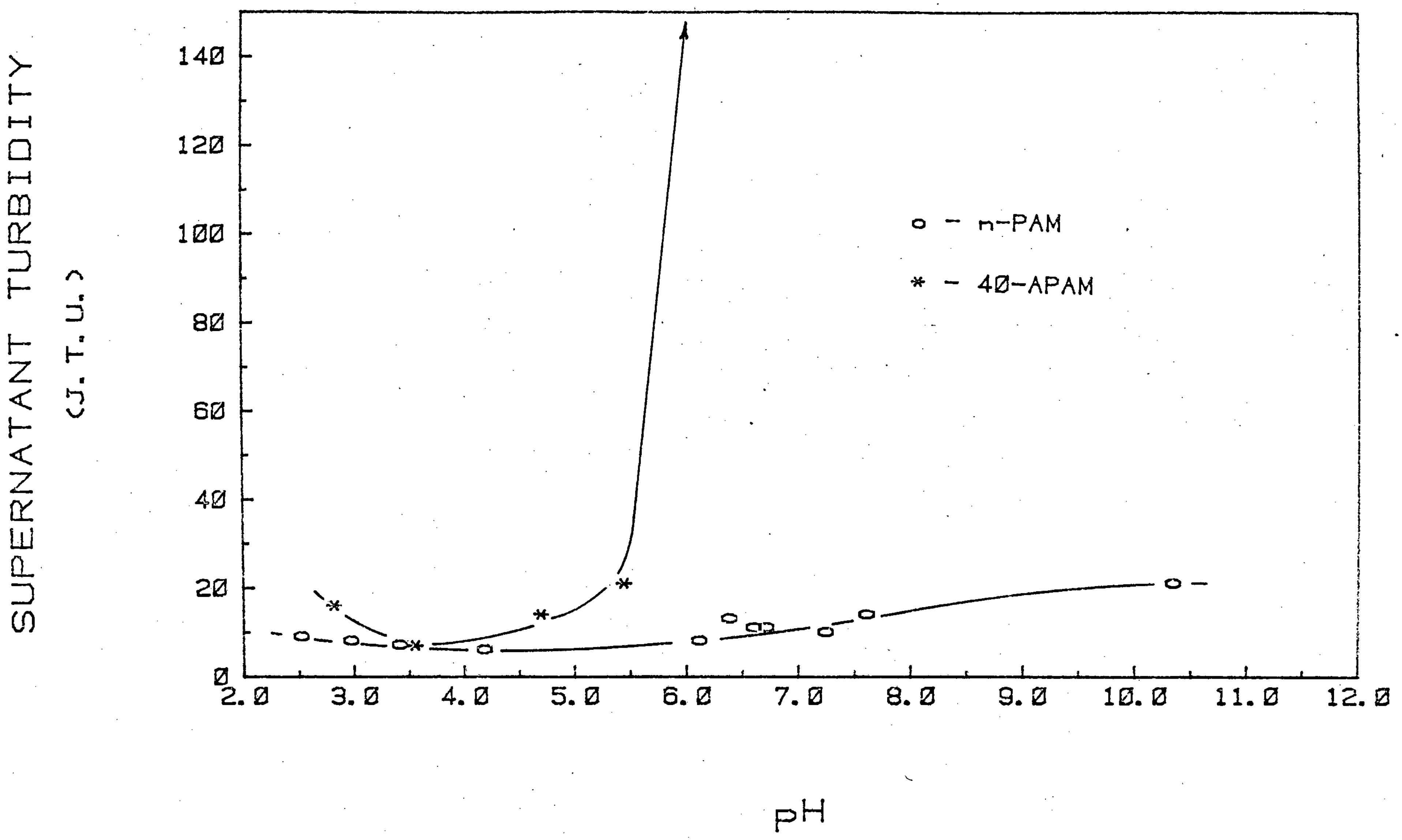


FIGURE 3.3.7

SUPERNATANT TURBIDITY vs pH for Na+ KAOLIN

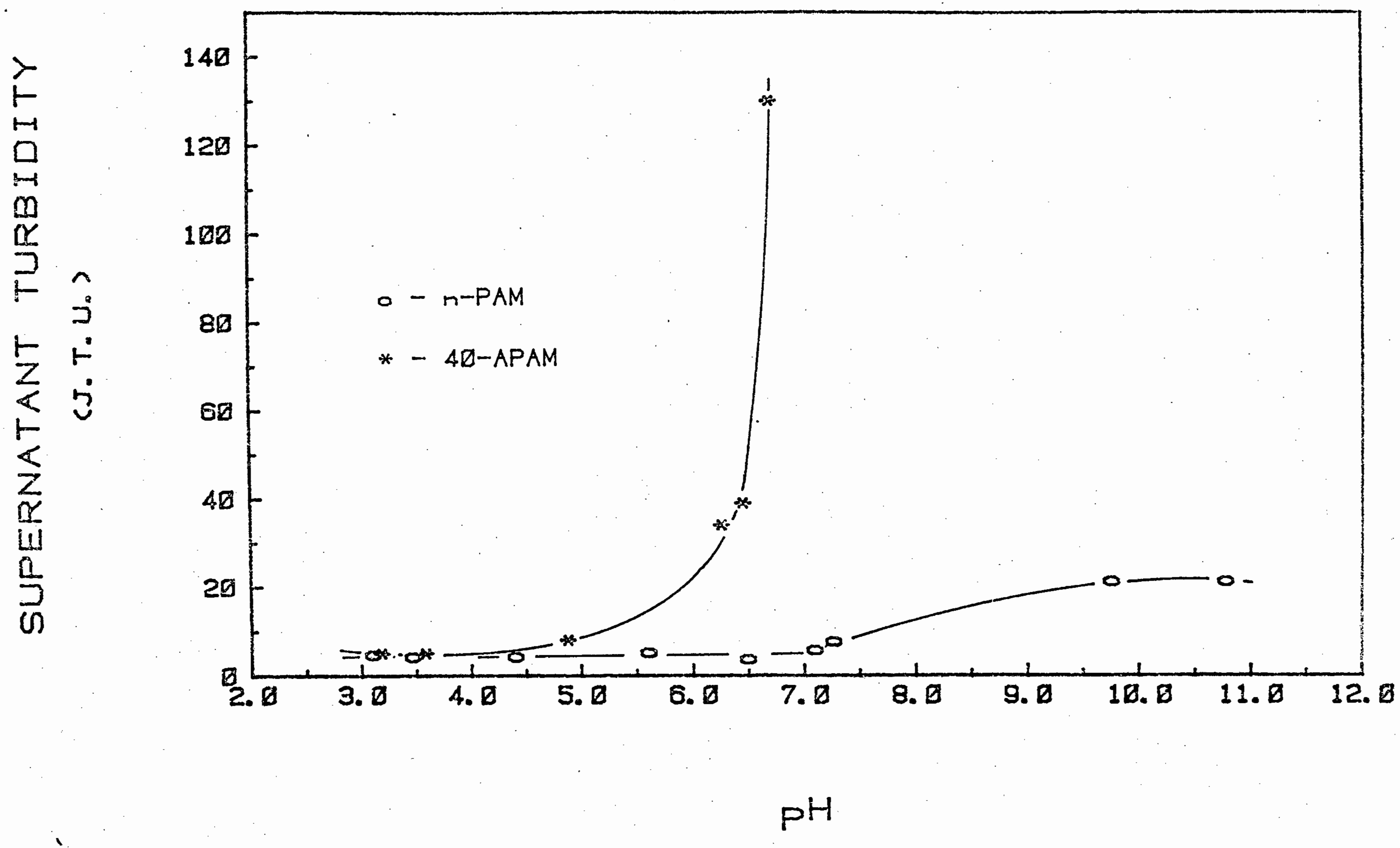


FIGURE 3.3.8

SUPERNATANT TURBIDITY vs pH for H+ KAOLIN

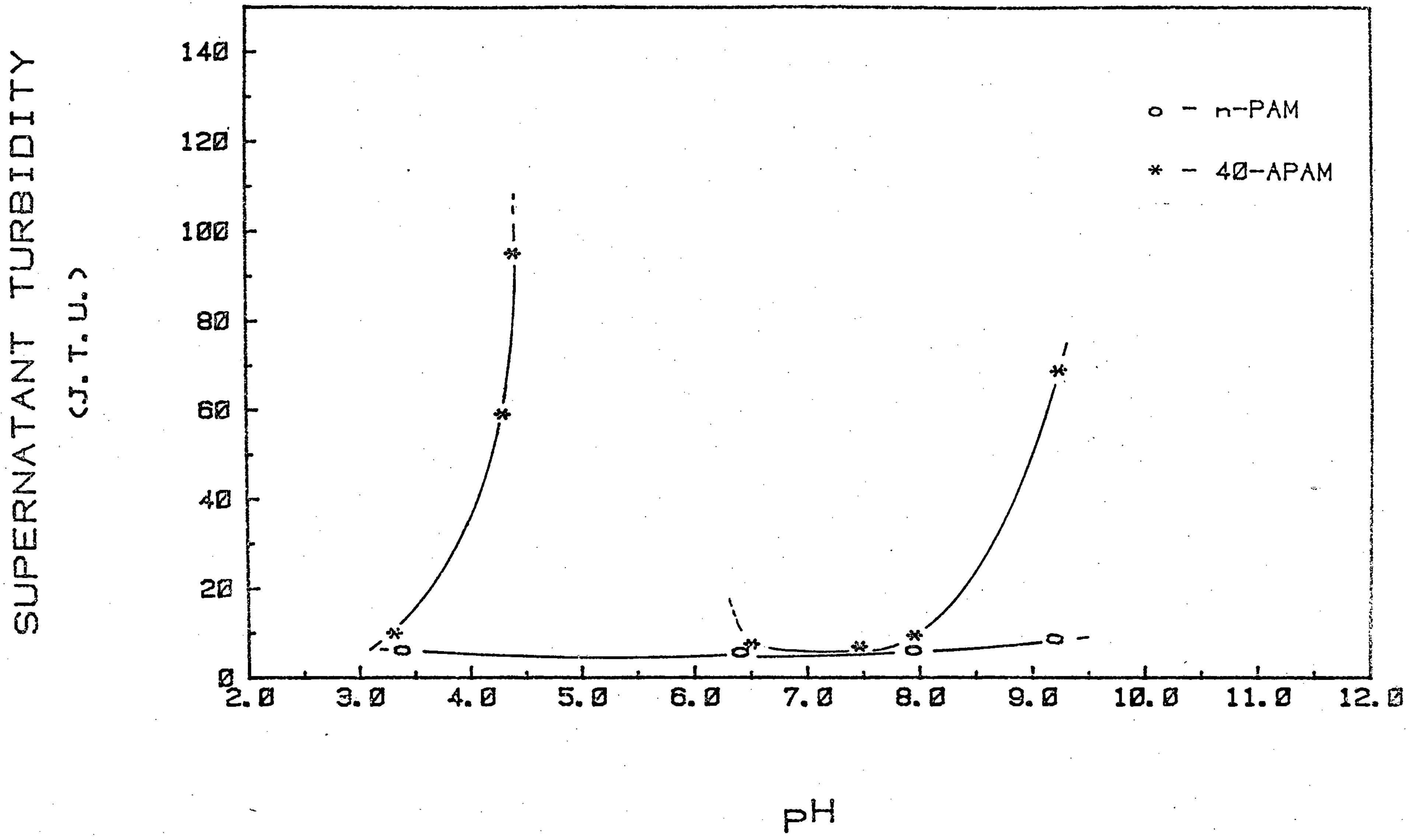


FIGURE 3.3.9

SUPERNATANT TURBIDITY vs pH for Ca^{2+} KAOLIN

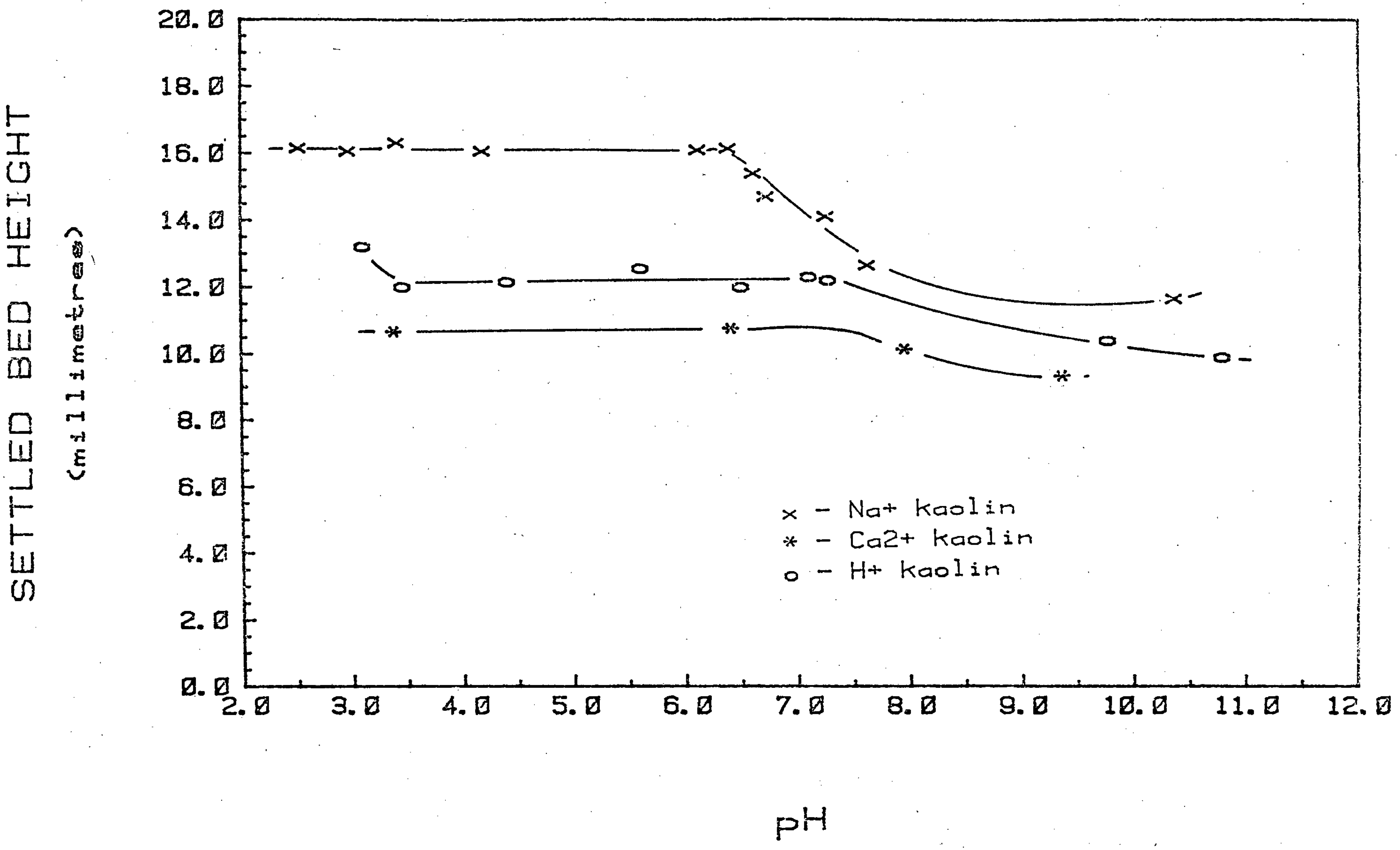


FIGURE 3.3.10

SETTLED BED HEIGHT vs pH for n-PAM

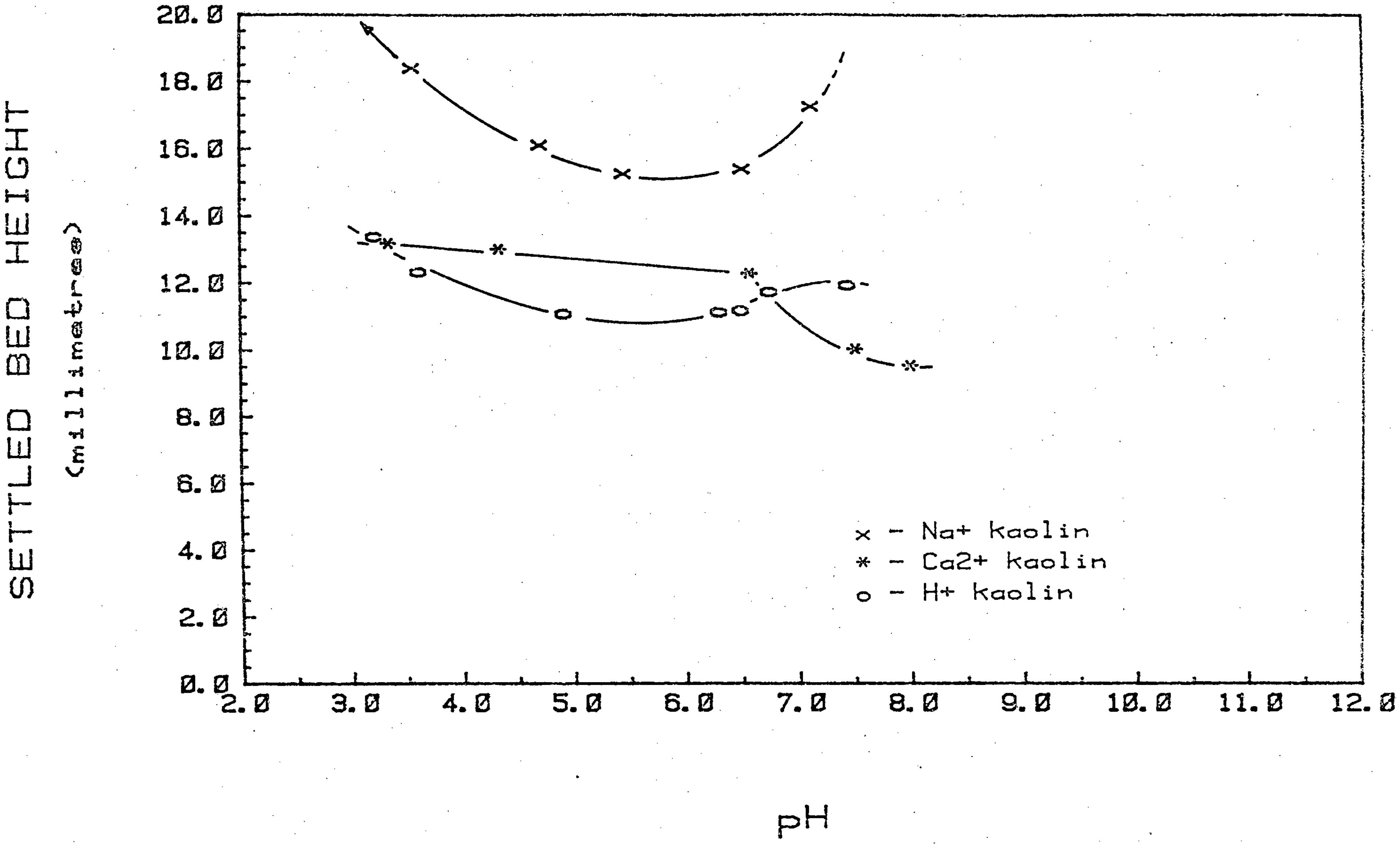


FIGURE 3.3.11

SETTLED BED HEIGHT vs pH for 40-APAM

case the Na^+ and H^+ clays have bowl shaped settled bed height curves with rather higher bed heights at low pH. The Ca^{2+} kaolin treated with 40-APAM has rather similar behaviour to the Na^+ and H^+ kaolin treated with n-PAM with decreasing bed height at higher pH.

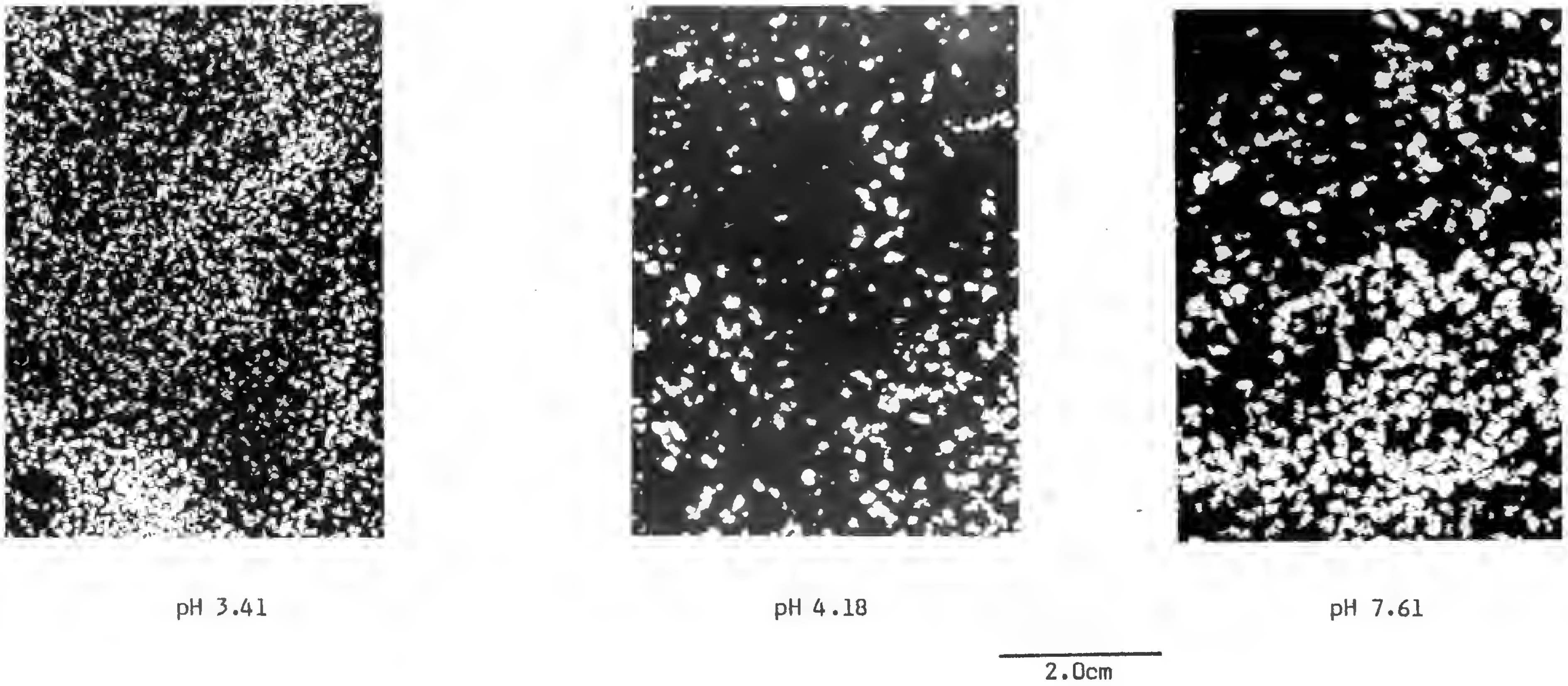
3.3.5 Floc Photography

Floc photography of Na^+ kaolin when treated with n-PAM reveals a progressive increase in floc size with increase in pH. This can be shown from the photographs at pH 7.61, 4.18 and 3.41 (Figure 3.3.12). By contrast the behaviour of the Na^+ kaolin treated with 40-APAM is more complex. At pH 7.1 the flocs are small and woolly and of the associative type. As the pH drops to pH 5.44 the flocs become larger and more coherent (i.e. discrete) but further drop in pH results in smaller flocs as is the case with the n-PAM. Figure 3.3.13 shows this at pH 7.1, 5.45 and 3.6. Note also the generally smaller size of flocs produced with the anionic flocculant on the Na^+ kaolin.

3.4 The Effect of Ionic Strength Variation on Flocculation

If flocculant concentration and pH can be conceived as two different axes along which results of adsorption studies may be projected a very obvious third is ionic strength. In the literature review it was seen that ionic strength modified both the behaviour of the kaolin, through compression of the double layer, and the behaviour of macromolecules where the role of the increased ionic strength is generally in the compression of the macromolecule and in reducing its solubility in some circumstances.

As with the work on the role of pH in adsorption the flocculant dosage chosen for the experiments was 2 mg/g kaolin. The "indifferent" electrolyte chosen was NaCl. It is possible to compute a minimum ionic strength that the clay itself will possess by virtue of its base exchange capacity. This is 3 m.e./100g kaolin (Heckroodt). Thus 1g of kaolin in 100 ml of water will contribute to an ionic strength of about 3×10^{-4} M. This value was chosen as the minimum ionic strength for this study. The pH was con-

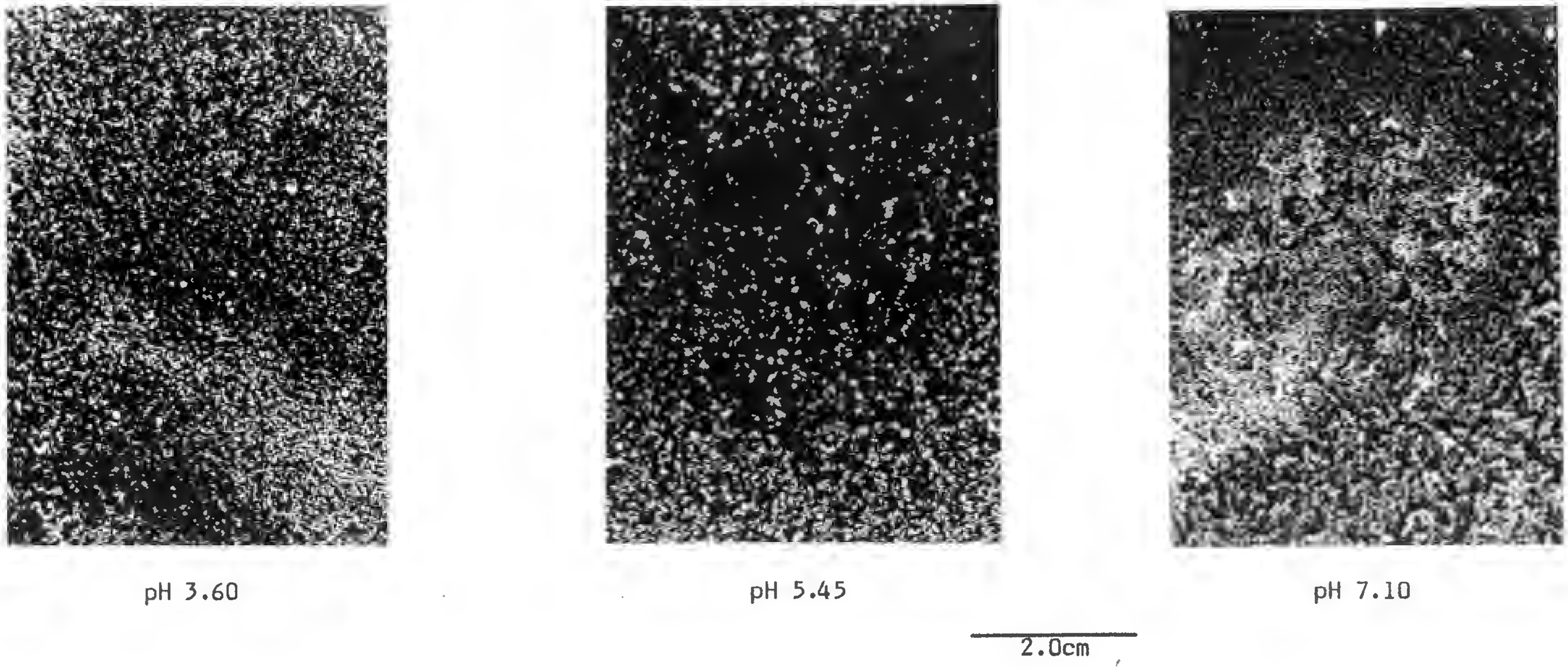


pH 3.41

pH 4.18

pH 7.61

Figure 3.3.12: Variation in floc size with pH for the Na^+ kaolin treated with n-PAM. Dosage 2mg/g.



pH 3.60

pH 5.45

pH 7.10

Figure 3.3.13: Variation in floc size and morphology across the pH range for Na^+ kaolin treated with 40-APAM. Dosage 2mg/g. Note the relatively smaller flocs generated in the presence of the anionic flocculant compared to the nonionic one (Figure 3.3.12).

trolled at 6.5 (± 0.3) for the Na^+ kaolin, 6.0 (± 0.4) for the H^+ kaolin and 7.0 (± 0.2) for the Ca^{2+} kaolin. These values were chosen as they resulted in the lowest additions of HCl and NaOH in order to stabilize the pH at the given level close to neutral pH.

The NaCl was added at the start of the aging stir (15 minutes) in the appropriate amount. The pH was controlled by an addition of HCl or NaOH one minute before the completion of the aging as was the case for the pH experiments. The experimental process followed the same routine as for the pH experiments from the addition of flocculant. The control samples (no flocculant added) showed very consistent bed volumes for the H^+ and Ca^{2+} kaolins, while the Na^+ showed an increase from 3×10^{-4}M to 1×10^{-3}M with a decreasing bed volume at higher ionic strengths. The Na^+ and H^+ kaolins showed the anticipated drop in supernatant turbidity while the Ca^{2+} kaolin showed an increase between 10^{-3} and 5×10^{-3}M.

3.4.1 Flocculant Adsorption, Supernatant Turbidity and Settled Bed Heights

The flocculant adsorption vs ionic strength is shown in Figure 3.4.1 for the n-PAM (H^+ and Na^+ kaolin) and the 40-APAM (H^+, Ca^{2+} and Na^+ kaolin). The similarity in the shape of the curves of the kaolins treated with the n-PAM is remarkable, there is an initial increase followed by a decrease in flocculant adsorption with a maximum at an electrolyte concentration of $5 - 7 \times 10^{-3}$M.

The Ca^{2+} and Na^+ kaolins treated with the 40-APAM are also similar in that they both exhibit a minimum in the range $3 - 5 \times 10^{-3}$M. The H^+ kaolin treated with 40-APAM has a continuously increasing flocculant adsorption across the range of electrolyte concentrations tested. The settled bed heights (Figure 3.4.2) of the various kaolins remain in the familiar order $Na^+ > H^+ > Ca^{2+}$ observed earlier. The Na^+ shows greater deviation which mimics the variation in the untreated bed volume for the 40-APAM though it does not for the n-PAM. The settled bed heights of the H^+ and Ca^{2+} samples are particularly stable as was the case for the pH results. The supernatant turbidities (Figure 3.4.3) follow similar trends to the untreated material for the 40-APAM, except that the minima achieved are lower. The Ca^{2+} shows an increasing supernatant turbidity with electrolyte concentration for the 40-APAM. The turbidities are consistently low for the Na^+ and H^+ kaolins treated with n-PAM.

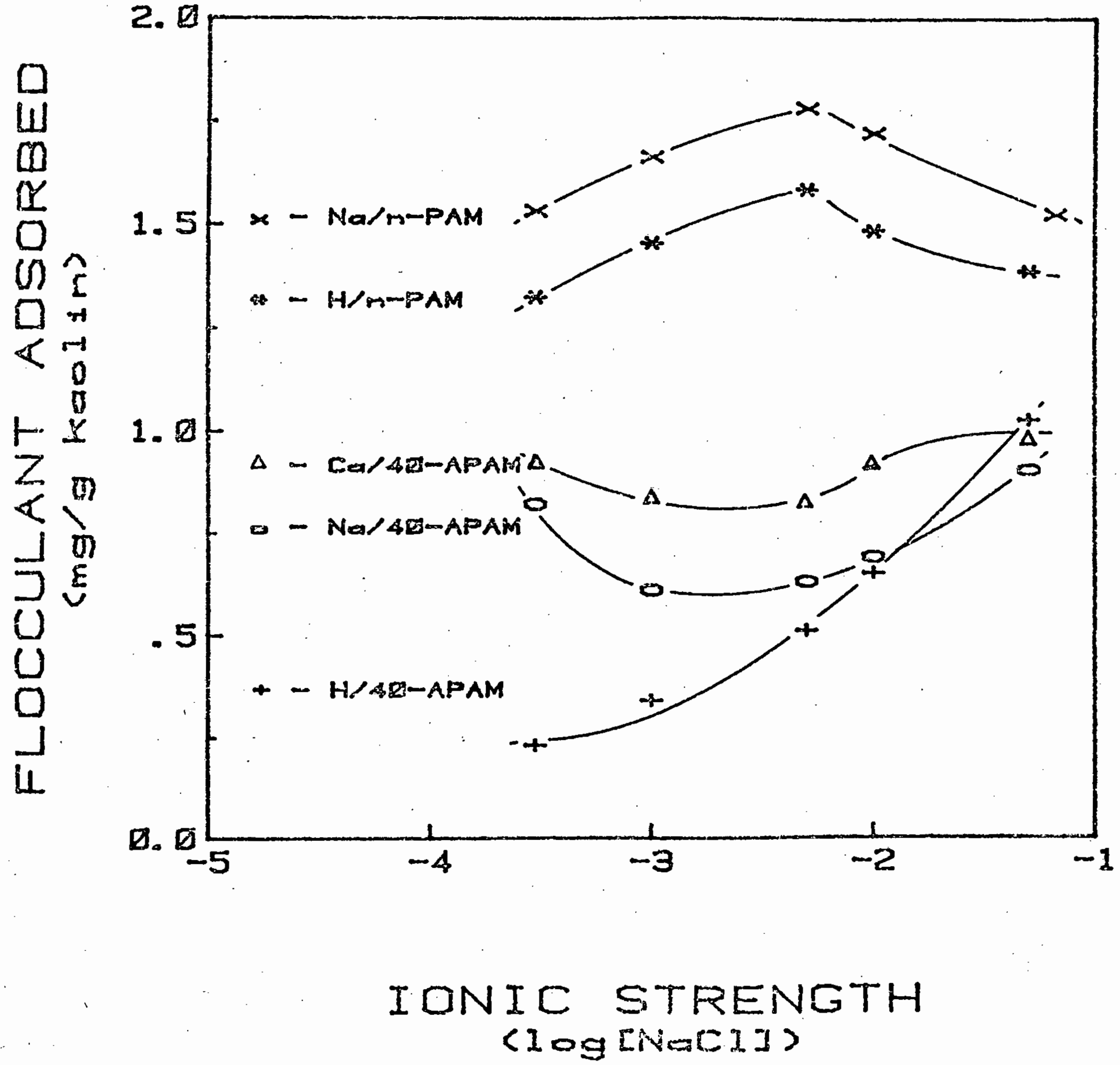


FIGURE 3.4.1

ADSORPTION vs IONIC STRENGTH

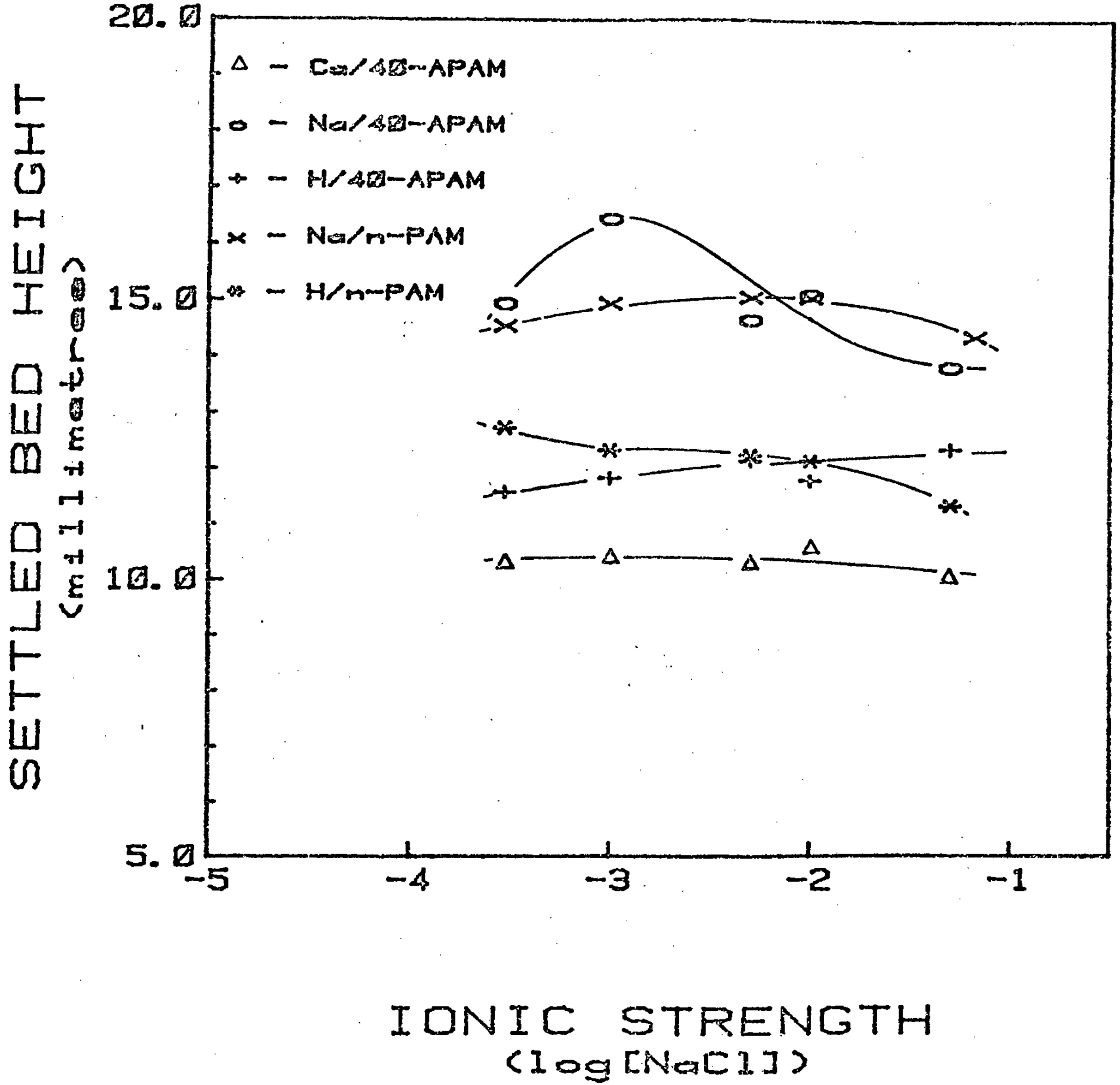


FIGURE 3.4.2

SETTLED BED HEIGHT vs IONIC STRENGTH

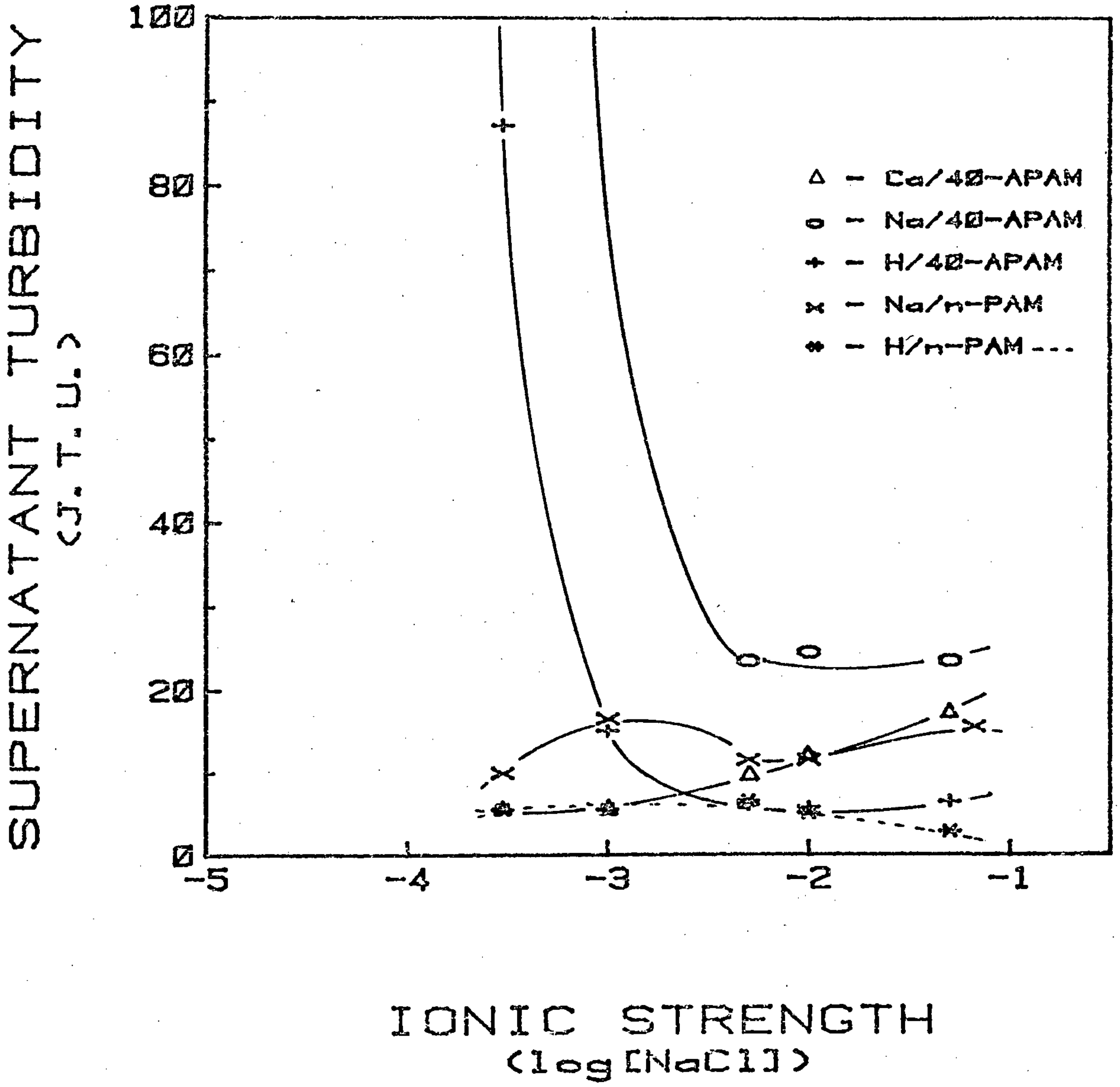


FIGURE 3.4.3

TURBIDITY vs IONIC STRENGTH

3.5 Discussion

3.5.1 Effect of ionic character of flocculant on adsorption and flocculation. Stability under agitation

The development of the experimental method was based on the response to agitation of the nonionic polyacrylamide. Thus it was anticipated that the flocs formed using different flocculants would be of different sizes under the same experimental conditions. The stability of some flocs under the given conditions of agitation, moreover, provides an assessment of their properties when compared with flocs that suffer degradation under the identical conditions of agitation. The method of floc photography used in this study can provide an indication of the stability of flocs generated with different flocculants. At a single dosage, using a range of flocculants, the photographic evidence of floc size suggests that larger flocs are more stable (since they have 'survived' the standard conditions of agitation) than flocs which appear either disrupted or have the form of flocs that are formed in the presence of insufficient flocculant.

This assessment of floc stability or instability decided by floc size criteria provides a basis for the description of how other flocculation parameters are affected by floc breakdown, and the role that flocculant adsorption plays in this process. Combined with this approach is the investigation of the variation of floc density with increase in flocculant concentration. Results from single floc settling experiments facilitated in particular the understanding of settled bed height variations.

3.5.2 Effect of Ionic Character of Flocculant on Adsorption

The characteristics of the adsorption vs flocculant dosage curves have been described. The most notable difference in these results is the behaviour of the Na^+ kaolin when compared with the H^+ and Ca^{2+} kaolins. This is the reduction in the level of flocculant adsorption for the Ca^{2+} and more markedly for the H^+ kaolin with increasing anionic character of the flocculant. This does not occur for the Na^+ kaolin. Floc photography of Na^+ kaolin treated with different flocculants showed that only the n-PAM generated large coherent flocs. This finding is confirmed by the high supernatant turbidities of the Na^+ kaolin treated with the anionic flocculants and the difficulties encountered in measuring the settled bed height of the material treated with the anionic flocculants. These findings indicate that anionic flocculants are extremely ineffective flocculants of Na^+ kaolin at its natural pH. However there is still a marked level of flocculant adsorption of the anionic flocculants, considerably more in fact than is necessary to flocculate the Ca^{2+} and H^+ kaolins. This assessment is further reinforced by the distinctive floc size/density behaviour of the Na^+ kaolin. As has been mentioned, the Na^+ kaolins achieve a maximum density as the dosage of flocculant is increased and higher dosages may result in a decrease in density. This can be shown graphically (Figure 3.5.1) for a floc diameter of 0.3mm. This observation when viewed in conjunction with the floc appearance for the material treated with the anionic flocculants suggests that the limit (and the decrease) in density may be due to floc disruption and resuspension of stabilised material (which is confirmed by the high supernatant turbidities and high levels of flocculant adsorption).

By contrast the flocs formed by the Ca^{2+} and H^+ kaolins and anionic flocculants at their natural pH are extremely stable. The large flocs formed by the H^+ kaolin treated with 20-APAM provide a contrast with the behaviour of the Na^+ kaolin treated with the same flocculant.

A comparison of the variation in floc density at the 0.3 mm floc size for the H^+ kaolin plotted against flocculant dosage (Figure 3.5.2) with the equivalent plot for the Na^+ kaolin (Figure 3.5.1) again reveals this difference. The density of the flocs generated from the H^+ kaolin increase with dosage and the densities of the flocs produced at each dosage also increase with increasing anionic character of the flocculant. Note however that at the lowest dosage in both cases the density of the flocs is nearly identical.

Earlier workers, in particular Linke and Booth; and Black, Birkner and Morgan (1965), found that optimum flocs were produced at the point of the adsorption graph where adsorption was no longer total (i.e. at the knee). The first study was concerned with settling rate and the second with minimum supernatant turbidity. In this study it also appears that there is a

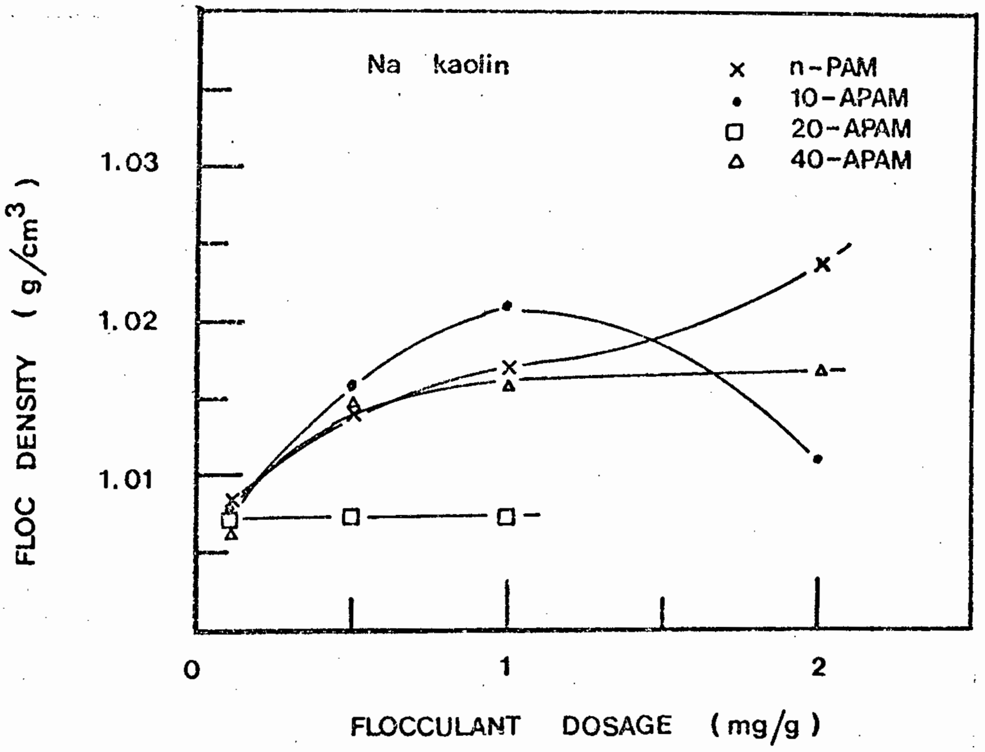


FIGURE 3.5.1: FLOC DENSITY vs FLOCCULANT DOSAGE for Na+ KAOLIN.

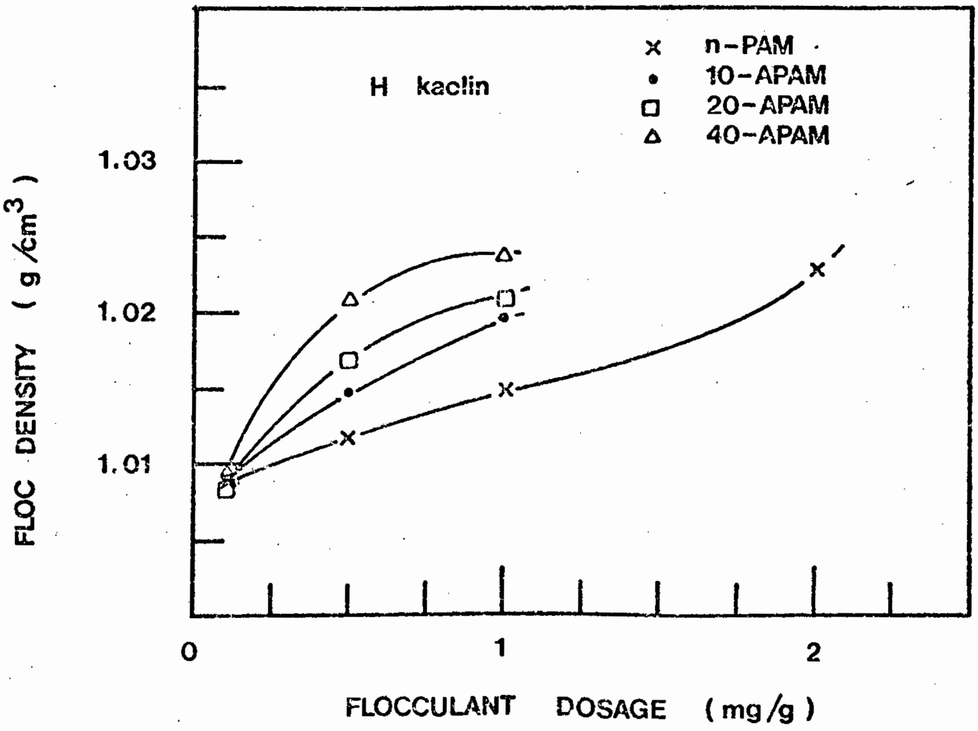


FIGURE 3.5.2: FLOC DENSITY vs FLOCCULANT DOSAGE for H+ KAOLIN.

relationship between the knee in the adsorption vs dosage plots and the maximum in the settled bed height and the minimum in supernatant turbidity. In the case of the H^+ kaolin the higher dosage region of the adsorption vs dosage data there is no increase in adsorption with increase in dosage. Linke and Booth also made the observation that, in the presence of excess flocculant, floc breakdown is facilitated with agitation. This has been confirmed by the results of the experiments on the effect of agitation on floc structure in this study. The level of flocculant adsorption at different dosages therefore provides an indication of the dosage at which coherent flocs are formed, if at all. This is confirmation of the instability of Na^+ kaolin flocs generated with anionic flocculants. The lack of a knee in the adsorption vs dosage data or the characteristic features of the stable adsorption plots (best exemplified by the H^+ kaolin) shows the way adsorption data may reflect the condition of suspensions treated with flocculants. An indication of the instability in a suspension of flocs could be found in the increase in the level of adsorbed flocculant at flocculant dosages above the characteristic knee in the adsorption vs flocculant dosage graphs. In addition the level of adsorption required to form stable flocs can be estimated from the knee. A series of three graphs for the H^+ kaolin (Figure 3.5.3) the Ca^{2+} kaolin (Figure 3.5.4) and the Na^+ kaolin (Figure 3.5.5) indicates how this assessment correlates with the present view that anionic flocculants are extremely inefficient with the Na^+ kaolin. The graphs are of flocculant adsorption at the 1 mg/g and the 4 mg/g dosages of flocculant plotted against the degree of anionic character of the flocculant. The difference between the two levels of adsorption for any one flocculant is an indication of the stability of the flocs (if the difference is small) or the relative instability (if it is large).

Figure 3.5.3 and 3.5.4 show that for the H^+ and Ca^{2+} kaolin the concentration of flocculant seems to affect the level of adsorption to a smaller degree as the anionic character of the flocculant is increased. In addition the level of adsorption itself falls as the anionic character is increased. This is not true for the Na^+ kaolin: the difference between the level of adsorption at the two different dosages remains large and the reduction in adsorption does not occur in the same way.

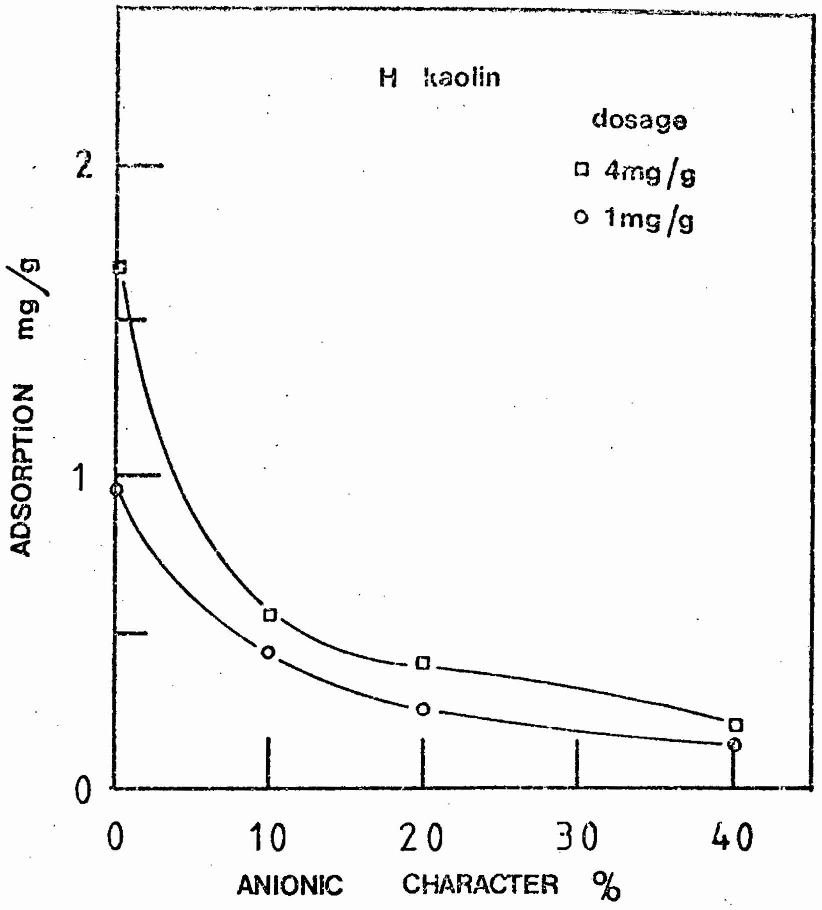


FIGURE 3.5.3: FLOCCULANT ADSORPTION vs ANIONIC CHARACTER for H+ KAOLIN

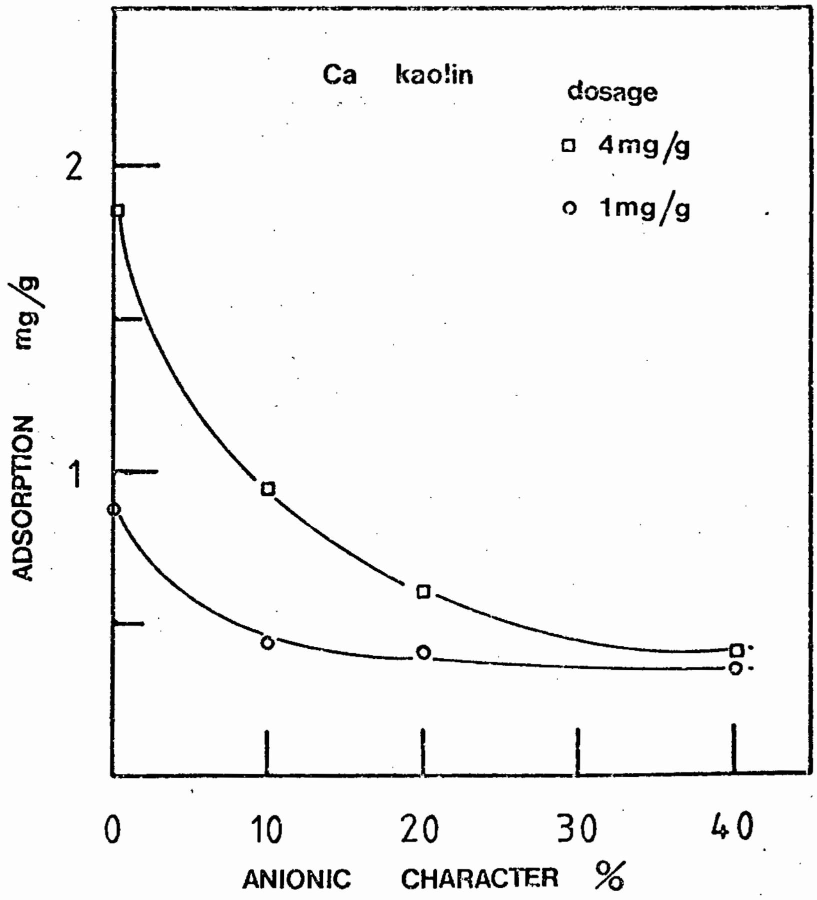


FIGURE 3.5.4: FLOCCULANT ADSORPTION vs ANIONIC CHARACTER for Ca2+ KAOLIN

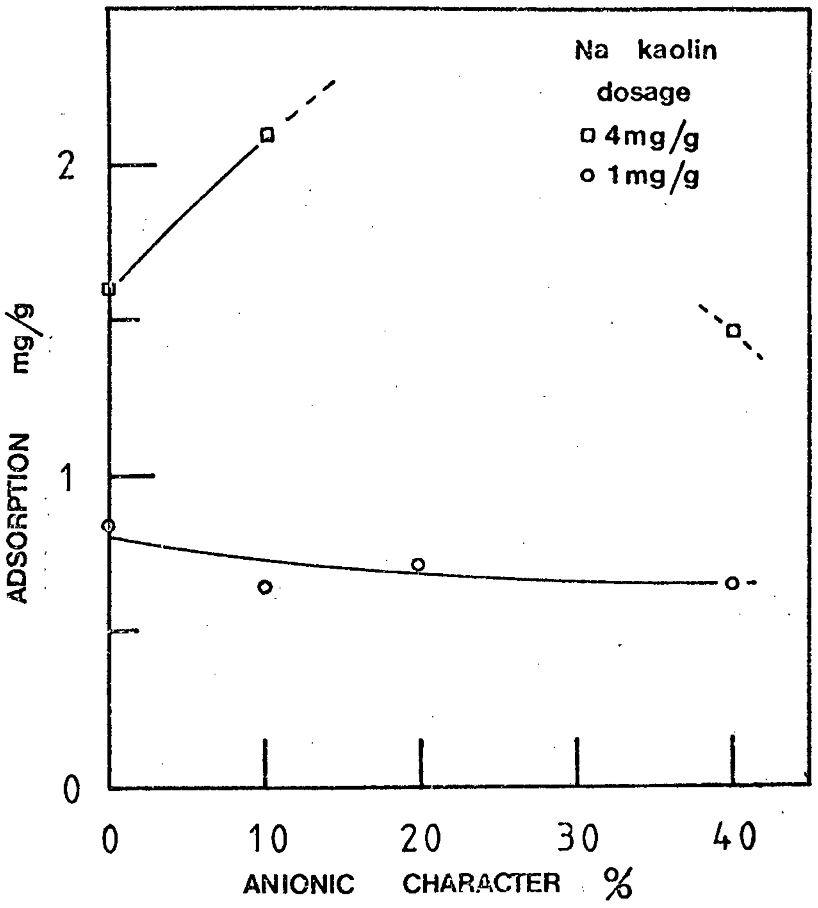


FIGURE 3.5.5: FLOCCULANT ADSORPTION vs ANIONIC CHARACTER for Na+ KAOLIN

3.5.3 The Interaction of Anionic Flocculants with Kaolin

The differences in behaviour discussed above may be in part due to the differences in the natural pH of the three homoionic forms of the kaolin. This will be examined in a subsequent section. However the level of flocculant adsorption is, in the case of the Ca^{2+} and the H^{+} kaolins decreasing substantially with no decrease in the stability of the flocs generated. Indeed, if the criterion for floc stability evaluation is floc size and the dosage at which stable flocs are formed, the increase in anionic character seems to improve the flocculation. This increase in floc stability must be associated with a more efficient bonding on the kaolin surface. This could result from a greater number of adsorbed segments of flocculant or a higher segmental bond energy. The first possibility is extremely unlikely as it would tend to reduce the length of loops extended into the diffuse layer and beyond and would thus inhibit rather than facilitate bridging events. Thus there must be an electrostatic contribution to the bonding. In the case of the H^{+} kaolin this could be the result of adsorption occuring at positively charged edge sites through ionised carboxyl groups on the flocculant. This would in addition cause charge neutralisation of the edges of the kaolin thus effectively reducing edge-edge repulsion between the particles. The lower levels of flocculant adsorption with increasing anionic character can also be attributed to the more extended conformation of the more anionic flocculants at the natural pH of the H^{+} kaolin and their greater charge density facilitating both the process of charge neutralization and effective interparticle bridging. In the case of the Ca^{2+} kaolin the higher pH makes it unlikely that many positive edge charges are available (otherwise the same mechanism could be suggested for the Na^{+} kaolin and this does not occur) and therefore it is necessary to postulate that the more effective bridging mechanism is related to the presence of the divalent Ca ion. The most likely mechanism of action is through the formation of electrostatic bonds between the surface and the flocculant (both negatively charged) by the formation of an ionic bridge. This role has been suggested for the Ca^{2+} ion by other researchers (van Lierde; Black 1960).

3.5.4 Effects of Agitation on Adsorption

In the case of the Na^+ kaolin there is no possibility of ionic bridging and there are few or no edge positive charges for electrostatic bond formation. Thus at this high pH the most efficient bonding would be hydrogen bonding, since both the kaolin and the anionic polyelectrolytes are highly negatively charged. However the level of adsorption is high. This is a result of the agitation of the suspension causing floc disruption. In the case of the Na^+ kaolin the weak bonds formed on addition of the extended, rigid polyelectrolyte are easily disrupted and thus flocs formed in the first moments of flocculant addition are broken down by agitation. This will not occur, of course, with the nonionic flocculant. Since new surfaces are exposed by the disruption process and an excess of flocculant is present more is adsorbed. However as more flocculant is adsorbed on newly exposed mineral surfaces the possibility of new efficient bridging events is reduced.

By contrast both the H^+ kaolin and the Ca^{2+} kaolin initially form stronger more enduring bonds since they have a marked electrostatic component. Thus the process of disruption and excess flocculant adsorption does not occur. The progressively lower levels of adsorption with increasing anionic character results from a combination of increased bridging efficiency, as a result of greater molecular volume (due to repulsion between the ionised acrylate groups on the polymer) and a bonding type that results in the formation of strong bonds on the surface that are not disrupted during agitation (which also suggests charge neutralization in the case of the H^+ kaolin). Flocculation in the presence of excess flocculant requires enduring bridges between particles that, by their manner of formation, specifically exclude certain regions of the mineral surface from polymer adsorption. This results in closed, convoluted particle-polymer arrangements called flocs. Levels of flocculant dosage that result in the adsorption of the bulk of the flocculant result in flocs that are smaller and more diffuse. It has been noted that the small flocs, when not agitated, form loose aggregates. These aggregates are easily disrupted on stirring. The above description of the flocculation process suggests that the small flocs are the stable unit under the dynamic conditions of agitation but that there remain exposed areas of mineral surface available for adsorption.

Extended polymer loops can undergo temporary association with other surfaces when agitation is stopped. This suggests that for each flocculant there will be a concentration of the flocculant which, under given conditions of agitation, will result in the formation of large stable flocs. In the case of the H^+ and Ca^{2+} kaolins photographic evidence showed that the more anionic flocculants formed large discrete flocs at lower dosages than the neutral or cationic types. This is further confirmed by the evidence of the settled bed heights.

3.5.5. Settled Bed Height

The characteristic form of the settled bed height vs dosage data is an increasing bed height to a peak with a subsequent decrease to a plateau level. The low bed heights at low dosages in all cases represent higher bed heights than those of the untreated control samples. This suggests the development of a structure in the kaolin suspension. The maximum in bed height represents the point at which flocs become discrete incompressible units under conditions of settling. Below this dosage the flocs are known to be less dense from single floc settling experiments, (suggesting a higher settled bed volume) but they have lower bed heights because they are compressible. Above the dosage at which the flocs have a maximum in settled bed volume the floc density is still increasing and this results in a reduction in settled bed height. In the case of the Ca^{2+} and H^+ kaolins a distinctive pattern of behaviour is observed as the anionic character of the flocculant is increased in that the peak in the settled bed height occurs at lower flocculant dosages and is also narrower. This mimics the reduced levels of adsorption required to produce coherent flocs. This suggests the density increases in the case of the H^+ and the Ca^{2+} kaolin more rapidly as the degree of anionic character of the flocculant is increased. This is evident from the graph of settled bed height for the H^+ kaolin vs flocculant dosage presented here in a slightly different form (Figure 3.5.6). The initial rise in settled bed height is not indicated but only the drop in settled bed height with increase in flocculant dosage is shown. It can be seen that the most anionic flocculant shows both the most rapid decrease in bed height and the lowest bed height and that the trend for the other flocculants is in decreasing order of anionic character. If this diagram is compared to Figure 3.5.2 which is from data for the single floc

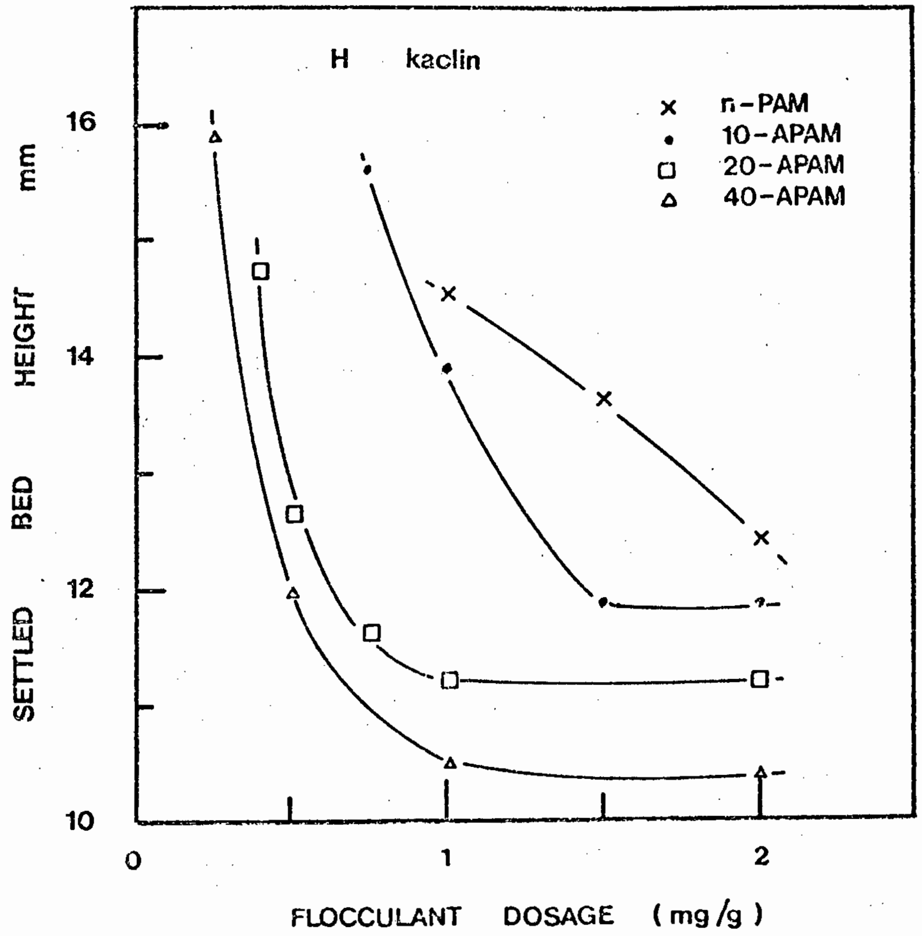


FIGURE 3.5.6: BED HEIGHT vs FLOCCULANT DOSAGE for H+ KAOLIN.

settling (floc size-density) experiments, it can be seen that the inverse relationship is followed for the floc density with dosage of flocculant over the same range. This provides an independant measurement of this phenomenon and confirms the explanation given above, based on an understanding of variations in floc density with increase in flocculant dosage. It is notable that the trend of these settled bed results follows the pattern of results observed by Dollimore and Horridge (1972), although a general characteristic of the results in that study was an increase in settled bed volume after the minimum (at which the sedimentation rate was a maximum). This may be due to the higher solids concentration used in that study. The present explanation of the settled bed data, relating it to the increase in density and coherence of the flocs is entirely consistent with the results of Dollimore and Horridge (1972). The increase in floc density may reach a limit at higher dosages of flocculant or alternatively the excess flocculant levels are so high that they contribute to the disruption of the floc structure.

3.5.6. Supernatant Turbidity

Examination of the supernatant turbidity results confirms the description of the processes by which the settled bed heights change with flocculant dosage. Below the dosages where significant excess flocculant is present the supernatant turbidity is high. It then drops to a plateau or to a minimum followed by a subsequent increase in turbidity. Before coherent flocs are formed (i.e. below the maximum in settled bed height) small flocs and unflocculated material contribute to the supernatant turbidity. At dosages just beyond the point where incompressible coherent flocs are formed excess flocculant appears in the supernatant. Thus no kaolin escapes interaction with flocculant and most material is incorporated into flocs, the result being a minimum in supernatant turbidity. Where this low level of turbidity persists it is clear that these processes are still efficient. However where there is an increase in supernatant turbidity with increase in dosage some other process must begin to operate. Results show that this occurs as the anionic character of the flocculant is increased. The increased turbidity may result in the case of the H^+ and Ca^{2+} kaolins, from stronger bonding taking place. Very fine particles could interact with a single or a number of flocculant molecules in such a way as to be stabilised in suspension before a successful bridging event takes place. The higher the flocculant concentration the more likely such events become, resulting in an increasing number of stabilised particles. Since the more anionic the flocculant the higher it's viscosity, it is likely that part of the increased turbidity is due to the lower settling rates that result from this increase.

It is noted that there is a progressive decrease in the dosage at which the minimum in supernatant turbidity is found as the anionic character of the flocculant is increased for the H^+ and Ca^{2+} kaolins. The dosage at which the minimum is achieved moves to lower dosages and this indicates that there is a relationship of the turbidity minimum to the settled bed peak and also to the knee in the adsorption vs dosage graphs for these two kaolins. It serves to confirm the increased flocculating efficiency of the anionic flocculants in that they achieve the low level of turbidity at much lower levels of adsorption.

The results of Dollimore and Horridge (1972) show much more dramatic decreases in light transmission (increases in turbidity) with dosage than are recorded in this study. This may be due to the higher particle concentrations used in their study.

3.5.7. The Anomalous Behaviour of Cationic Flocculants

A major point of difference between the findings of the present study and those of Dollimore and Horridge is in the behaviour of the kaolin flocculated with cationic flocculants. Unfortunately the method used to determine the adsorption of the polyacrylamides could not be used to determine the level of adsorption of the cationic flocculants, but it is clear from the settled bed results and the supernatant turbidities that the cationic flocculant is less efficient than the nonionic and anionic polyacrylamides. By contrast the results of Dollimore and Horridge suggest that the cationic flocculants were the most efficient. In addition the settled bed maximum in this study was highest for the cationic flocculant but lowest in the study of Dollimore and Horridge. A possible reason for this difference is to be found in the different methods of agitation. The method used by Dollimore and Horridge is of short duration compared to the 15 minute agitation using the impeller stirrer. Thus it is possible that the endurance of the bonding of the cationic flocculant to the kaolin surface is less than that of the nonionic and anionic flocculants. As a consequence the flocs may break down more easily. This is however a problematic explanation. In particular it does not explain why the characteristics of floc breakdown observed with the Na^+ kaolin (treated with anionic flocculants) are not repeated. The bed heights decrease (as does the supernatant turbidity) in a manner that suggests that the cationic flocculant only requires a higher dosage of flocculant to perform the task of flocculation. Theng (1982) has indicated that cationic polyelectrolytes interact strongly with negatively charged clay surfaces and that polymer collapse occurs. In a flocculating system the agitation time would critically affect this process with longer agitation favouring the rupture of bridges and the collapse of the polymer. Higher dosages would tend to reduce this process because of steric factors becoming more important. This may also contribute to the discontinuity in the turbidity data if the change in adsorption behaviour (suggested by Hesselink) from predominantly adsorbed polymer segments to extended loops occurs at this dosage. This could be related to two different processes of reducing the degree of dispersion of the kaolin, - the first being the neutralization of surface charge (recorded electrophoretically by Black et al 1966) and the second, turbidity reduction accomplished by bridge formation. This explanation must however remain somewhat speculative as it was not possible in this study to record the level of adsorption of the flocculant. The present results suggest that polycations are not good flocculants in kaolin slurries under conditions of extended agitation.

3.5.8 Flocculant Molecular Mass

Differences in molecular mass of the two 10-APAM flocculants resulted in differences in behaviour being observed for the H^+ and Ca^+ kaolins. The photographic evidence for the H^+ kaolin shows that the higher molecular mass flocculant generated larger flocs while in the case of the Ca^{2+} kaolin the floc sizes are very similar. It is notable from the adsorption vs dosage graphs for the two kaolins that the level of adsorption of the two flocculants is different in the case of the H^+ kaolin and similar in the case of the Ca^{2+} kaolin. The adsorption results for the different molecular masses show no consistent pattern in the adsorption data whether efficient flocculation occurs or not. The settled bed height maximum of the H^+ kaolin treated with the low molecular weight flocculant appears to be broader than that of the higher one. If the width of the peak is a reflection of the level of adsorption then this interesting result is borne out to some extent by the similarity in peak widths in the case of the two flocculants with the Ca^{2+} kaolin. The difference in behaviour observed for the H^+ and Ca^{2+} kaolins is related to the difference in pH. We note that at the natural pH of the Ca^{2+} kaolin both the low m.w 10-APAM and the 10-APAM will be fully ionized and therefore equally rigid hydrodynamically speaking. Thus the controlling element of floc stability will be the cumulative strength of the interparticle bonds to the surface. This seems to demand a greater number of molecular chains of the low molecular mass flocculant to ensure floc stability and it is probably coincidental that a similar mass is required for both flocculants. However in the case of the H^+ kaolin it is immediately obvious that a considerably greater concentration of the low m.w. flocculant is required. This must be in part due to the higher molecular volume of the highest molecular mass flocculant providing more efficient bridging under the conditions of lower pH where the flocculant molecules are more flexible. The difference in behaviour between the Ca^{2+} and H^+ kaolins is a matter of degree rather than a matter of difference in mechanism, though in the case of the H^+ kaolin treated with 10-APAM the larger floc size seems to suggest that the higher molecular mass flocculant is playing an enhanced role that may be related to the kinetics of floc formation. It is clear that the higher molecular mass flocculant is to be favoured if floc stability is to be ensured.

3.5.9. Further Comparison with Earlier Studies

Some of the points of contact of the present study and the extensive work of Dollimore and Horridge have been mentioned. It has been noted in particular that the pattern of the settled bed data and the evaluation of the condition of the supernatant is remarkably similar in spite of the solids concentrations being different by an order of magnitude. These points of similarity do not extend however to the internal variations between different types of flocculant tested. In particular differences appear in the efficiency of cationic flocculants, which appear in this study to be poor, in that the small size of flocs and the high dosages required in order to generate them is distinctly worse than the behaviour of the nonionic flocculant in the case of the Na^+ kaolin and the nonionic and anionic flocculants in the case of the H^+ and Ca^{2+} kaolins.

There is however agreement with the findings of Dollimore and Horridge in that the dosage at which efficient flocculation occurs is lower for the anionic flocculant than the nonionic one. Secondly the width of the settled bed peak is narrower in the case of the anionic flocculant and it also occurs at a lower dosage. The slope of the light transmission curves for the supernatant is steeper in the case of the anionic flocculant on both sides of the maximum in the study of Dollimore and Horridge as is the case for the equivalent supernatant turbidity minimum in the present study.

This last finding is again confirmed in the study of Black, Birkner and Morgan (1965) who used two anionic flocculants of 4 and 30% anionic character, the one with the higher degree of anionic character having a narrower turbidity trough and achieving it at a lower dosage. It is also noted that the results of Black, Birkner and Morgan indicate that in the absence of added electrolyte no floccuation at all occurs with anionic flocculants. The kaolin concentrations in their study were two orders of magnitude lower than those in the present one.

Findings in two other studies confirm results in this study - Slater and Kitchener show remarkable similarities in settled bed and clarification trends in their study of fluorite suspensions. Healy in his work on flocculation of quartz notes the correspondence of floc size development and reduction of supernatant turbidity.

This study, therefore, substantially confirms the findings of earlier workers except in the case of cationic flocculants. The additional information provided by single floc settling tests and floc photography and a standardized method of agitation allows a description of the basic mechanisms that give rise to variations in bed height and supernatant turbidity using a range of flocculants. In addition the relationship of these variations to flocculant adsorption have been elucidated.

Three different homoionic forms of kaolin tested at their natural pH have revealed differences in behaviour. In particular the inefficiency of anionic flocculants in the case of the Na^+ kaolin is noted. It was necessary therefore to evaluate to what extent pH contributed to these differences and subsequently to investigate the effect of variations in the electrolyte concentration.

3.5.10 Discussion of pH Results

3.5.10.1 Unflocculated Control Samples

The untreated control samples that were used as part of the investigation of the effect of pH reveal that the type of cation that is present on the kaolin surface profoundly affects the suspension behaviour across the pH range studied. This is exemplified by the extremely high settled bed heights of the Na^+ kaolin below pH 5.5. This seems to indicate that the classical cardhouse structure is most efficiently formed in the presence of singly valent counter ions that do not play a potential determining role, since, in the presence of the H^+ ion and the Ca^{2+} ion, the settled beds of the unflocculated controls are much lower.

The role of the predominant counterion is also shown in the supernatant turbidities of the control samples. In particular the supernatant turbidity of the Ca^{2+} kaolin at pH 6 increases as it does for the Na^+ and the H^+ kaolins; however at a pH of 7 and above the supernatant turbidity of the Ca^{2+} kaolin drops to about 170 J.T.U. This behaviour can be related to the doubly valent nature of the Ca^{2+} ion. It is much more efficient in balancing the surface negative charges thus reducing the thickness of the diffuse layer and promoting coagulation. It is not possible to explain the increase in supernatant turbidity around pH 6 from a simple physical view of the electrical double layer. It may result from coprecipitation of the Ca^{2+} ion with a silicate or aluminate radical thus preventing it from performing its role as a counterion in the electrical double layer. It has not been the purpose of this study to identify the mechanism that gives rise to this phenomenon. In this context the importance of having untreated control samples in all flocculation studies is noted. Where no controls have been used in other studies the underlying assumption has been either that the modification of the flocculant conformation has a more profound effect on flocculation than the nature of the surface with which the flocculant interacts or, alternatively, that the behaviour of different homoionic forms of kaolin is already sufficiently well understood from the qualitative descriptions based on the DLVO theory. The careful study by van Lierde of the flocculation-dispersion behaviour of quartz in the presence of polyacrylate and the calcium ion is an example of the complexities of behaviour that can be found when pH is introduced as a variable.

3.5.10.2 Flocculant Adsorption across the pH Range

The different adsorption characteristics of the n-PAM and the 40-APAM across the pH range on the three homoionic forms of kaolin has been noted. It can be seen, however, that the general characteristics of the adsorption of flocculant on the H^+ and Na^+ kaolin are similar and that in the case of the Ca^{2+} kaolin treated with the 40-APAM the adsorption of flocculant is markedly different.

The adsorption of flocculants on the Na^+ kaolin can be more easily interpreted when the effect of pH variation on floc size is observed. The floc size of the kaolin treated with the n-PAM decreases with decrease in pH. This suggests that the higher pH is producing conditions that favour more stable flocs. The settled bed height also decreases at higher pH suggesting that there is an increase in floc density. At the same time there is a decrease in the level of flocculant adsorption of about 20% as the pH is increased. The previous discussion of the relationship between the type of adsorption and floc stability suggests that as the pH is increased some bonding mechanism between the kaolin and the polyacrylamide is becoming more efficient. The major change in the kaolin under these conditions is hydroxylation to produce edge negative charges.Another mechanism that may contribute to more efficient flocculation is an increase in flocculant coil volume if a small number of amidic groups have been hydrolysed. This would contribute to more efficient bridging. In the case of the Na^+ kaolin treated with the 40-APAM the photographic evidence shows small disrupted flocs at high pH, an increase in floc size near neutral pH, and smaller flocs at low pH. Flocculant adsorption shows a minimum at a pH of 5 with an increase in adsorption with increase or decrease in pH. At low pH the adsorption of 40-APAM is of the same order as the n-PAM. This is expected since at low pH the anionic flocculant behaves essentially as a nonionic one (because of the protonation of its carboxylate groups). As the pH is increased more and more groups become ionised. This causes internal repulsion between the polymer coil segments and results in an increase in the dimensions of the coil. This facilitates bridging. At the same time many positively charged groups are present on the edges of the kaolin that can form electrostatic bonds with the flocculant's ionized carboxylate groups. This process of charge neutralisation combined with the more efficient bridging means that stable flocs are formed at much lower levels of flocculant adsorption. The flocculant adsorption falls to one sixth of what it was at pH 3. Above pH 6 increase in adsorption and floc degradation go hand in hand. As the population of edge positive charges drops with increase in pH a larger number of non-electrostatic bonds are required to ensure floc stability. However as the flexibility of the polymer chains is reduced by ionization the possibility of those bonds forming before a large floc becomes disrupted is smaller. Thus although adsorption is still taking place inter-particle bridging becomes less efficient, flocs are disrupted and new surfaces are exposed to flocculant. Smaller flocs form with higher levels of adsorbed flocculant. Physically this causes less dense flocs (higher settled beds) and an increase in supernatant turbidity as material is resuspended. The above description completes the understanding of why the Na^+ kaolin was not flocculated by the anionic flocculants at its natural pH. Identical arguments can be applied to the flocculation of the H^+ kaolin with the two different flocculants. However the results show that the particular counterion does have some role to play in the exact shape and position of the adsorption-pH curves especially above pH 4. Thus in the case of the H^+ kaolin the level of flocculant adsorbed reaches a minimum at pH 6.3 and is about one twelfth of the amount of flocculant adsorbed at pH 3. This suggests that positive edge charges on H^+ kaolin persist to higher pH thus facilitating electrostatic bond formation at the same time as the number of ionised groups is increased thus extending the coil and improving bridging between particles.

It has been remarked that the adsorption vs pH curves for the kaolins with singly valent counterions are coincident at a pH of about 3.3. At this pH these kaolins are probably at or very near their point of zero charge (pzc) and the flocculants are essentially nonionic. Thus the variations in the properties of the kaolin due to surface charge modification and coil dimension variations of the flocculants are at a minimum, therefore the level of adsorption of both flocculants on the two kaolins is identical. Even though this is the case, the settled bed heights are different showing that the counterion is still playing a role. The supernatant turbidities are practically identical.

3.5.10.3 The Behaviour of the Ca^{2+} Kaolin Across the pH Range

The Ca^{2+} kaolin treated with n-PAM shows a constant level of adsorption across the pH range. This is associated with a constant turbidity and a very constant settled bed height. All this indicates that the same mechanism of floc formation is occuring in all cases across the pH range.

However, the adsorption of the 40-APAM departs from the pattern established by the singly valent homoionic kaolins. Up to a pH of 4.5 there is a high and increasing adsorption of flocculant that is associated with an increasing supernatant turbidity. There is then a drop in adsorption to pH 8 that is almost linear. This is associated with a low turbidity, and a drop in settled bed volume. At pH 4.3 the turbidity of the treated Ca^{2+} kaolin is higher than the turbidity of the untreated control. This suggests that, instead of flocculation taking place, the presence of the Ca^{2+} ion is causing the stabilisation of the kaolin and that this is, as would be anticipated, associated with a higher (almost total) level of flocculant adsorption. This could occur in two ways. Either the rate of adsorption of flocculant onto the kaolin is so high that it is complete before effective bridging events take place or the nature of flocculant adsorption on kaolin in the presence of Ca^{2+} ions is different in a manner that does not promote flocculation. At pH 3 the kaolin is flocculated; as the pH is increased the flocculant coil begins to ionise and expand. This permits the counterions on the kaolin faces (balancing the pH-independant surface charge) to form ionic bridges with the ionized flocculant thus forming strong bonds on the faces and on the kaolin edges. If this process is more rapid and irreversible than the normal formation of nonspecific bonds by displacement of singly valent counterions on the faces then it is possible that stabilization competes with the normal process of flocculation. In addition it should be noted that doubly valent ions not only have the ability to form ionic bridges between the kaolin and the flocculant molecule but that ionic complexes can be formed between the cation and two acrylate groups on the flocculant molecule. This will have the effect of reducing the charge density of the coil, thus reducing its dimensions and because of the ionic nature of the Ca-acrylate bonds the flexibility of the coil will also be reduced. At low pH these effects will tend to make the coil behave as a nonionic one and at a higher pH the dimensions of the coil will not be as large as would be expected in the absence of the Ca^{2+} ion. In the following discussion this additional complication will be ignored as the majority of the Ca^{2+} ions are expected to be associated with the kaolin surface. If the Ca^{2+} ions were added as free electrolyte however it would not be possible to ignore this effect (Black 1961; Hesselink 1977).

At higher pH flocculation is again favoured. The increase in flocculant coil volume with ionisation will favour the formation of interparticle bridges with strong ionic links formed by Ca^{2+} ions on each surface. This will tend to cause flocculation rather than stabilization. The unique stability of the Ca-ionic link is attested by the fact that the level of flocculant adsorbed continues to drop beyond pH 7.8 and that stable flocs are formed and low supernatant turbidities are present under conditions where singly valent homoionic kaolins have high levels of flocculant adsorption and supernatant turbidities that cannot be measured after 15 minutes. The compression of the diffuse layer by the specifically adsorbed Ca^{2+} ions also contributes to floc stability.

3.5.10.4. Comparison of pH Results with Published Literature

Dollimore and Horridge (1973) undertook an investigation of the effect of pH on the flocculation of kaolin by polyacrylamides. The data in this study and in theirs are basically in agreement. Again the pattern of increasing settled bed heights to a pH of about 6 is observed. Across the common pH range the supernatant clarity data are also comparable. In particular the results for the anionic flocculant in their studies were similar to that for the Na^{+} and H^{+} kaolins rather than the Ca^{2+} kaolin.

However differences are noted in the settled bed heights for the Na^+ and H^+ kaolins treated with the anionic flocculant. The results of Dollimore and Horridge follow a pattern of slowly increasing bed height to a pH of 5.8 with a subsequent rapid decrease in bed height. The initial slow increase is attributed to packing of flocs being different as the floc size increases and this is consistent with the present analysis. However the results of this study show a characteristic trough shaped curve for the settled bed results when the 40-APAM is used. This difference arises from the type of agitation applied in the two different studies. In the less aggressive and shorter period of agitation applied in the study of Dollimore and Horridge floc breakdown may not have occured. In this study the long period of agitation results in the disruption of unstable flocs which are formed initially at higher pH. This disruption results in small flocs of lower density and thus the settled bed heights are higher. The present study therefore tends to associate low settled bed volumes with floc stability. Caution must be observed however at low dosages of flocculant or with beds of highly disrupted flocs.

The study of van Lierde on flocculation-dispersion of quartz suspensions in the presence of polyacrylate shows that in the presence of the Ca^{2+} ion dispersion takes place below a pH of 5.5, and that above pH 5.5 the quartz tends to flocculate. Although the systems are not entirely comparable (in particular because of the flocculating role of amidic groups on the polyacrylamide) the similarity in behaviour is an indication that the phenomenon of stabilization of Ca^{2+} kaolin by the highly anionic polyacrylamide occurs in the manner described. The interpretation of van Lierde is very similar to the one given above.

Slater, Clark and Kitchener in their investigation of the flocculation of fluorite with an anionic polyacrylamide measured the level of adsorption of flocculant. There is a notable reduction in the level of adsorbed flocculant (an anonic polyacrylamide) in the same manner as was observed in this study with increase in pH and improvement in flocculation. At higher pH where flocculation became less effective adsorption did not increase - possibly inhibited by mineralogical factors or because of the short and gentle agitation applied.

The classical study of Micheals and Morelos on polyelectrolyte adsorption by kaolinite demands some re-evaluation in the light of the present study. In particular their findings with regard to the level of anionic polyacrylamide adsorption at high pH are by their own admission liable to be in error. Thus the zero adsorption found in their study at pH 7 and above is not found in the present one. However as they used a hydrolysed polyacrylamide and their method of agitation was "gentle shaking" it is quite probable that the level of flocculant adsorption was extremely low; as is the case with the hydrogen kaolin and the anionic flocculant at a similar pH in this study. The settled bed vs pH data resemble those of Dollimore and Horridge (1973) but the changes also appear to be more dramatic even though the solids concentration was similar to that used in this study. This suggests that the difference is the result of the gentler agitation in the case of the study of Micheals and Morelos.

3.5.11 Ionic Strength

The primary reason for the investigation of the role of ionic strength was to determine the effect that this variable would have on the adsorption of flocculant in particular. It is already known from DLVO theory that the addition of increasing concentrations of electrolyte reduces the stability of a dispersion. This was observed in the control samples. The Na^+ kaolin at neutral pH has, at low electrolyte concentrations, a high supernatant turbidity which was observed to drop with increase in the electrolyte concentration. The supernatant turbidity of the Ca^{2+} kaolin increased gradually at higher electrolyte concentrations probably as a result of the Na^+ ions displacing Ca^{2+} ions and being less effective in compressing the diffuse layer. A maximum in the settled bed height of the control samples was noted in the case of the Na^+ kaolin with increase in ionic strength.

The adsorption of the nonionic flocculant increased to a maximum and then decreased for the H^+ and the Na^+ kaolin with increase in ionic strength. The adsorption of anionic flocculant initially dropped with the Na^+ kaolin and then increased as the ionic strength was increased. The adsorption of the anionic flocculant on the H^+ kaolin increased. In each of these cases the initial behaviour mimics what occurred with decrease in pH. This is expected to happen since both reducing the pH and increasing the ionic strength of kaolin reduces the degree of dispersion of the material. However since the basic mechanism is not identical with the two cases the behaviour is also not identical. Increased ionic strength will also reduce the dimensions of nonionic flocculant molecules to a small degree (the effect is larger for the anionic flocculant) and this should tend to increase adsorption. The analysis of Hesselink suggests an increasing adsorption where the adsorption is not ionic in character as the ionic strength is increased. However the tendency for an increase in adsorption operates in competition with the more effective interaction of the flocculant molecule with the kaolin surface as the charge at the OHP is reduced (with increasing ionic strength). This tendency will reduce the amount of flocculant that is required to produce stable flocs. It is quite likely that in the pH results the drop in the level of adsorption of nonionic flocculant close to the pzc for the Na^+ kaolin occurs for similar reasons. The steep slope of the adsorption of the 40-APAM is consistent with the expected reduction in repulsion between the ionised groups on the molecule and the favouring of nonionic interactions with the kaolin surface. (It also confirms the findings reported by Somasundaran).

The Ca^{2+} kaolin in the presence of the anionic flocculant would have an increasing adsorption if it mimicked the behaviour of the pH results. Instead there is an initial drop in adsorption followed by a slight increase. The stability of the settled bed heights and the gradual increase in the supernatant turbidity gives no clue as to the reasons for this behaviour. The increase in the ionic strength will tend to decrease the dimensions of the flocculant molecule but there is no big change in the Ca^{2+} kaolin stability to offset this. It is possible that the decrease in the thickness of the diffuse layer will favour a greater contribution of nonionic bonding thus resulting in greater floc stability (lower flocculant adsorption). However this must remain the least satisfying of the explanations of adsorption of flocculant until the behaviour of polyelectrolytes in the presence of doubly valent ions is better understood. The fact that the pattern of adsorption does not mimic the results for the lowering of pH is an indirect confirmation that the Ca^{2+} ion is playing a specific chemical role in the peculiar adsorption behaviour observed across the pH range.

3.6 Floc Size Studies using Image Analysis

Floc photography had shown that under controlled conditions individual flocs could be photographed and numbers of individual flocs against a background could give an assessment of the floc sizes and a feeling for the distribution of floc sizes. In order to further quantify some of these parameters some flocculated samples were prepared for floc photography. These were Na^+ kaolin treated with n-PAM and 40-APAM at 0.25, 1, 2 and 4 mg/g dosages. This was done at the natural pH of the kaolin. Macrophotographs and micrographs, where appropriate, were enlarged and floc outlines were digitized using an image analysis technique called areal analysis (Frith). A digital planimeter is used to digitize the perimeter of the flocs in a photographic field and the co-ordinates are used to compute a single floc area and its apparent diameter (using a spherical model). The results of these computations were stored on a flexible disc. A second program was used to compute histograms of the fractional cummulative floc area across each diameter interval. Thus if the flocs with diameter 0.4 - 0.5 mm constituted 8% of the total area of flocs digitized in a sample the fractional cummulative floc area would be 0.08. The modes of the histogram (floc diameters in mm) could then be used as a measure of the floc diameter (weighted in favour of larger floc diameters by the process of accumulating the areas over each diameter division). In some instances it is difficult to observe on a photograph whether a floc is a single unit or an aggregate of smaller flocs. In general the solution to this problem depended to a degree on the choice of the planimeter operator and to that extent the evaluation of the data is subjective. For this reason the significance of the absolute values of the modes must be treated with some care, but the trends of floc size with flocculant dosage have obvious significance. Most of the histograms with the exception of the 0.25 mg/g dosage appeared to be bimodal suggesting two distinct regimes of floc sizes. A very obvious example of this is the 4 mg/g dosage of 40-APAM with the sodium kaolin (Figure 3.6.1). Some distributions of the cumulative floc area are difficult to assess since both modes may be within the standard deviation of an assumed normally distributed unimodal distribution. Bearing this in mind it is possible to examine the data for the two flocculants for the three different homionic forms of kaolin (Figures 3.6.2, 3.6.3 and 3.6.4). The

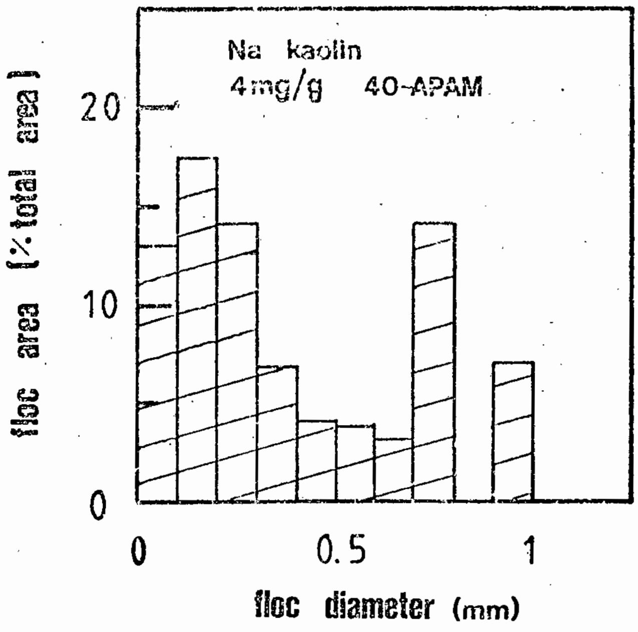


FIGURE 3.6.1: FLOC AREA vs FLOC DIAMETER SHOWING BIMODAL FORM.

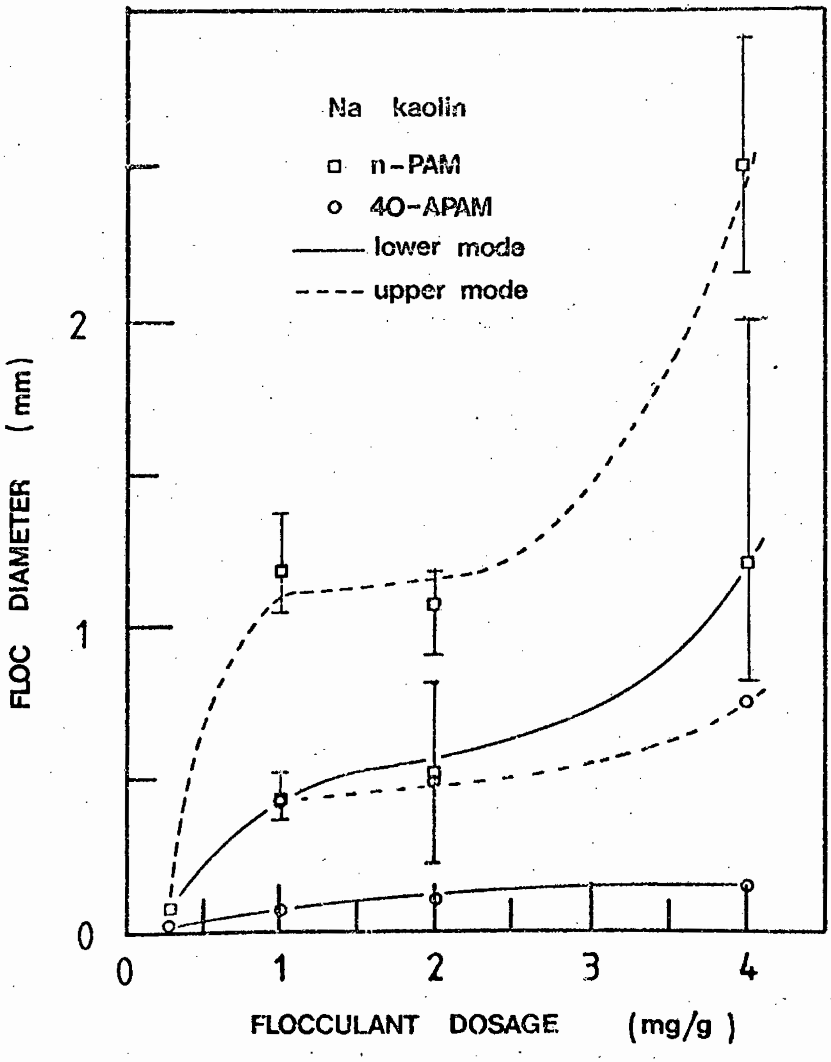


FIGURE 3.6.2: FLOC DIAMETER vs FLOCCULANT DOSAGE for Na+ KAOLIN.

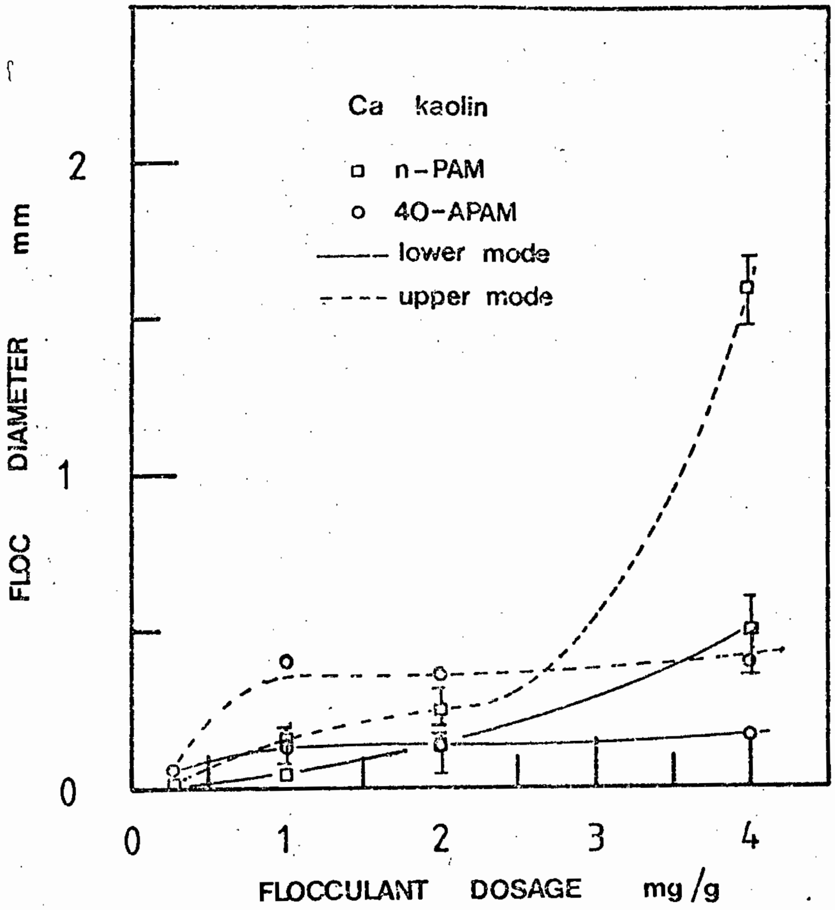


FIGURE 3.6.3: FLOC DIAMETER vs FLOCCULANT DOSAGE for Ca2+ KAOLIN.

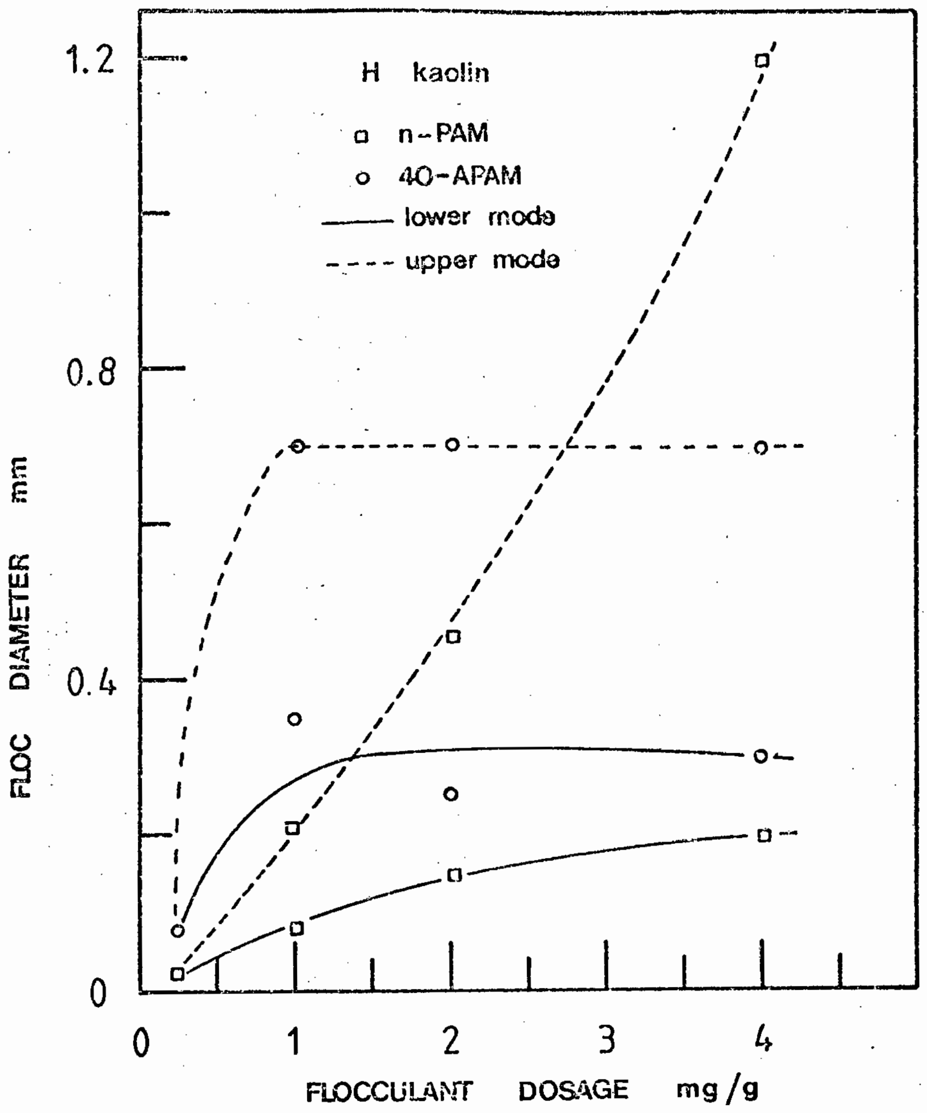


FIGURE 3.8.4: FLOC DIAMETER vs FLOCCULANT DOSAGE for H+ KAOLIN.

Na^+ kaolin with n-PAM shows a rapid increase in the magnitude of the upper mode with dosage that follows the pattern of the results for the lower mode. The same pattern is followed for the Ca^{2+} and the H^+ kaolin. The Ca^{2+} and the Na^+ kaolin may exhibit a point of inflection between 1 and 2 mg/g for the n-PAM. The 40-APAM results seem to show a rapid increase to a stable floc size across the range 1 - 4 mg/g. In this sense the behaviour of the two different flocculants is distinctively different.

Another way to observe this difference is to plot the unweighted logarithm of the averge floc area against the flocculant dosage . This is shown in Figures 3.6.5 and 3.6.6. The average floc area continues to increase with dosage in all cases with the n-PAM (Figure 3.6.5) but a limit that is very similar for the three kaolins is reached when the material is treated with the 40-APAM. Average areas are of the same order for the Ca^{2+} and H^+ treated with n-PAM and the three homoionic forms treated wth 40-APAM. The Na^+ kaolin treated with n-PAM has an average area nearly an order of magnitude higher.

3.6.1 A Note on the Measurement of Floc Size using Image Analysis

It seems clear that the floc size distributions, when weighted for the larger floc sizes by summing the areas, are bimodal. However by far the largest number of flocs are small as it requires comparatively few large flocs to provide a fairly high fraction of the total cumulative area. This may suggest that the larger flocs are in the process of being disrupted by the agitation. This would be consistent with the observations made of the process of floc disruption in the studies where the agitation time was varied.

Most noticeable in this regard is the small floc size of the smaller Na^+ kaolin flocs resulting from flocculation by the anionic flocculant. The pH results and the natural pH flocculation parameters both suggest that a process of floc disruption takes place. This is confirmed by the present results. In addition it is noted that the floc size of the H^+ and Ca^{2+} kaolins treated with the anionic flocculant achieve their limiting size at a much lower dosage than the same kaolins treated with the nonionic flocculant. This is confirmation of the earlier finding that did not rely on measurements of floc size. Thus the method of floc size measurement based

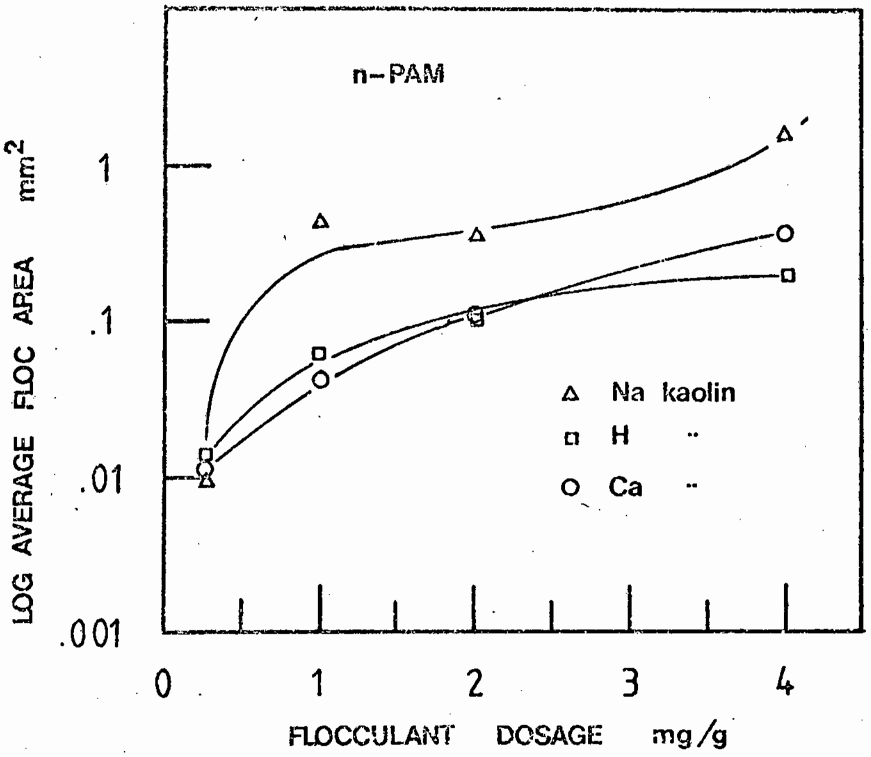


FIGURE 3.8.5: LOG AV. FLOC AREA vs FLOCCULANT DOSAGE for n-PAM

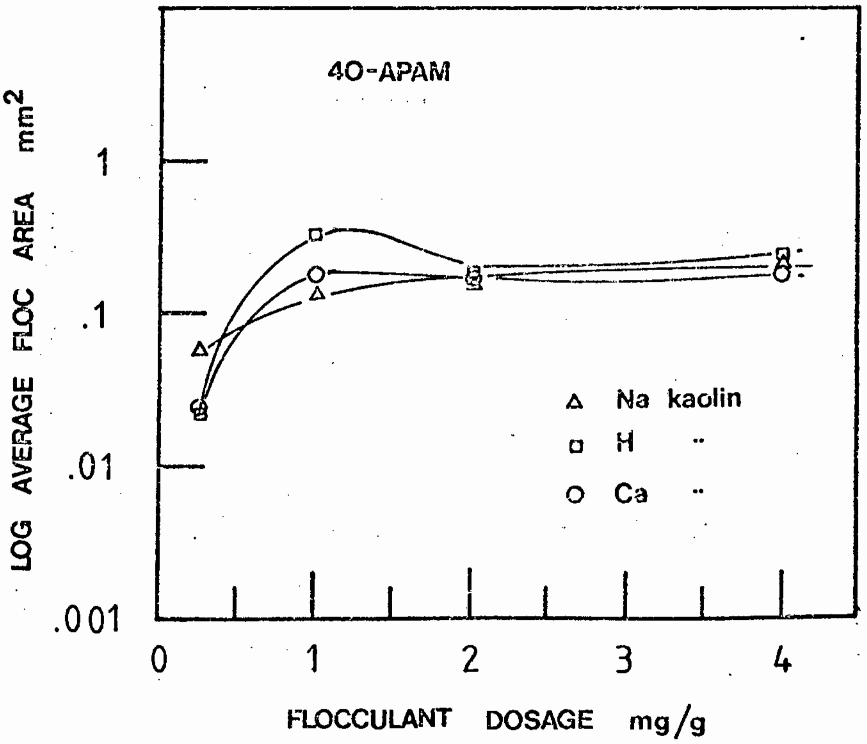


FIGURE 3.8.6: LOG AV. FLOC AREA vs FLOCCULANT DOSAGE for 40-APAM.

on image analysis reinforces the initial impressions gained from examination of the undigitised floc photographs. If this method could be suitably automated it could provide the basis of a more analytical modelistic assessment of the effectiveness of different flocculants under different conditions. At present it is a slow and tedious process that serves to reinforce the qualitative judgements of the photographic record in the present study.

CHAPTER FOUR

GENERAL DISCUSSION

4. GENERAL DISCUSSION

A number of elements of the discussion are more profitably expressed in a more general section. Important among these are (i) the applicability of Hesselink theory of polyelectrolyte adsorption to adsorption in flocculation studies and (ii) the applicability of the different flocculation models of Walles and, La Mer and Smellie in the investigation of flocculation.

4.1 The Theory of Polyelectrolyte Adsorption

The results of the agitation time studies (and the earlier work of Jankovics) indicate that stable flocs are formed at levels of adsorption considerably lower than the total possible adsorption of polyacrylamides. In addition the higher levels of flocculant adsorption are associated with disruption of the floc structure and redispersion of the material in the presence of excess flocculant. The process of disruption also occurs where the flocculant is totally adsorbed. These findings indicate that the level of flocculant adsorption at any moment is a dynamic interaction between the agitation conditions, the level of flocculant excess and the strength of the flocs present. This was earlier the finding of Linke and Booth. Thus it cannot be expected that the theory of polyelectrolyte adsorption can be directly applied in flocculation studies. This in turn casts doubt on the modified DLVO approach to colloid stability in flocculation which aims at determining the modification of the terms of the stability expression in the presence of polyelectrolyte. In these systems, at best, only pseudo-equilibria are established (as exemplified by plateaus in flocculant adsorption with agitation time at a given flocculant dosage). At present the V_{sr} and V_b terms of the stability expression are inaccesible experimentally and even at the pseudo-equilibrium the V_R term (modified by the presence of polyelectrolyte) is almost impossible to evaluate unless some indication of the surface coverage is available.

However the theory has proved valuable in one area already discussed (when evaluated in terms of flocculation).

This is the verification of the reason for the increased effectiveness of anionic flocculants on H^+ kaolins when compared with nonionic flocculants. The theory indicates that a combination of charge neutralization (of edge positive charges) and chain extension due to ionization (both pH dependant) gives rise to this phenomenon, since stronger bonds are required to allow the lower levels of flocculant adsorption required to produce stable flocs.

4.2 The Evaluation of the Role of the Flocculant in Flocculation

The theory of Smellie and La Mer suggested that half surface coverage by flocculant was the ideal condition for most efficient flocculation. The work of Jankovics indicates however that flocs were formed at levels of flocculant adsorption about 1/2 to 1/6 of the final level of total adsorption. The lower the molecular mass the greater the fraction of total flocculant adsorbed.

This indicates that the higher molecular mass the further optimum flocculation moves from the half surface coverage condition. This would seem to be consistent with the present study, where the molecular mass of the n-PAM, 10-APAM, 20-APAM and 40-APAM was the same. Considering the case of the H^+ kaolin, there is a consistent drop in the level of the flocculant adsorbed with increase in anionic character. Since the natural pH of the H^+ kaolin suspension is ∿5.00 it is possible to compute the number of ionized groups on each flocculant chain. This gives an assessment of the coil dimensions. The number of ionized groups on the chains at pH 5 is presented in tabular form below:

Polymer	Fraction of ionized segments / chain
n-PAM	0
10-APAM	0.025
20-APAM	0.05
40-APAM	0.1

This will necessarily result in coil volume expansion and increasing rigidity of the coil with increase in anionic character. Both of these trends would tend to reduce the level of adsorption on the kaolin (and therefore reduce the surface coverage). This suggests that the length of the extended loops of the flocculant are much more important in flocculation than the surface coverage. Thus the model of Walles (who considered the joint radius of the polymer-particle as a basis for the measurement of collision frequency) is probably a more viable approach to the study of flocculation kinetics. However his simple model will have to become considerably more sophisticated before it can be used to predict flocculation efficiency.

It is clear that under certain circumstances flocculant chain extension becomes inefficient in promoting flocculation (as was the case with H^+ and Na^+ kaolins above pH 7). This is because the bonding of the flocculant molecule to the particle becomes important under the dynamic conditions of agitation. As the number of possible electrostatic bonds drops, with increase in pH, the excessive chain rigidity (now with all ionizable groups ionized) inhibits flocculation. Under the dynamic conditions of agitation a simple picture of the initial stages of flocculation would be two particles (comparatively massive) being held together by a tenuous extended "string". The turbulence found near the impeller can be imagined to whip one particle off the end of the "string" and so flocculation is inhibited. It is possible however for a large number of single particle-single polymer molecule units (and multiple polymer attachments to a single particle) to survive leading to the high levels of flocculant adsorption and the characteristic stabilization of the singly valent homoionic forms of the kaolin. In the case of the Ca^{2+} kaolin this does not occur because of the unique nature of the Ca^{2+} ionic link which provides a strong bond with the kaolin surface (and may also reduce the polymer coil dimensions). It is clear that the flocculation of the Na^+ kaolin at its natural pH by the nonionic flocculant is related to the flexibility of the molecule which is maintained across the pH range as much as to the hydrogen bonding which takes place, since there is no electrostatic repulsion of the nonionic molecule by the negatively charged kaolin surface (face and edges).

It seems therefore that two criteria must be fulfilled for efficient flocculation to take place and that these criteria are necessarily interrelated. They are the rigidity of the polymer molecule and the strength of the particle-polymer bond. The persistance of bridges under the dynamic conditions of agitation defines an efficient flocculating system and this requires bonding on the surfaces of both particles which is sufficiently strong to resist rupture. Thus where the bonding is weak it is necessary to have a flexible flocculant molecule which will allow the formation of a sufficiently large number of bonds on each surface (without the steric problems that arise with more rigid coils). The corresponding large number of bridges between each surface implied by this significantly reduces the possibility of all bridges being ruptured at the same instant. However under agitation there must be a continual breaking and reformation of bridges, which may, with changes in flocculant conformation, eventually result in floc rupture, or the diffusion of excess flocculant into the floc structure. This description supports the time dependant model of floc rupture developed in this study. Polymer molecules of greater rigidity require correspondingly stronger bonds in order to form enduring bridges between particles. (This also suggests a more extended molecular conformation if rigidity is generated by ionization or a less extended conformation if it is generated by crosslinking or the presence of divalent and trivalent ions.)

Levels of adsorption are reduced in particular by stronger bonds associated with electrostatic bonding between the flocculant molecule and the mineral surface.

The model of Walles therefore provides a useful basis for interpretation of the results of flocculation studies conducted under controlled conditions of agitation.

CHAPTER FIVE

CONCLUSIONS

5. CONCLUSIONS

5.1 Conclusions based on physical observation

1. An impeller based system of suspension preparation and flocculation that admits itself to empirical analysis is a useful basis for the investigation of the effect of agitation on mineral slurries.

2. Photographic records of flocs can provide the basis for useful qualitative and quantitative assessments of the nature of the floc structure, the efficiency of different flocculants and the effect of other variables such as agitation, pH and flocculant dosage.

This study has identified three basic floc 'morphologies'.

a) Associative small flocs, characterised by a woolly structure that generally arise from small dosages of flocculant.

b) Discrete (coherent) denser flocs that are larger and appear more reflective. They are characteristic of higher dosages of flocculant.

c) Disrupted flocs. They have fibrillar appendages that result from long periods of agitation. They are less reflective than discrete flocs and are characterised by a larger size than the associative flocs described above.

3. Single floc settling experiments provide a basis for evaluation of floc density relationships.

Where efficient flocculation takes place there is an increase in density of flocs of a given size with increase in flocculant dosage. Flocculants of increasing anionic character show higher and more rapid floc density increases with dosage if efficient flocculation takes place. At low dosages (where small associative flocs are formed) floc density is almost independant of the flocculant type and the homoionic form of the kaolin.

(For a given kaolin) larger flocs have lower densities than smaller flocs at a single dosage of flocculant. The floc size-density relationship appears to follow a power law. These findings were consistent with the interpretation of variations in settled bed heights.

4. When efficient flocculation occurs with anionic flocculants the following was found :-

a) The dosage required to produce discrete flocs is lower as the degree of anionic character of the flocculant is increased.

b) The settled bed height maximum occurs at lower dosages for increasing anionic character of the flocculant.

c) The minimum supernatant turbidity is achieved at lower dosages for increasing anionic character of flocculant.

d) The amount of flocculant adsorbed decreases with increase in anionic character for H^+ kaolin and Ca^{2+} kaolin at their natural pH.

5. Anionic flocculants did not flocculate Na^+ kaolin at its natural pH although substantial amounts of flocculant were adsorbed.

6. Increasing the efficiency of the flocculation process by the modification of some variable in the system (except dosage) tends to reduce the level of flocculant adsorption.

a) Increasing the anionic character of the flocculant reduces the level of flocculant adsorption for the H^+ and Ca^{2+} kaolins.

b) Increasing the pH increases the floc size of kaolin flocculated with nonionic flocculant. The level of flocculant adsorption drops by about 20%.

c) With a 40% anionic flocculant adsorption is at a minimum at a slightly acidic pH when floc size is at a maximum for the Na^+ and H^+ kaolins.

5.2 Interpretive Conclusions

1. The Ca^{2+} counter ion interacts with ionised anionic flocculants by a process of ionic bridging. This mechanism of interaction may result in either flocculation or stabilisation of the kaolin suspension depending on the pH under the conditions applied in this study.

2. The relationship between polyelectrolyte chain extension as a result of ionisation and the pH controlled positive edge charges on kaolin is critical (i.e. the controlling element) in the flocculation of singly valent homoionic kaolins by anionic flocculants under the agitation conditions used in this study.

3. At the point of zero charge of singly valent homoionic kaolins the adsorption of flocculant is apparently independant of the ionic character of the flocculant.

4. In flocculation studies the criterion for floc stability is a dynamic interaction between the prevailing conditions of agitation and the stability of the floc suspension under those conditions. Floc rupture under conditions of excess flocculant results in a reduced floc size and adsorption of flocculant by newly exposed surfaces. Under controlled conditions of agitation for a constant time the largest floc size in any series of tests represents the most stable floc structure. This gives indications in some circumstances of the mechanisms of particle-flocculant interactions that give rise to floc stability.

5. Floc degradation under specified conditions of agitation is a time dependant process. Two different agitation systems when analysed led to the postulation that the rupture process is therefore slow and dependant on the energy input into the system rather than the instantaneous turbulent intensity of the agitation.

6. Floc rupture appears to be by macroscopic rupture rather than an erosion process in the presence of excess flocculant.

Where no excess is present rupture and erosion may both occur.

APPENDICES

Appendix 1 : Preparation of Homoionic Kaolins

The kaolins used in this study were produced from a material mined at Serina, near Fishoek, in the Western Cape. At that time, February 1979, the kaolin was beneficiated at the mine by blunging, mica trap and settling, followed by screening and filter pressing. The cakes were air dried. The predominant exchangeable cations on the kaolin were Na^+, Ca^{2+} and Mg^{2+} in fairly equal proportions. This kaolin suspended in water is alkaline at a concentration of 1g/100ml. In addition the kaolin readily coagulates under these conditions. The as-received kaolin was dry mixed in a clean ¼ ton cement mixer. Three homoionic forms of the kaolin were prepared for use in the present study. These were a hydrogen kaolin (which is in all probability a mixed hydrogen-aluminium kaolin (Banin and Ravikovitch)) a sodium kaolin and a calcium kaolin. They were generated using a strong acid cationic resin (I.R. A200). The method of preparation was based on that of Worrall and Ryan. It involved stirring the clay at low intensity with the resin for a period of 24 hours. There was no evidence of attrition of the resin during the stirring process. At the mixing concentrations used the relative exchange capacities of the resin and the clay respectively was about 100:1. Following the ion exchange process the kaolin was washed twice with deionised distilled water. The hydrogen kaolin (H^+ kaolin) was generated from a resin prepared with an excess of HCl. The Na^+ kaolin and the Ca^{2+} kaolin were generated with a resin prepared in the presence of the appropriate chlorides. The use of ion exchange resins in the preparation of homoionic clays has been criticised by Bolt and Frissel. The study of Worrall and Ryan and the early results of the present study seemed to indicate that the desired ion exchange phenomena did indeed take place. The drying was accomplished in the same manner suggested by Worrall and Ryan. The kaolins were stored in sealed plastic containers in a constant temperature laboratory.

Appendix 2 : The Determination of Polyacrylamide by Quantitive Precipitation of Residual Polymer and Subsequent Turbidimetric Measurement

A method due to Macefield forms the basis of the determination of polyacrylamides in this study. It involves the quantitative precipitation of polyacrylamide from solution by reaction with chlorine radicals evolved from the reaction of sodium hypochlorite with glacial acetic acid.

Two stock solutions are used. 1ml of the acid solution (26.3ml glacial acetic acid, 4.2ml conc. HCl and 73.7ml deionised water) is added to a 20ml aliquot of the supernatant after the turbidity has been determined. After brief agitation (15 sec) a bleach solution (sodium hypochlorite; 1.3% available chlorine) is added (1ml). The solution is allowed to stand and is briefly agitated for 5 seconds every two minutes following an initial agitation of 10 seconds duration. The turbidity is determined after 8 minutes.

Calibration graphs can be constructed for each type of polyacrylamide. The method used in this study depended on the linearity of the calibration graphs initially determined. Since this was established it was possible to use the turbidity of the diluted stock solution as a basis for evaluating the residual polyacrylamide following flocculation. It became necessary to correct for the dilution of the remaining suspended solids with addition of the reagents when the turbidity of the solids was more than 1% of the turbidity of the residual flocculant. This provides an assessment of the accuracy of the technique. In general for total turbidities less than 200 JTU the accuracy of the individual readings was better than 1%. However the uncertainty of the results is greater where there remained substantial flocculant in the supernatant in conjunction with suspended solids and when there was significant solid in suspension and very little flocculant (which occured infrequently).

The following equation used to calculate the level of flocculant adsorption was :-

$$A = F\ [1 - (T - (20/22\ R)/N)\ ]$$

where A is the adsorbed flocculant in mg/g

F is the flocculant concentration in mg/g

T is the final turbidity after addition of reagents (JTU)

R is the residual turbidity after centrifuging (JTU).

N is the turbidity of the solution concentration F.

Appendix 3 : Floc Photography

Floc photography was undertaken with the use of plastic petri dishes. Two camera systems were used:-

1) A camera mounted on a copy board with macro lens,
2) A camera mounted on a stereo-optical microscope.

With the camera mounted above the copy board an aliquot of the slurry was placed into the petri dish. The scale was either a washer of known internal diameter (4.4mm) or was derived from a photograph of a millimetre rule taken under the same conditions as the flocs were photographed.

In the stereo-optical microscope it was found to be necessary to place a slightly smaller plastic petri dish over the floc suspension in order to eliminate reflection at the air/water interface and to minimise floc movement due to thermal variations under microscope illumination.

The separation between the two petri dishes was greater than 0.5mm and varied with the amount of liquid present. Closer separations were avoided by shims on the edges of the upper petri dish. In this way floc collapse under the weight of the petri dish was avoided.

Appendix 4 : Variable Stirring Conditions

The basis of the method was to use two different stirring apparatuses to generate flocs and evaluate the performance of the stirrers in relationship to the effect on floc structures and common flocculation criteria.

1. Impeller:

The impeller had 4 vertical blades (paddles) of length 25mm and height 5mm. This impeller was driven using a variable speed Heidolph stirrer. The flocculation vessel used was a 250ml pyrex beaker.

The performance of the stirring system was evaluated by empirical stirrer criteria (Chapter 2).

1g samples of kaolin in the sodium homoionic form were placed in the beaker and 90ml distilled, deionized water was added. The impeller was lowered until 4mm above the base of the beaker and the stirrer secured. The kaolin was stirred at 240 rpm for 15 minutes.

10ml of appropriately diluted stock flocculant was added from a pipette to the stirred slurry. The flocculated suspension was stirred for 15 minutes (240 rpm). At this time it was separated into two aliquots of equal volume, in separate 50ml measuring cylinders.

After 2 minutes a 20ml aliquot was pippetted from the 25ml level using a pipette with its tip bent through 90° (to make it horizontal).

The turbidity of the sample of supernatant liquor was determined using a Hach turbidimeter (Model 1850A). The aliquot was then transferred to a centrifuge tube and the liquor was centrifuged at 1380 rpm for five minutes.

15 minutes after decantation a 20ml aliquot was taken (by pipette) from the second measuring cylinder and the turbidity determined.

The settled bed heights were measured with vernier calipers after 5 minutes and 15 minutes.

Following centrifuging the turbidity of the first aliquot was again determined and the residual flocculant in the aliquot was determined.

Thus this basic experimental procedure yielded the following data relevant to the flocculation process -

1) Supernatant turbidity (2 minute and 15 minute)
2) Settled bed height (5 minute and 15 minute)
3) Centrifuge turbidity
4) Flocculant adsorption.

In addition photographs were taken of the bulk floc structure using methods described above.

2. Magnetic Stirrer

In the case of the magnetic stirrer the experimental procedure was substantially the same, except that the suspension was stirred by a magnetic stirrer from the time immediately prior to flocculant addition (i.e. after the initial 15 minute aging of unflocculated material). The magnetic stirrer (also analysed according to empirical stirrer formulations) had a teflon coated stirrer bar with a width of 25.5mm and a height of 4mm. The stirring speed was 960 rpm.

Appendix 5 : Adsorption and Flocculation Studies

The study of the adsorption characteristics with different flocculants and the gathering of flocculation data was conducted using the 4 bladed impeller and stirring conformation described above.

The methods applied differed somewhat in detail but not in basic concept.

The kaolin was prepared in 1.5g samples in either the Na^+, Ca^{2+} or H^+ homiionic form.

The kaolin was stirred in 135ml water (distilled, deionized) for 15 minutes at which time a 45ml aliquot was decanted into a 50ml cylinder to constitute a control.

The remaining 90ml was flocculated (by addition of 10ml of flocculant) and stirred for 15 minutes. In the case of these experiments the flocculant was added to the slurry at an elevated stirring speed to reduce the possibility of local overdoping. The elevated speed was maintained for 30 seconds following the flocculant addition. The floc suspension was divided following stirring and the supernatant turbidities determined as described. A centrifuge time of 10 minutes was chosen. Settled bed height was measured only after 15 minutes (and sometimes after 1 hour early in the experimental program).

Adsorption was determined by difference from the residual flocculant in the supernatant (using the method described in Appendix 2.) Floc photography was carried out routinely.

Appendix 6 : Single Floc Settling Determinations

A simple apparatus consisting of a short settling tube with a vertical, flat polystyrene window was used in the investigation of the relationship between floc size and floc density as determined by the modified Stokes law.

The flocs were generally counted in the size range 0.5mm - 0.1mm.

This was done using a horizontally mounted stereo-optical microscope with a calibrated graticule.

A small amount of flocculated material was introduced into the top of the distilled water filled settling tube and the flocs were timed over appropriate graticule divisions and the size of the flocs estimated from the graticule. In general at least 60 and often more flocs were counted to reduce the statistical errors due to the variability of the estimates, both of settling time and floc size.

The counting of 60 flocs generally took 20 - 40 minutes and the data reduction on a mini-computer another 30 minutes. Thus the method could be considered to be slow, but the results generally justified the effort.

1. The settling tube had to be illuminated with a cold light source to avoid generation of convection currents.

2. The introduction of large flocs or a large amount of flocculated material at once sometimes generated turbulence giving rise to non-systematic errors. Experience however allowed this condition to be recognized rapidly and a short wait of 1 - 2 minutes was generally sufficient to allow the system to stabilize.

3. The introduction of large amounts of flocculated material sometimes gave rise to bulk fluid movement resulting in anomalously high settling rates. This condition could generally be identified from the instability of weak flocs or alternatively the unstable settling characteristics of coherent discrete flocs.

Appendix 7 : Floc Size Determination by Image Analysis

The method of image analysis has not been used previously in studies that have been made of floc size. The use of image analysis in mineralogy and physical metallurgy has grown in the past years. This growth has been accelerated by the introduction of automatic and semi-automatic computer based systems. A semi-automatic system developed for areal and lineal analysis has been used in this study (Frith). The basic requirement for image analysis in this instance is photographic records that allow the analyst unambiguous evaluation of the observed field (i.e. no agglomerates of flocs and well defined floc edges) and photographic floc sizes that are significantly larger than 2mm in diameter. In most cases the second condition was easily met. However it is difficult to be certain what constitutes a single floc, especially as some flocs are not nearly spherical. This in turn complicates the analysis of what constitutes a floc diameter as some model has to be assumed to calculate this parameter from areal analysis data. Given this reservation the method was applied. Between 40 and 150 flocs were digitized using a digital planimeter for each homoionic form of the kaolin and dosage of flocculant. This data was reduced to accessible parameters such as area and apparent (spherical) diameter by the computer. The subsequent treatment of the data is described in the body of the thesis.

REFERENCES

References

Akers R.J. (1978) Experimental Methods (1); in The Scientific Basis of Flocculation. NATO Advanced Studies Institute Series E - No. 27 (ed. Ives K.J.) Sijhoff and Noordhoff - Netherlands, 131 - 163.

Akers R.J. (1972) Factors affecting the rate of polyelectrolyte-flocculation reaction. Filtration and Separation vol. 9, 423 - 425 and 466.

Alston E. (1979) Allied Colloids - Personal Communication.

Argaman Y. and Kaufman W.J. (1970) Turbulence and flocculation. Proc Am. Soc. Civ. Eng; Jou Sanitary Eng. Div. vol 96, 223 - 241.

Ash S.G. and Clayfield E.J. (1976) Effect of polymers on the stability of colloids. Flocculation of polystyrene latex by polyethers. Jou. Coll. Int. Sci. vol 55(3), 645 - 657.

Banin A.B. and Ravikovitch S. (1966) Kinetics of reactions in the conversion of Na or Ca saturated clay to H-Al clay. Proc. 14 Nat. Conf. on Clay Clay Min., 193 - 209.

Bhatty J.I., Dollimore D. and Zahedi A.H. (1978) The aggregation of kaolinite suspensions in gum tragacanth solutions. Trans.Brit. Ceram. Soc. vol 77, 126 - 131.

Black A.P. (1960) Basic mechanisms of coagulation. Jou. Am. Wat. Works Assn., vol 52, 492 - 503.

Black A.P. and Hannah S.A. (1961) Electrophoretic studies of turbidity removal by coagulation with aluminium sulphate. Jou. Am. Wat. Works Assn. vol 53, 438 - 452.

Black A.P., Birkner F.B. and Morgan J.J. (1965) Destabilization of dilute clay suspensions with labelled polymers. Jou Am. Wat. Works Assn. vol 57, 1547 - 1560.

Black A.P., Birkner F.B. and Morgan J.J. (1966) The effect of polymer adsorption on the electrokinetic stability of dilute clay suspensions. Jou.Coll. Int. Sci. vol 21, 626 - 648.

Bockris J. O'M, Conway B.E. and Yaeger E. (1980) Comprehensive Treatize of Electrochemistry. Vol 1: The Double Layer. Plenum Press, New York.

Bolland M.D.A., Posner A.M. and Quirk J.P. (1976) Surface charge on kaolinites in aqueous suspension. Aust. J. Soil Res. vol 14, 197 - 216.

Bolland M.D.A., Posner A.M. and Quirk J.P. (1980) pH independant and pH dependant surface charges on kaolinite. Clay Clay Min. vol 28(6), 412 - 418.

Bolt G.H. and Frissel M.J. (1960) The preparation of clay suspensions with specified ionic composition by means of exchange resins. Soil Sci. Soc. Am. Proc. vol 24, 172 - 177.

Buchanan A.S. and Oppenheim R.C. (1968) The surface chemistry of kaolinite. I. Surface leaching. Aust. J. Chem. vol 21, 2367 - 2371.

Buchanan A.S. and Oppenheim R.C. (1972) The surface chemistry of kaolinite III. Microelectrophoresis. Aust. J. Chem. vol 25, 1857 - 1861.

Camp T.R. (1955) Flocculation and flocculation basins Proc. Am. Soc. Civ. Eng. vol 120, 1 - 16.

Davies J.T. (1972) Turbulence Phenomena. Academic Press, N.Y. and London.

Dixon J.K. and LaMer V.K. (1967) Effect of the structure of cationic polymers on the flocculation and the electrophoretic mobility of crystalline silica. Jou. Coll. Int.Sci. vol 23, 465 - 473.

Dollimore D., Griffiths D.L. and Miller D. (1969) The effect of polyacrylamide on the sedimentation of dense silica suspensions. Proc. Brit. Ceram. Soc. No. 13, 67 - 78.

Dollimore D. and Horridge T.A. (1971) The floc sizes of kaolinite flocculated by polyacrylamide. Trans. Brit. Ceram. Soc. vol 70, 191 - 194.

Dollimore D. and Horridge T.A. (1971/72) The filtration of beds of china clay flocculated by polyacrylamides. Powder Tech. vol 5, 111 - 114.

Dollimore D. and Horridge T.A. (1972) The optimum flocculant concentration for effective flocculation of china clay in aqueous suspension. Wat. Res. vol 6, 703 - 710.

Dollimore D. and Horridge T.A. (1973). The dependance of the flocculation behaviour of china clay - polyacrylamide suspensions on the suspension pH. Jou. Coll. Int. Sci. vol 42, 581 - 588.

Dollimore D. and Horridge T.A. (1977) The effect of hydration of the exchangeable cation on the flocculation behaviour of china clay - polyacrylamide suspensions. Powder Tech. vol 17, 207 - 212

Estcourt A. (1981) The filtration of flocculated kaolin suspensions. Chem Eng. Undergraduate Project, University of Cape Town, unpublished.

Ferris A.P. and Jepson W.B. (1975) The exchange capacities of kaolinite and the preparation of homoionic clays. Jou. Coll. Int. Sci. vol 51, 245 - 259.

Flegmann A.W., Goodwin J.W. and Ottewill R.H. (1969) Rheological studies on kaolinite suspensions. Proc. Brit. Ceram. Soc. No. 13, 31 - 45.

Frith V. (1981) Image analysis using a digitizing planimeter. Honours Project - University of Cape Town, unpublished.

Gregory J. (1969) Flocculation of polystyrene particles with cationic polyelectrolytes. Trans. Farad. Soc. vol 65, 2260 - 2268.

Gregory J. (1973) Rates of flocculation of latex particles by cationic polymers. Jou. Coll. Int. Sci. vol 42, 448 - 456.

Gregory J. (1978) Flocculation by inorganic salts. in The Scientific Basis of Flocculation. NATO Advanced Studies Series E - No 27 (ed Ives K.J.) Sijthoff and Noordhoff - Netherlands, 89 - 98.

Gregory J. (1978) Effects of polymers on colloid stability in The Scientific Basis of Flocculation. NATO Advanced Studies Series E No27 (ed Ives K.J.). Sijtoff and Noordhoff - Netherlands, 101 - 130.

Grim R.E. (1968) Clay Mineralogy. McGraw Hill Book Company New York (1st edition revised) particularly 193 - 225.

Griot O. and Kitchner J.A. (1965) Role of surface silanol groups in the flocculation of silica suspensions by polyacrylamide. Trans. Farad. Soc. vol 61, 1026 - 1038.

Habib M.A. and Bockris J. O'M (1980) Specific adsorption of ions. in Comprehensive Treatize of Electrochemistry vol 1 (ed Bockris J. O'M, Conway B.E. and Yaeger E.) Plenum Press, New York, 135 - 220.

Hall E.S. (1965) The zeta-potential of aluminium hydroxide in relation to water treatment coagulation. J. Appl. Chem. vol 15, 197 - 205.

Hall E.S. (1966) Electrokinetic studies of dispersions of clay in hydrolysed aluminium solutions. Disc. Farad. Soc. No. 42, 197 - 203.

Healy T.W. (1961) Flocculation - dispersion behaviour of quartz in the presence of a polyacrylamide flocculant. Jou. Coll. Sci. vol 16, 609 - 617.

Healy T.W. and LaMer V.K. (1962) The adsorption - flocculation reactions of a polymer with an aqueous colloidal dispersion. Jou. Phys. Chem. vol 66, 1835 - 1838.

Healy T.W. (1971) General Discussion. Disc. Farad. Soc. No 52, 313.

Heckroodt R.O. (1979) Ann. Geol. Survey of South Africa, 9 - 13.

Hesselink F.Th. (1977) On the theory of polyelectrolyte adsorption. Jou. Coll. Int. Sci. vol 60, 448 - 466.

Hinze J.O. (1959) Turbulence - An introduction to its mechanism and theory. McGraw Hill Book Company, New York.

Hudson H.E. (1965) Physical aspects of flocculation. Jou. Am. Wat. Works Assn. vol 57, 885 - 892.

Hudson H.E. and Wagner E.G. (1981) Conduct and uses of jar tests. Jou. Am. Wat. Works. Assn. vol 73, 218 - 223.

Hughes M.A. (1977) Coagulation and Flocculation, in Solid-liquid Separation (ed Svarvosky L.) Butterworths London.

Hunter R.J. and Alexander A.E. (1963) Surface properties and flow behaviour of kaolinite Parts I, II and III. Jou. Coll. Sci. vol 18, 820 - 832; 833 - 845; 846 - 862.

Hunter R.J. (1966) The interpretation of electrokinetic potentials. Jou. Coll. Int. Sci. vol 22, 231 - 239.

Hunter R.J. and Wright H.S.L. (1971) The dependance of electrokinetic potential on concentration of electrolyte. Jou. Coll. Int. Sci. vol 37, 564 - 580.

Iler R.K. (1973) Effect of adsorbed alumina on the solubility of amorphous silica in water. Jou. Coll. Int. Sci. vol 43, 399 - 420.

Ives K.J. (1978) Experimental methods (2). in The Scientific Basis of Flocculation. NATO Advanced Studies Institute Series E, No. 27 (ed Ives K.J.) Sijthoff and Noordhoff, Netherlands, 165 - 191.

Jankovics L.(1965) Effect of agitation and molecular weight on polymer adsorption and deflocculation. Jou. Appl. Polymer Sci. vol 9, 545 - 552.

Jepson W.B., Jeffs D.G. and Ferris A.P. (1976) The adsorption of silica on gibbsite and its relevance to the kaolinite surface. Jou. Coll. Int. Sci. vol 55, 454 - 461.

Kane J.C., LaMer V.K. and Linford H.B. (1963) The filtration of silica dispersions flocculated by high polymers. J. Phys. Chem. vol 67, 1977 - 1981.

Kane J.C., LaMer V.K. and Linford H.B. (1964) Filtration and electrophoretic mobility studies of flocculated silica suspensions. J.Am.Chem Soc. vol 86, 3450 - 3453.

Kitchener J.A. (1978) Flocculation in mineral processing. in The Scientific Basis of Flocculation. NATO Advanced Studies Institute Series E, No. 27 (ed. Ives K.J.) Sijthoff and Noordjoff. Netherlands, 283 - 328.

LaMer V.K. and Healy T.W. (1963) Adsorption - flocculation reactions of macromolecules at the solid liquid interface. Review Pure Appl. Chem. vol 12, 112 - 133.

LaMer V.K. (1966) Filtrations of colloidal dispersions flocculated by anionic and cationic polyelectrolytes. Disc. Farad. Soc. No 42, 248 - 254.

Levine S. and Smith A.L. (1971) General discussion. Disc. Farad. Soc. No 52, pg 312.

Linke W.F. and Booth R.B. (1960) Physical chemical aspects of flocculation by polymers. Trans. Am. Inst. Min. Mech. Pet. Eng. vol 217, 364 - 371.

Lyklema J. (1976) Inference of polymer adsorption from electrical double layer measurements. Pure and Applied Chem. vol 46, 149 - 156.

Lyklema J. (1978) Surface chemistry of colloids in connection with stability. in The Scientific basis of Flocculation. NATO Advanced Studies Series E No. 27 (ed Ives K.J.) Sijthoff and Noordhoff - Netherlands, 3 - 36.

Lyklema J. (1981) Progress in interfacial chemistry in relation to colloid stability. Pure and Applied Chem. vol 53, 2199 - 2209.

Macefield I.R. (1978) Determination of polyacrylamide using a turbidimetric technique. Allied Colloids Communication (unpublished).

MacKenzie J.M.W. (1971) Zeta-potential studies in mineral processing : measurement techniques and applications. Min. Sci. Eng. Vol 3, 25 - 43.

Matijevic E.(1966) General Discussion. Disc. Farad. Soc. No.42, 106 - 107.

Matijevic E. (1977) The role of chemical complexing in the formation and stability of colloidal dispersions. Jou. Coll. Int. Sci. vol 58, 374 - 389.

McCarthy M.F. and Olson R.S. (1959) Polyacrylamides for the mining industry, Mining Engineering. vol. 10, 61 - 65.

Michaels A.S. and Morelos O. (1955) Polyelectrolyte adsorption by kaolinite. Ind. Eng. Chem. vol. 47, 1801 - 1809.

Michaels A.S. and Bolger J.C. (1962) Settling rates and sediment volumes of flocculated kaolin suspensions. I and EC Fund. vol 1, 24 - 33.

Mori S., Okamoto H., Hara T. and Aso K. (1980) An improved method of determining the zeta-potential of mineral particles by microelectrophoresis. Int. Sym. of Fine Particle Processing. Las Vegas. Nevada (ed. Samasundaran P.), 632 - 651.

Mortensen J.L. (1957) Adsorption of hydrolysed polyacrylonitrile on kaolinite:I Effect of exchangeable cation and anion. Proc. Soil. Sci. Soc. Am., vol 21, 385 - 388.

Mortensen J.L. (1959) Adsorption of hydrolysed polyacrylonitrile on kaolinite : II Effect of solution electrolytes. Proc. Soil Sci. Soc. Am., vol 23, 199 - 202.

Napper D.H. and Hunter R.J. (1972) Hydrosols. in Surface Chemistry and Colloids; vol 7, Physical Chemistry Series One. (Kerker M. volume editor. Buckingham A.D. series editor) Butterworths, London, 241 - 300.

Ninham B.W. (1981) Surface forces - the last 30A. Pure and Appl. Chem. vol 53, 2135 - 2147.

Overbeek J.Th.G. and Lyklema J. (1959) Electric Potentials in Colloidal Systems. in Electrophoresis. vol I, (ed Bier M.) Academic Press New York. Chapter 1.

Overbeek J.Th.G. (1976) Polyelectrolytes, Past, Present and Future. Pure and Appl. Chem., vol 46, 91 - 101.

Overbeek J.Th.G. (1977) Recent developments in the understanding of colloid stability. Jou. Coll. Int. Sci., vol 58, 408 - 422.

Overbeek J.Th.G. and Wiersma P.H. (1979) The interpretation of electrophoretic mobilities. in Electrophoresis vol 2, (ed Bier M.) Academic Press, New York, Chapter 1.

Overbeek J.Th.G. (1980) The Rule of Shulze and Hardy. Pure Appl. Chem. vol 52, 1151 - 1161.

Packham R.F. (1965) Some studies of the coagulation of dispersed clays with hydrolysing salts. Jou. Coll. Sci. vol 20, 81 - 92.

Packham R.F. (1972) The laboratory evaluation of polyelectrolyte flocculants. Br. Polymer J. vol 4, 305 - 315.

Parker D.S., Kaufman W.J. and Jenkins D. (1972) Floc breakup in turbulent flocculation processes. Jou. San. Eng. Div: Proc. Am. Soc. Civ. Eng. vol 98, 79 - 99.

Parks G.A. (1965) The isoelectric points of solid oxides, solid hydroxides and aqueous hydroxo complex systems. Chem.Rev. vol 65, 177 - 198.

Quirk J.P. (1960) Negative and positive adsorption of chloride by kaolinite. vol 188, 253 - 254.

Reich I. and Vold R.D. (1959) Flocculation - deflocculation in agitated suspensions I. carbon and ferric oxide in water. Jou. Phys. Chem. vol 63, 1497 - 1501.

Richardson M.J. (1964) The direct observation of polymer molecules and determination of their molecular weight. Proc.Royal Soc. A279, 50 - 61.

Ries H.E. and Meyers B.L. (1968) Flocculation mechanism: charge neutralization and bridging. Science, vol 160, 1449 - 1450.

Ries H.E. (1970) Microelectrophoresis measurements on polymer flocculants alone and in excess with model colloids. Nature, vol 226, 72 - 73.

Roberts K., Kowalewska J. and Friberg S. (1974) The influence of interactions between hydrolysed aluminium ions and polyacrylamides on the sedimentation of kaolin suspensions. Jou. Coll. Int. Sci. vol 48, 361 - 367.

Rochon T.G. (1961) Resinography of high polymers. Anal. Chem. vol 33, 1810 - 1816.

Rushton J.H., Costich E.W. and Everett H.J. (1950) Power characteristics of mixing impellers, Part I and II. Chem. Eng. Progress, vol 46, 395 - 404 and 467 - 476.

Sakaguchi K. and Nagase K. (1966) The flocculation of kaolin and precipitated $CaCO_3$ by polymers. Bull. Chem. Soc. Japan vol 39, 88 - 91.

Sarkar N. and Teot A.S. (1973) Coagulation of negatively charged colloids by anionic polyelectrolytes and metal ions. Jou.Coll. Int. Sci. vol 43, 370 - 381.

Schamp N. and Huylebroeck J. (1973) Adsorption of polymers on clays. Jou. Polym. Sci. Symposium No. 42, 553 - 562.

Scholfield R.K. and Samson H.R. (1954) Flocculation of kaolinite due to the attraction of oppositely charged crystal faces. Disc. Farad. Soc. No. 18, 135 - 145.

Shyluk W.P. and Stow F.S. (1969) Aging and loss of flocculation activity of aqueous polyacrylamide solutions. J. Appl. Polym. Sci. vol 13, 1023 - 1036.

Silberberg A. (1962) The adsorption of flexible macromolecules. Part I and II. J.Phys. Chem. vol 66, 1872 - 1883 and 1884 - 1907.

Silberberg A.(1967) Adsorption of flexibile macromolecules. III. Generalized treatment of the isolated macromolecule; the effect of self exclusion. J. Chem. Phys.vol 46, 1105 - 1114.

Slater R.W. and Kitchener J.A. (1966) Characteristics of flocculation of mineral suspensions by polymers. Disc. Farad. Soc. No. 42, 267 - 283.

Slater R.W., Clark J.P. and Kitchener J.A. (1969) Chemical factors in the flocculation of mineral slurries by polymeric flocculants. Proc. Brit. Ceram. Soc. No 13, 1 - 12.

Smith B.H. and Emerson W.W. (1976) Exchangeable aluminium on kaolinite. Aust. J. Soil. Res. vol 14, 43 - 53.

Somasundaran P. (1980) Principles of Flocculation, Dispersion and Selective Flocculation. Int. Symp. of Fine Particles Processing (2 vols) Society of Mining Engineers (ed. Somasundaran P.) 947 - 976.

Spielman L.A. (1978) Hydrodynamic aspects of flocculation. in The Scientific Basis of Flocculation. NATO Advanced Studies Institutes Series E, No.27, (ed Ives K.J.) Sijthoff and Noordhoff Netherlands, 63 - 88.

Stromberg R.R. (1968) Polymer adsorption on substrates. in Interface Conversion for Polymer Coatings (ed Weiss P. and Cheever G.D.) Elsevier, N.Y.

Stumm W. and Morgan J.J. (1962) Chemical aspects of coagulation. Jou. Am. Wat.Works Assn. vol 54, 971 - 994.

Stutzmann Th. and Siffert B. (1977) Contribution to the adsorption mechanism of acetamide and polyacrylamide on clays. Clay Min, vol 25, 392 - 406.

Sutherland D.N. and Tan C.T. (1970) Sedimentation of a porous sphere. Chem. Eng. Sci., vol 25, 1948 - 1950.

Swartzen-Allen S.L. and Matijevic E. (1974) Surface and colloid chemistry of clays. Chem. Rev. vol 74, 385 - 400.

Swift D.F. and Friedlander S.K. (1964) The coagulation of hydrosols by Brownian motion and laminar shear flow. Jou. Coll.Sci; vol 19, 621 - 624.

Szczypa J., Monies A. and Sprycha R. (1976) Some remarks on flocculation of calcium carbonate in aqueous suspension with a nonionic flocculant and electrical surface charge of flocculated particles. Coll. and Polym. Sci. vol 254, 606 - 607.

Theng B.K.G. (1982) Clay-Polymer Interactions: Summary and Perspectives. Clay Clay Min. vol 30, 1 - 10

Thomas D.G. (1964) Turbulent disruption of flocs in small particle size suspensions, J. A.I.Ch E. vol 10, 517 - 523.

Tomi D.T. and Bagster D.F. (1978) The behaviour of aggregates in stirred vessels. Parts I and II, Trans. Inst. Chem. Eng. vol 56, 1 - 8 and 9 - 18.

Tomi D.T. and Bagster D.F. (1980) The behaviour of aggregates in stirred vessels. Mat. Sci. Eng. vol 12, 3 - 19.

van Lierde A. (1980) Behaviour of quartz suspensions in the presence of calcium ions and acrylate polymers. Int. Jou. Min. Processing vol 7, 235 - 243.

van Mengen W. and Snook I. (1978) Statistical mechanical approach to phase transitions in alloys. Disc. Farad. Soc., No.65, 92 - 100.

van Olphen H. (1963) An Introduction to Clay Colloid Chemistry, Wiley Interscience, New York.

Vincent B. (1974) The effect of adsorbed polymers on dispersion stability. Advances in Colloid and Interface Science, vol 4, Elsevier, Amsterdam, 193 - 277.

Vrij A. (1976) Polymers at interfaces and the interactions in colloidal dispersions Pure and Appl. Chem. vol 48, 471 - 483.

Walles W.E. (1968) Role of flocculant molecular weight in the coagulation of suspensions Jou. Coll. Int. Sci. vol 27, 797 - 803.

Wiese G.R., James R.O. and Healy T.W. (1971) Discreteness of charge and solvation effects in cation adsorption at the oxide water interface. Disc. Farad. Soc. No. 52, 302 - 323.

Williams D.J.A. and Williams K.P. (1978) Electrophoresis and zeta potential of kaolinite. Jou. Coll. Int. Sci, vol 65, 79 - 87.

Worrall W.E. and Ryan W. (1960) Flow properties of monoionic clay suspensions. Trans. VII International Ceramic Congress, 421 - 433.