

A STUDY OF THE FLOCCULATION OF
MINERAL SUSPENSIONS BY POLYMERS

A thesis submitted for the degree of Doctor
of Philosophy in the University of London

by

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September 1967

SUMMARY

The thesis opens with a review of the literature concerning flocculation of mineral suspensions by polymer compounds. Concepts of flocculation are considered from two points of view - namely, the physical and chemical aspects. The gaps and apparent contradictions found in the literature led to the greater part of the present study.

An apparatus has been developed to determine, on the same sample, the several established empirical indices of flocculation. The polyacrylamide-fluorite system has been studied in detail. The results showed that, while the permeability of the filter-cake provides a comparative index of flocculation, the quantitative theory developed by La Mer, Smellie and Healy, relating the permeability to the degree of flocculation and polymer concentration, is invalid. This theory was shown to rest on an erroneous assumption about the origin of the permeability maximum and an incorrect physical model of flocculation. Further data obtained from the flocculation characteristics of fluorite and hematite suspensions, with a range of flocculants derived from polyacrylamide, provided support for the bridging theory of flocculation. The influence of the method of mixing and polymer addition was also investigated.

A technique was devised to determine trace concentrations of an anionic polyacrylamide in solution, and this was used in a detailed investigation of the flocculation characteristics of the

fluorite - hydrolysed polyacrylamide system. The effects of pH and of a neutral salt were determined and the results clearly indicated that, while adsorption was indispensable, optimum flocculation was obtained only with maximum extension of the polymer molecules. This property, itself, was strongly dependent on the pH and the ionic strength of the medium.

The mechanism of adsorption of polyacrylamide on ionic crystals, such as calcium fluoride, has been considered and the possibility of dipole interaction of amide groups with the electrostatic field of the lattice has been suggested.

The flocculating action of anionic polyacrylamides with silica suspensions and of cationic polyacrylamides with alumina suspensions was found to be strongly influenced by the concentration of Ba^{++} and $(\text{HPO}_4)^{--}$ respectively. A possible adsorption mechanism has been suggested, based on the interplay of electrostatic forces of repulsion and attractive chemical forces.

ACKNOWLEDGEMENTS

I should like to express my sincere gratitude to Dr. J.A. Kitchener for his guidance and encouragement over the past three years.

I should like to thank my friends and colleagues in the Royal School of Mines for their many assistances and useful discussions. My thanks also to Mr. E.A. Gill of B.T.I. Limited for his provision of information and experimental polymer samples.

Finally I should like to thank Rio Tinto Zinc Limited for the provision of a Research Bursary held during the tenure of this work.

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CHAPTER I

INTRODUCTION

The separation of suspended solids from a liquid is an important process in the beneficiation of minerals, the purification of water and the treatment of industrial effluents. Agglomeration of the dispersed particles is usually beneficial to the solid-liquid separation and is commonly induced by addition of electrolytes or water-soluble polymers. The mechanism of aggregation in the two cases is different and it has been proposed (1) that the action of polymers should be known as flocculation. This convention will be followed in the present thesis.

The first flocculating agents (flocculants) were based on naturally occurring polymeric materials (starches, glues etc.). More recently, synthetic flocculants have been developed which are even more efficient, and this class is potentially the most important. It is generally accepted that such flocculants act by adsorption on to the surface of the suspended particles followed by the formation of physical "polymer bridges" between the particles. However, the choice of a flocculant for a particular suspension is still largely determined by trial and error. In order to be able to forecast a suitable flocculant in any particular suspension a more detailed understanding is required of the surface chemistry of the dispersed phase and the adsorption characteristics of the polymers. In most industrial operations such systems are ill defined.

Suspensions of essentially insoluble material can be classified according to the size of the particles. Very persistent, if not actually stable, suspensions may be formed with fine colloidal particles (equivalent diameter less than about 1μ). The sedimenting effect of gravity is then overcome by the dispersing effect of Brownian motion. Coarser particles are relatively unaffected by Brownian motion and settle under the force of gravity according to Stokes's law. Suspensions of finely ground minerals fall into this category.

Colloidal systems have been the subject of considerable laboratory investigation and, in principle, the factors governing their stability should extend to the suspensions of coarser particles. It has long been established that particles in a stable aqueous suspension are electrically charged, either positively or negatively, and the electrostatic forces of repulsion prevent the particles coagulating.

The surface charge on a particle may arise from three basic mechanisms:

- 1) Dissociation of the surface of an ionic lattice into constituent ions renders the surface charge very dependent on those ions which can be incorporated into the lattice e.g. Ca^{++} in a CaF_2 sol. The concentration of these "potential determining ions" may be adjusted so that the average charge on the particle surface is zero - the so-called zero point of

charge (z.p.c.). Under these conditions no forces of repulsion exist and rapid coagulation occurs.

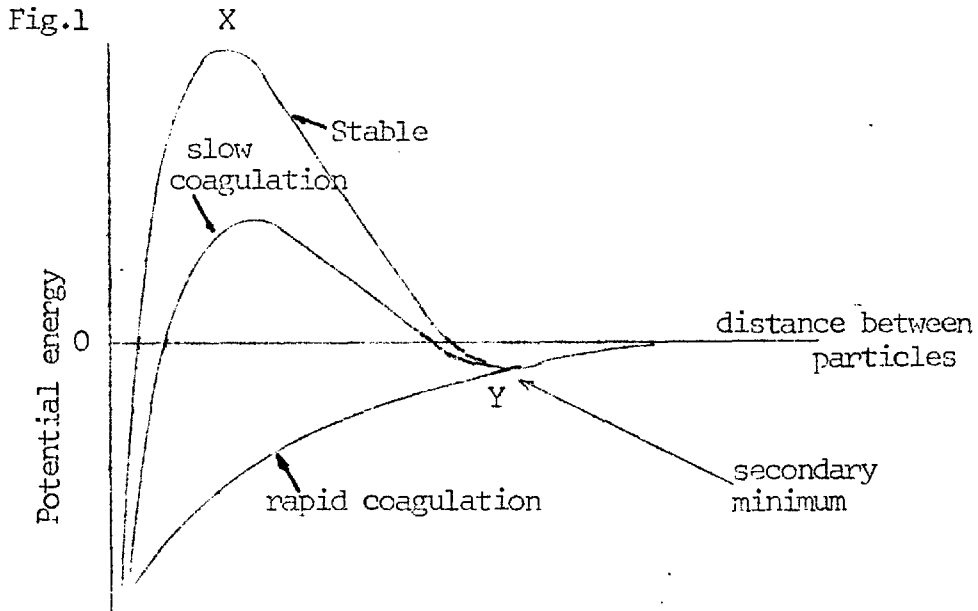
- 2) The charge may alternatively be determined by the chemisorption of a specific ion from solution, e.g. phosphate ions in an alumina sol.
- 3) Of a different nature, an internal lattice defect or ion substitution can be the source of a charge at a particle surface, e.g. clays and zeolites.

Current theories place little emphasis on surface defects although the high surface energy associated with edges, cleavage planes, dislocations etc., may be expected to influence the surface charge. This might be of considerable importance in suspensions of finely ground minerals, as these are virtually always impure, heterogeneous, and mechanically disturbed solids.

The "electrical charge" exhibited by small particles is not a net electrostatic charge but an electrical double layer, one set of ions fixed to the surface of the particle while the "counter-ions" of equal and opposite charge exist in the surrounding solution. It is an overlapping between the diffuse parts of the electrical double layers of two particles which gives rise to the electrostatic forces of repulsion. In a stable suspension these forces predominate; in a coagulating system a force of attraction is the operative factor. This has been identified as the London-van der Waals force of attraction (2).

The net force between two particles is obtained by summing the forces of repulsion and London-van der Waals force of attraction. Whilst the latter is determined only by the nature of the solid particles and the dispersion liquid, the former is strongly dependent on electrolyte concentration and composition, and if the intensity of the double layer is sufficiently reduced coagulation occurs. Indifferent electrolytes (i.e. not potential - determining ions) act by collapsing the diffuse part of the electrical double layer. With reduced thickness the repulsive forces may operate only at shorter inter-particle distances and in a coagulating system the force of attraction predominates. Compression of the double layer increases, at a particular electrolyte concentration, with increasing valency of the counter-ions (Schulze-Hardy Rule). Therefore suitably charged polyelectrolytes should be very efficient in causing coagulation.

The interplay of attractive and repulsive forces between colloidal particles is generally represented by potential energy curves (Fig. 1). The height of the energy barrier X determines the stability against coagulation during collisions brought about by Brownian motion. With relatively large particles (7μ) there is a "secondary minimum" (Y) of significant depth ($> 1 KT$) at large separations.



For 10μ particles of polystyrene in dilute salt solutions Schenkel and Kitchener (3) showed that coagulation takes place in this secondary minimum in the potential energy curves. The inter-particle distance was calculated to lie at $500 - 1000 \text{ \AA}$ in that system. This is explained as a balance between the London-van der Waals force and the repulsive force. The bonding of the particles in the secondary minimum is easily broken by a weak impulse, therefore this state of coagulation is reversible, whereas particles coagulated into the deep primary minimum are difficult to separate again.

The Adsorption of Polymers from Solution.

The efficiency of a flocculant is largely determined by its adsorption characteristics. The adsorption of macromolecules from solution differs considerably from that of monomers. This is due to two basic properties:

- 1) The free polymer molecule possesses a large number of internal degrees of freedom.
- 2) Adsorption is possible at a large number of adsorption sites along the polymer chain.

As a consequence, even after adsorption the polymer molecule still possesses a large number of degrees of freedom in comparison with an adsorbed monomer. Also, an adsorbed segment enhances the chances of adsorption of neighbouring segments by bringing them into close proximity of the surface.

Adsorption experiments show that a polymer can adsorb much more than a "monolayer" (all segments adsorbed) yet the shape of the isotherm precludes multilayer adsorption. It is postulated that adsorption occurs at only a fraction of the available segments and the unadsorbed segments extend into the solution (4)

The structure of the adsorbed layer is more completely discussed on Page 33.

Mechanism of Flocculation.

Simple qualitative tests indicate that flocculation is very different from coagulation. Efficient flocculation can be effected by very low dosages of polymer (in the order of a few p.p.m. in the liquid) and occurs within seconds of mixing the flocculant with the suspension. The large, loosely-textured, fluffy aggregates (flocs) settle rapidly and occupy a large final volume (under conditions of good flocculation).

These observations indicate that the effect of a flocculant is twofold - firstly, to increase the "stickiness" of the particles and secondly to form stronger inter-particle bonds than those present in coagulated systems. These requirements are satisfactorily incorporated into the "bridging" theory of flocculation whereby a macromolecule adsorbed by one particle extends sufficiently far into solution and is capable of being adsorbed also by another particle. This bridge is the basic link in the formation of the large, three dimensional, network of flocs.

There is considerable experimental evidence which although not absolutely proving this theory supports the hypothesis:-

a) Effect of Concentration of Polymer. At high-concentrations flocculants become ineffective. As more and more polymer is adsorbed the number of extended loops increases but at the same time the number of surface sites available for bridge formation is reduced and at high surface coverage this leads to a reduction in flocculation. La Mer and Smellie (5) calculated that for optimum flocculation the surface coverage should be about 50%. Adsorption studies, performed on a number of flocculant - mineral systems, report values between 10 and 33%. (6,7,8).

b) Effect of Molecular Weight of Flocculant. The influence of molecular weight has been the subject of extensive laboratory study. All workers have reported a continued improvement in flocculation with increasing molecular weight of the flocculant (9,10,11,12) apart from Healy and La Mer who found an optimum value (13). The

dimensions of a macromolecule increase with molecular weight. Therefore, with increasing size, the adsorbed molecule should extend further into solution and thus improve its inter-particle bridging capacity. This effect has been more closely examined by Sakaguchi and Nagase (11), using the polyacrylamide - calcium carbonate system. They have established a relationship between the size of a macromolecule (characterised by its intrinsic viscosity) and its efficiency as a flocculant. A steady improvement was noted which became much more rapid when the size of the free, unperturbed macromolecule was the same as, or greater than, the average distance between the dispersed particles.

Studies of various flocculant types have shown that for polymers of similar chemical nature a linear molecular chain is more effective than a cross-linked (14) or highly branched (15) one of similar molecular weight. This is also in accord with the idea of bridging.

c) Electron Micrographs. An electron micrograph of a kaolin suspension flocculated by a polysaccharide has been prepared by Audsley (16). It was considered likely that if flocculation is due to polymer bridging then the orientation of polymer chains in proximity to the particle surface would be observed by this technique. Although most of the structure was lost during sample preparation, a polysaccharide bridge extending between two particles was clearly visible. This work correlates with that of Fischer (17) who, using an equivalent technique, observed similar structures when a

polystyrene dispersion was treated with the calcium salt of a copolymer of vinyl acetate and the partial methylester of maleic acid.

d) Strength of the Floc. The coagulated sediment of a coarse suspension is readily redispersed by vigorous agitation (17) while similar flocculated material is far more resistant to shear. Although Read and Kitchener (18) have directly confirmed the mutual "adhesiveness" of flocculated particles by measuring the effect of flocculants on the adhesion of individual quartz particles to a polished silica plate no absolute measurements of adhesiveness are known.

Weitser and Paskutskaja (20) attempted to measure the mechanical strength of flocs in a clay - polyacrylamide system. Their method consisted of allowing the flocs to form and settle and then subjecting them to intensive agitation until the former dispersed state was regained. The results indicate that the resistance of the flocs to shear increased rapidly at low concentrations of polyacrylamide to an optimum value. Higher dosages of flocculant did not reduce the strength of the floc. An absolute measure of floc strength would be a considerable advantage in defining the fundamental properties of the flocculated state.

Many dilute solutions of flocculants are viscoelastic, but the possibility of flocculation occurring by extended segments entangling, physically or chemically (21) (e.g. H bonded), is

considered to be very limited (22), if it exists at all. In general, flocculation occurs at fairly low surface coverages and at high surface coverage stabilisation occurs when this mechanism would be imagined to be most effective. After all the polymers are spontaneously soluble in water.

Physical Aspects of Flocculation.

An important practical problem is assessing the effectiveness of flocculation with suspensions containing not only different size distributions but also different shape factors and densities. The classical methods of light-scattering and particle-counting are unsuitable and various authors have used different empirical indices of flocculation such as rate of fall of the division between flocculated material and the supernatant liquid, the clarity of that supernatant liquid, the volume of settled flocs and the filtration characteristics of those flocs. There does not appear to have been a full correlation between these various parameters and their usage is often controlled by their applicability to a particular system e.g. under laboratory conditions settling rates are visible only at fairly high solids concentration in the suspensions.

The filtration method developed by La Mer and Smellie (5,22-25) is the only parameter which has been subjected to theoretical analysis. These authors have presented considerable data in support of their various hypotheses and a critical assessment of their work is presented in Chapter IV.

Concentration of Flocculant.

It has already been reported that the flocculation of a colloidal system cannot be increased indefinitely. Beyond a certain "optimum concentration" the use of additional flocculant is detrimental. This effect has been related to the ability of adsorbed macromolecules to form a bridge to other particles. This is so reduced at high surface coverage that stabilisation of a suspension can occur.

The stabilising action of flocculant-type polymers in aqueous suspensions has two principal sources. The adsorption of a highly charged polyelectrolyte on to the surface of a particle could provide a high surface potential and charge density so that the electrostatic force of repulsion between similar particles would prevent their mutual approach to the distance at which van der Waals force of attraction could act. For non-ionogenic macromolecules a different mechanism is believed to exist. The van der Waals constant of the adsorbed layer is close to that of the solution so that the net van der Waals attractive force (solid plus adsorbed layer) is drastically reduced. "Steric" stabilisation is suggested when the adsorption of sufficiently large, flexible macromolecules may increase the distance of closest approach of two colliding colloidal particles to such an extent that the thermal energy would at any possible distance remain in excess of the negative potential energy (26,27). Steric stabilisation would, however, be ineffective unless the van der Waals constant for the adsorbed layer was close to that of the dispersion medium.

Addition of Polymer.

Industrial operating manuals giving instructions on the use of flocculants stress the importance of the conditions of addition on subsequent flocculation (28,29). For the most efficient use of the flocculant it should be uniformly distributed throughout the suspension. For, if localised excess concentrations do occur, then some particles may be undertreated while others may adsorb an excess and pass into stabilised state. This is most likely to occur when a concentrated solution of flocculants is used or the suspension is inadequately stirred during addition (or both). Linke and Booth (9) showed that the "haze" of suspended particles left in the supernatant liquid after flocculation had occurred, even at low concentrations, was due to particles which had adsorbed a disproportionately large amount of flocculant and become stabilised.

McCarty and Olsen (30) presented data showing the improvement in flocculation occurring when multistage addition of dilute flocculant solutions is employed. Kuz'kin and Nebera (31) suggest that vigorous agitation during polymer addition should improve distribution. This, however, should be carefully applied as polymer degradation can occur at high shear rates.

These findings, however, do not exclude the possibility of obtaining successful flocculation by other techniques; in one unusual case solid flocculant was added to a pulp "with good results" (32), although it is likely that a more conventional method would have been more efficient.

The Effect of Agitation.

a) During floc formation - In a slowly coagulating colloidal suspension collision frequency between the particles is determined by Brownian motion (perikinetic flocculation). Brownian motion has little effect, however, on the diffusion of larger particles, of the order of $1 - 10\mu$ (34, 35) and it is necessary to apply gentle agitation to the suspension to attain a convenient rate of flocculation (orthokinetic flocculation). This is especially important in dispersions of low solids content and, in the treatment of potable water, floc growth is prolonged for a considerable time. This has the advantage of not only producing large flocs but also promoting the "scavenging" action of these flocs where individual particles are "swept up" and united with the larger floc. It is a justifiable criticism of most industrial operations that the large flocs, once formed, are allowed to settle and that no attempt is made to use their scavenging action on particles which remain in suspension.

The kinetics of flocculant adsorption are diffusion-controlled (35) and agitation would promote more rapid adsorption which could be beneficial to flocculation.

b) The flocculated suspension - The effect of agitation on a flocculated suspension is complex. It is generally agreed that, although flocs are resistant to immediate redispersion, prolonged or intense agitation can cause considerable deflocculation (7, 9, 30, 36) (i.e. floc breakdown and redispersion). Nevertheless, although

some workers have found an optimum time of agitation to produce maximum flocculation(22,37,39)and Kane et al (38)reported that the polyacrylamide-silica system was independent of duration of agitation.

Various suggestions have been made to explain mechanical deflocculation.

1 - Polymer Desorption.

The adsorption of most flocculants is substantially an irreversible reaction. For desorption to occur it would be necessary for all or almost all of the adsorbed segments to be simultaneously released and statistically this is considered to be an unlikely eventuality (39). Also, most of these systems are irreversibly deflocculated (7). and this indicates some other mechanism.

2 - Rupture of the Polymer Chain.

If a polymer bridge were to be broken during agitation then the reduced bridging capacity of the remaining adsorbed fragment of the chain could lead to permanent deflocculation. The energy required to break a C-C bond is considerable and bridges presumably contain many molecules: however, it is difficult to define the hydraulic forces present within a floc while it is being stirred.

3 - Reduction in Bridging Capacity.

The initial floc breakdown is usually accepted as a rupture through the weakest point in the floc. Linke and Booth (9) suggested that when this breakdown occurs in the presence of excess polymer in solution this is adsorbed on the fresh surfaces presented. The

floc would be unable to reform because of a reduction in the number of surface sites available for bridge formation. Jankovics (40) envisaged that, in the presence of large excess dosages, deflocculation would result in stabilised primary particles.

La Mer and Healy (39) and Kragh and Langston (7) considered deflocculation when there is no unadsorbed polymer present. If the particles are kept apart by agitation over a long period there could be a slow re-arrangement of the polymer molecule at the interface; involving the adsorption of extended chains on to the surface of the particle so that they are no longer able to span the gap between the particles and form bridges.

Linke and Booth (9) reported that the stability of flocs to agitation (at a particular flocculant to solids ratio) increases with increasing solids content. They considered re-formation of broken flocs as being determined by their time of "free travel" between collisions. When the number of flocs is small the time between collisions is longer and these authors also envisaged a "flattening" of the adsorbed polymer under such conditions, which further increases the difficulty of flocculating low solids content suspensions.

This viewpoint is supported by the adsorption data of Peterson and Kwei (41) for polyvinylacetate adsorbed on to chrome plate and also by the theoretical work of Silberberg (42). These workers postulated that under equilibrium conditions much of the chain will lie flat at the surface, except when there is rather weak

segment-surface interaction. However, these findings were disputed by Eirich et al (43,44). In a recent series of papers they have measured the thickness of the adsorbed layer for a number of different polymers. They found little distortion of the solvated macromolecule when it is adsorbed and, therefore, they concluded that under equilibrium conditions the polymer does not lie flat at the surface. If the number of adsorbed segments were to increase with time this could presumably occur in a static floc where the polymer chain has formed a bridge between two particles, this would result in the particles being brought into closer contact, i.e. a spontaneously dewatering floc and low floc volume. This is not the case.

4 - Exposure of Fresh Surface.

Whilst the possibility of "flattening" of the adsorbed polymer is not precluded, the effect of heterogeneous polymer adsorption within a floc has not been fully considered. Few suspensions are made monodisperse simply by stirring, and, flocs will consist of aggregates of "clumps". The occlusion of untreated particles into a floc network and multistage addition of flocculant would also provide an uneven distribution of polymer within a floc. If such a structure were to be mechanically degraded, the adsorbed macromolecule, by virtue of its large number of degrees of freedom, could penetrate into regions of low polymer concentration, e.g. adsorption occurring on the interlamellar surfaces of clays (45). This would reduce the number of macromolecules available for

bridging when agitation was stopped. This model would also explain the restoration of a mechanically degraded floc to its original flocculated condition by addition of a small f_k^* fraction (10-20%) of the original flocculant dosage (30). Similarly, the essentially non-porous, siliceous suspensions encountered in South African gold mine processing are almost entirely unaffected by agitation; although some reduction in floc size occurs during agitation large flocs reform rapidly on standing (46). Similar non-porous material was employed in the experimental work of Kane et al (38) where no deflocculation was observed. The other three theories, already mentioned, would not account for these observations.

Solids Content of Suspensions.

The importance of orthokinetic flocculation on the flocculation of low solids content suspensions has been mentioned above. At higher solids content the increased frequency of particle collisions should provide a more efficient usage of the polymer, but this would be very dependent on the uniformity of mixing. In fact, at very low solids content (less than 0.1% by weight solids), a linear relationship between solids content and optimum polymer concentration has been found (8,6). Similar relationships have been established, for solids content of up to 50%, for the polyacrylamide-silica system (9,47). However, La Mer et al (38,23) found that such relationships are very dependent on the system and they suggested that "the strength of polymer adsorption" is an important parameter (38).

Particle Size.

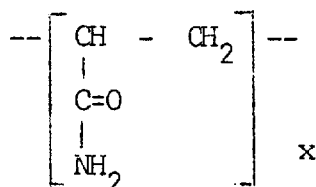
Again there is no uniformity of opinion on the relationship between specific surface area and optimum polymer concentration. While Linke and Booth (9) found that the optimum polymer concentration to solid ratio was directly proportional to the specific surface area, La Mer et al(23) found the ratio proportional to the square of the specific surface area. However, the conclusions of the former authors that the mechanism of polymer adsorption and floc formation are independent of particle size are probably justifiable in both instances.

Chemical Aspects of Flocculation.

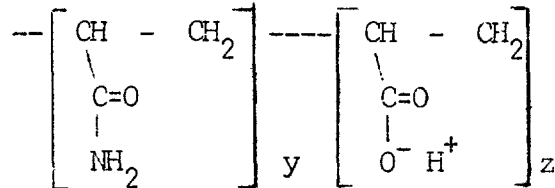
A wide range of natural and synthetic polymeric materials are effective as flocculants. They may be classified as cationic or anionic polyelectrolytes or non-ionic polymers.

The most extensively employed naturally occurring polymers are based on polysaccharides (gums, starches etc.) (15) and gelatine (7). These are generally of a complex nature and may be chemically modified to fit into any of the above categories.

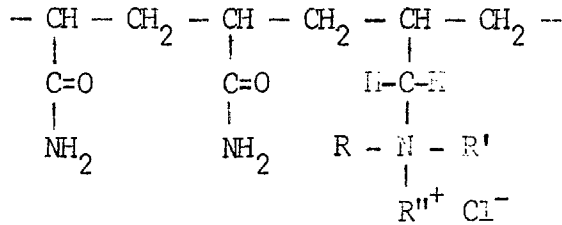
Of greater effectiveness (on weight basis) are the new synthetic polymers many of which are based on polyacrylamide.



Polyacrylamide itself is non-ionic but can be converted by controlled alkali hydrolysis to a complete or partial anionic character.



Cationic polymers can be prepared by copolymerising acrylamide with varying amounts of quaternary amines (9).



Although pure polyacrylamide is presented as being non-ionogenic, in its commercial preparation a small percentage, generally less than 1%, of the amide groups are hydrolysed to carboxyl groups.

Many other synthetic flocculants based on polyethylene oxide (48), copolymers of maleic anhydride, (49) polyethyleneimine (50) etc. are also available.

The importance of the groups along the polymer chain does not rest solely with providing functional groups for adsorption. A polyelectrolyte possesses a large number of similarly charged, mutually repelling groups along the polymer chain and this can result in considerable extension of the chain i.e. an effective

increase in the dimensions of the macromolecule. The close relationship between size of the flocculant molecule and its ability to flocculate have been previously reported (c.f. Page 15) therefore, it would appear that the nature of the functional groups could be equally important.

Adsorption Mechanisms.

When a macromolecule is adsorbed from solution bonds between polymer segment and the surface are formed in preference to the existing segment-solvent and solvent-surface bonds. Thus, although the driving force for polymer adsorption is the polymer-surface interaction energy, the solvent can exert a considerable influence.

Various polymer segment-surface interaction mechanisms have been postulated for a number of different mineral-flocculant systems.

Electrostatic Interaction.

Where a particle and a polyelectrolyte are of opposite sign adsorption always occurs. Kuz'kin and Nebera (31) suggested that electrostatic adsorption can also occur when only part of the surface is oppositely charged to the polyion, the mechanism being independent of the value of the average surface potential.

Hydrogen Bonds.

This is a common type of bond for organic compounds which contain a hydrogen atom attached to a strongly electro-negative atom (O,S,N). This mechanism has been shown to be responsible for

the adsorption of polyacrylamide and other flocculants on to fresh silica (51) and various clays (52,53,54,55). The bond energy for one segment-surface site interaction is 3.5 - 10 kcal/mole depending on the compounds involved (56); but as the adsorbate molecules are originally hydrogen-bonded to water, the difference in bonding energy is probably rather small.

Formation of Ionic Bonds.

Polyelectrolytes^{tes} which contain carboxylate, phosphate or sulphonate groups in their chains could, theoretically, be adsorbed by solids, having di or trivalent ions in their lattices, through the influence of ionic bonds. This mechanism has been cited for the adsorption of polyacrylic acid on to calcite and other minerals containing calcium where the formation of an insoluble deposit of calcium polyacrylate can be postulated (56). This mechanism is analogous to the use of minerals (e.g. Pb^{2+} with carboxylate soaps). However, no indisputable proof of this mechanism is known.

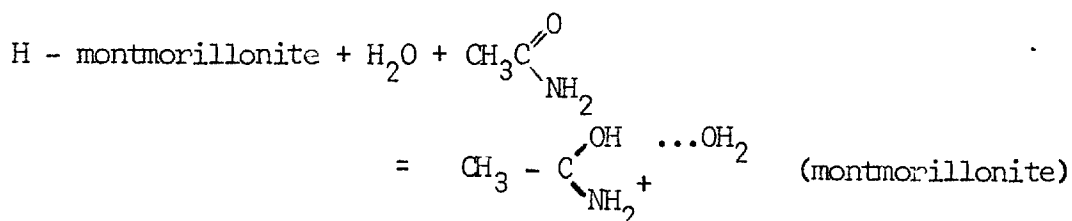
La Mer and Smellie (22) postulated that phosphorylated starches adsorbed on to solid calcium phosphate by the formation of an insoluble calcium complex. This has not been confirmed by recent work of Audsley (51) who considers adsorption of such polysaccharides to occur by hydrogen bonding.

Similarly, lime has been reported to increase the adsorption of guar gum on siliceous minerals(101) but this might alternatively

arise from a reduction of its solubility, rather than the participation of Ca^{2+} in the adsorption bond (57).

Adsorption of Amides.

The recent work of Talcun and Mortland (59,60) on the adsorption of primary, secondary and tertiary monomers on to various forms of montmorillonite indicates that a further mechanism may be responsible for the adsorption of polyamides. Although amides in aqueous solutions act as extremely weak bases these authors obtained evidence from infra-red spectroscopy that with aluminium and hydrogen forms of the clay the "highly acidic" nature of the surface may lead to protonation of the carbonyl bond so that the amide is electrovalently attached to the edges of the clay platelets. Viz.



They postulated a different mechanism for the adsorption of amides on to the copper, calcium and sodium forms of the clay. They considered that the amide group possesses a dipole $\text{R} - \text{C} \begin{array}{l} \nearrow \text{O}^- \\ \searrow \text{NH}_2 \end{array} +$ which interacts with the adsorbed ion to form an electrostatic bond.

Complex Formation.

Another possible contribution to the adsorption of polymers based on polyacrylic acid could be by complex association (110) with transition metal ions in mineral lattices. A similar possibility

exists for the adsorption of polyethylenimine. However, no examples of this mechanism are definitely known.

Although the basic driving force for the adsorption of a polymer is the segment-surface interaction energy, other independent parameters can effect the adsorption characteristics - notably the influence of the aqueous medium on the dissolved polymer.

Kinetics of Adsorption.

All published adsorption-time curves show the anticipated increase in the amount adsorbed with time, with an asymptotic approach to an "equilibrium" value. The initial adsorption of flocculants is very rapid, as successful flocculation is frequently observed within seconds of mixing the polymer solution with the suspension, whereas equilibration is slow.

The kinetics of adsorption are related to diffusion of the macromolecules; the adsorption rate rises sharply when the solution is intensely stirred (35,40). This rate rises with increasing temperature and diminishes as the molecular weight becomes greater (35). However, Healy (37) showed that adsorption of a partially hydrolyzed polyacrylamide was reduced at high shear rates and deduced that the polymer was adsorbed by only a small proportion of the segments and controlled by the shear rate at the surface of the particle. However, these results have not been confirmed.

Dependence on Molecular Weight.

The equilibrium amount of polymer adsorbed (weight per unit area) increases with increase in molecular weight (35).

The diffusion coefficient of macromolecules decreases with a rise in molecular weight, therefore, in a polymer solution showing a range of molecular weights preferential adsorption of the lower molecular weight species may occur (60). These molecules would be replaced later by larger molecules, in accordance with the equilibrium thermodynamic state (35).

Effect of Solvent.

More polymer is adsorbed from a 'poor' solvent than a 'good' one (4). In a poor solvent polymer coils are more tightly bunched together and may be expected to form more closely packed layers. Whilst desorption cannot often be effected by washing with pure solvent, replacing a bad solvent with a good one can remove the adsorbed layer.

Influence of the Adsorbent.

The effect of the adsorbent upon polymer adsorption is difficult to assess, since the detailed interactions of adsorbent, solvent, and polymer remain comparatively obscure. However, indirect studies on flocculation suggest that this is one of the most important parameters. The primary function of the adsorbent is to provide sites for polymer-surface interaction.

All available evidence supports the generalization that polyions will always adsorb on particles of opposite charge in aqueous suspensions. Where there is a marked variation in charge density on one particle (e.g. the surface and edges of clays) the polyions can adsorb on the local areas having the opposite charge, e.g. dispersion of clays by the adsorption of polyphosphates on the positive edges.

Hydrogen-bonding on to clay minerals occurs by surface hydroxyl (52,53,54,55) or oxygen groups (45). Griot and Kitchener (51) have shown that polyacrylamide is adsorbed on to silica at "isolated silanol groups." They found that certain forms of thermal silica powder and also freshly ground quartz lost their sensitivity to flocculation by non-ionic polyacrylamide after long immersion in water. This was shown to be associated with the disappearance of a bond in ^{the} infra-red spectrum ascribed to isolated silanol groups and although the "aged" suspensions were no longer susceptible to flocculation with polyacrylamide they were still amenable to flocculation by cationic polyelectrolytes. These authors found that the suspensions of talc (an aluminosilicate) behaved like silica; on the other hand alumina, kaolin and bentonite did not lose their susceptibility even after months of immersion in water. This aging process could account for some of the contradictory evidence found in the literature, as silica suspensions have been extensively studied, and the effect of sample treatment preparation has been ignored.

The adsorption of partially hydrolysed (anionic) polyacrylamide on to negatively charged kaolin (61,52) or silica (31) introduces a new complication. In this case there is a competing mechanism between hydrogen bond adsorption by the amide component and electrostatic repulsion between the particle and the similarly charged, ionised carboxyl groups. Adsorption can occur but this is dependent on both the charge of the particle and the degree of hydrolysis of the polymer. Kuz'kin and Nebera (31) suggested that a threshold zeta potential exists which determines whether adsorption can occur in a particular system, flocculation in such systems can be obtained only when the zeta potential has been reduced sufficiently to allow close approach of the polyelectrolyte molecules.

Schmidt and Eirich (63) also reported that increasing the number of ionized carboxyl groups in a series of vinyl acetate-crotonic acid copolymers reduces adsorption on anatase (TiO_2) bearing a like (negative) charge.

Structure of the Adsorbed Layer.

The work of Sakaguchi and Nagase (11) (see Page 15) indicates that the configuration of the solvated and the adsorbed macromolecules are closely related. The problem of the shape of non-ionic polymer molecules in solution can be treated in terms of a statistical coil in which there is an almost random distribution of segments. The average dimensions of the coil are dependent on the polymer-

solvent interaction, the size and number of the segments and any specific intra-molecular interaction (e.g. hydrogen-bonding) in the polymer (63).

The treatment given to polyelectrolytes in solution is modified by the change in shape occurring when their electrical free energy is altered by ionization and the presence of neutral salts. If the polymer molecule can undergo ionization (e.g. by changing the pH of a solution of polymethacrylic acid) electrostatic repulsion between the like charges introduced along the chain leads to a modification in its shape. When ionized, and in the absence of salts, these molecules are highly extended threads. Their effective length is sensitive to electrolyte concentration as this can cause a collapse of the electrical double layer surrounding the molecules and a consequent reduction in length.

Until recently (44) it has not been possible to measure the thickness of the adsorbed polymer layer directly. The theory of Simha, Frisch and Eirich (43) suggests that the thickness may be of the same order as the dimensions of the macromolecule in solution. Fontana and Thomas (64), however, concluded that 36% of the segments of poly-lauryl methacrylate were adsorbed from decalin on to silica. This is more in accord with the theory of Silberberg (42) who supposed that such interaction energies

(H-bonding) would result in almost all of the segments being adsorbed under equilibrium conditions. However, a theoretical study by Clayfield and Lumb (65) has indicated that the thickness of the adsorbed layer is a high fraction of the dimensions of the solvated molecule.

The recent work of Rowland and Eirich (44), based on measuring the flow of polymer solution through sintered filter discs, provides an accurate measure of the thickness of the adsorbed layer. These authors arrived at film thicknesses which were of the order of magnitude of the free coil diameters of the polymer in solution. They concluded that polymers adsorbed from solution in monolayers of compressed or inter-penetrating coils and that adsorbed films may consist of a dense layer immediately adjacent to the surface and a deep layer of loops extending into the solution. Also, that it is the segment-solvent interaction rather than the segment-surface interaction which dominates the conformation of the adsorbed chain. Finally, below some critical molecular weight, which varies with polymer and solvent, a much higher proportion of the segments lies directly at the surface.

This concept is of considerable importance in explaining the increased bridging capacity of higher molecular weight polymers. In the same way, increasing the size of a polyelectrolyte, by increasing the proportion of ionized groups, should also influence its bridging capacity. This was studied by Michaels and Morelos (52).

for the clay + hydrolysed polyacrylamide system. They found improved flocculation occurred when the number of carboxyl groups was increased. However, at high degrees of hydrolysis, the effect of increased polymer dimensions was offset by a reduction in adsorption (cf. page 33) and an optimum degree of hydrolysis for flocculation was about 30 %. This has been confirmed in recent work by Sakaguchi and Nagase (66).

The effect of Electrolytes on Flocculation.

The preliminary destabilisation of a suspension by the addition of an electrolyte prior to the use of a flocculant is a common industrial practice. Different types of electrolyte can be used although alum and ferric chloride are most widely employed. The function of these electrolytes is not simple; it is generally considered that their hydrolysis products lead to the formation of inorganic polymers which bind the particles together (67). This action is akin to bridge formation and these electrolytes should strictly be classified as flocculants.

Simple electrolytes can also be used to reduce the flocculant dosage, causing preliminary destabilisation to occur by a reduction in the surface potential or the thickness of the double layer. In such circumstances the flocculant would then form bridges between aggregates of coagulated particles instead of primary particles. A further effect of increased ionic strength could rest solely with reducing the thickness of the double layer without subsequent coagulation.

The adsorbed polymer might then be able to extend through the diffuse double layers of two particles to form a bridge. Previously the polymer might have been adsorbed within the double layer and double layer interaction would have resulted in stabilisation. This mechanism would explain the results of Robhun and Wachs (6) who found that although anionic polyacrylamide was adsorbed by both kaolinite and montmorillonite flocculation did not occur unless NaCl or CaCl₂ was present.

The major influence of electrolytes appears to be in modifying the surface of the particles so that adsorption can occur. In the literature two different mechanisms are cited:

- 1) Jones et al (14) found that at pH 7 unhydrolysed polyacrylamide was an ineffective flocculant for silica suspensions and that hydrolysed polyacrylamide acted as a dispersant unless calcium chloride was present, when the suspension could then be flocculated. Calcium ions were adsorbed on to silica, without causing charge reversal, and their action in this system was interpreted as providing an "ion bridge" between the silica and the polymer, presumably through the formation of calcium polyacrylate. However, the fact that hydrolysed polyacrylamide acted as a dispersant, in the absence of calcium ions, suggests it was already adsorbed and that calcium ions influenced bridging capacity rather than adsorption. Kuzkin and Nebera (31) also reported adsorption without subsequent

flocculation under similar conditions.

Mortensen (68,69) has suggested that a possible mechanism for the adsorption of hydrolysed polyacrylonitrile on to kaolinite would be through functional carboxyl groups interacting with divalent metal cations incorporated into the edges of the clay crystals.

2) Alternatively, the mechanism could be considered in terms of the change in surface potential which occurs in the presence of potential-determining ions. Mortensen found that there was a higher degree of adsorption in the presence of certain potential-determining ions. This was in the order $\text{Th}^{4+} > \text{Ca}^{2+} > \text{Ba}^{2+} > \text{H}^+$ $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+$ and this is approximately the same order as such cations reduce the zeta potential of kaolinite. Therefore, the mechanism could be represented as the competition between the electrostatic forces of repulsion between particle and polymer and a non-ionic force of adsorption, e.g. hydrogen bonding. Kuz'kin and Nebera (31) stated that the surface potential of silica has to be reduced, by adsorption of Ca^{++} , Fe^{3+} etc., before hydrolysed polyacrylamide can be adsorbed.

The same authors (12) also made a study of the adsorption of hydrolysed polyacrylamide on to alumina (corundum) and found a close relationship between the charge on the alumina particles (dependent on pH) and the amount adsorbed. When the suspension was highly positively charged (zeta potential $\approx +60\text{mV}$) there was 100% adsorption. The amount adsorbed remained almost constant until the

sign was reversed, (at pH 8.3) when a sharp decrease in adsorption occurred, corresponding to the increasing negative charge. Zero adsorption at pH 11 corresponded to a zeta potential of - 120 mV. At this pH the carboxyl groups are fully ionised therefore the polyion also has a maximum negative charge and the alumina is also negative. The adsorption energy is probably provided by hydrogen bonding between the amide group and Al - OH groups on the alumina surface (51). Flocculation was shown to be closely related to the amount of polymer adsorbed.

Griot and Kitchener (51) found that an "aged" suspension of silica (cf. page 32) whilst not sensitive to non-ionic polyacrylamide could be flocculated by it in the presence of high concentrations of NaCl. This effect they ascribed to an enhancement of the activity coefficient of the solvated polymer (incipient "salting out") so that adsorption could occur. A concentration of 4 - 5 N NaCl was needed.

The influence of salts and pH on the configuration of a polyion (cf. page 34) and its subsequent flocculation characteristics has been largely neglected. Although changing the size and conformation of a polyelectrolyte should have considerable influence on its bridging capacity and on its consequent flocculation characteristics no direct correlation has been attempted. MacKenzie (112) has been alone in suggesting that the suitability of certain flocculants may be established by referring to their configuration (by viscosity measurements) at different pH's.

Electrophoretic Mobility of the Floccs.

The problem of relating the electrophoretic mobility of a particle, carrying an adsorbed polymer layer, to its zeta potential is complicated, as viscous drag due to the thickness of the solvated sheath can provide anomalous results. Nevertheless apparent zeta potentials of floccs have been extensively measured and Riddick (70) has suggested that they correlate with overall flocculation characteristics.

In view of the wide range of flocculant types, varying from pure polyelectrolytes to completely non-ionic polymers, a constant relationship between apparent zeta potential and degree of flocculation would not be expected. The adsorption of a polyion on to an oppositely charged particle is determined by electrostatic forces of attraction. A consequent reduction in the surface potential could cause classical coagulation. With a large molecule, "bridging" could still contribute to flocculation but with low molecular weight material a reduction in the bridging capacity would increase the relative importance of coagulation. Any attempt to assess the significance of bridging with a low molecular weight polyion would be speculative. Using a low molecular weight (about 50,000) cationic polyelectrolyte Black et al (8) found that optimum flocculation of a negative clay suspension corresponded with very low electrophoretic mobility of the floccs. Similar observations have been made by Kane et al (71). When hydrolysed polyacrylamide (molecular weight 3

million and 30% carboxyl groups) is used to flocculate positive alumina suspensions, a dual adsorption mechanism of electrostatic interaction and hydrogen bonding is present. In this system considerable bridging would be expected and the lack of correlation between electrophoretic mobility and optimum flocculation (12) is in accord with this. The action of non-ionic polymers can be envisaged to be only by the bridging mechanism and thus could be independent of the true surface potential— but even the adsorption of a non-ionic polymer probably lowers the zeta potential of charged particles.

The initial rate of change of electrophoretic mobility with the amount of polymer adsorbed would be determined by both the charge and size of the macromolecule. The former could act by charge neutralization and the latter by viscous drag effects associated with its extension into solution. At high surface coverage the electrophoretic mobility of a particle or floc is determined almost wholly by the adsorbed polymer layer and is only slightly dependent on the charge of the underlying particle (12).

Aim of the present work

The various parameters used to measure the degree of flocculation of a suspension (see page 17) are to be regarded as empirical indices. On the other hand, when La Mer and Smellie (5, 22-25), introduced the permeability of the filter-cake as an index of flocculation, they developed quantitative relationships between the degree of flocculation and the concentration of the

flocculant which offered a fundamental interpretation. The theory was later slightly modified by Healy (82) but the final expressions were unchanged. There does not appear to have been an independent study of the theoretical model or of the fundamental assumptions on which the theory is based. This has been attempted in the present thesis.

Previous workers have been mainly concerned with the flocculation of oxide and clay minerals. An important omission is the ionic class of minerals which are of considerable industrial and academic interest. Fluorite was chosen as typical of such minerals and readily available. It was also found to be susceptible to flocculation with polyacrylamide and its derivatives — the principal class of modern commercial flocculants.

The flocculation characteristics of the systems were considered from two points of view — namely, the physical and the chemical aspects of flocculation. In the former, the effect of polymer concentration, the molecular weight of the polymer, method of mixing, and the concentration of solids in the suspensions was investigated.

In the latter half of the project, attempts were made to establish the relevant surface chemistry of the system. Various aspects were considered, including adsorption mechanisms and characteristics, the configuration of the polymer molecule in solution.

and the effect of pH and ionic strength on flocculation. It was hoped that the results would help remove some of the apparent contradictions that are to be found in the literature.

CHAPTER II

EXPERIMENTAL PROCEDURE

Sample Preparation

a) Fluorite - the starting material was pieces of hand-picked translucent British fluorite, some slightly iron-stained. This was passed through a laboratory jaw crusher set at $\frac{1}{8}$ ins and then ground in a vibratory disc mill to -350 mesh ($\approx 44 \mu$)

A steel pot was used but as the fluorite is relatively soft negligible contamination by iron was incurred. The number-average particle size was 10μ , as indicated by Coulter counter. The specific surface area was estimated to be 0.78 sq.m/g by a B.E.T. nitrogen ^{adsorption} analysis, giving rise to an equivalent particle diameter of 2.3μ .*

b) Hematite - a hematite concentrate, -200 mesh, was prepared by tabling and then deslimed. A microscopic examination showed only hematite to be present. This material was then ground in an agate pot in the vibratory mill to -350 mesh.

Other mineral powders were similarly prepared. The use of the agate or steel pot was determined by the relative hardness of the mineral, its purity and its chemical nature. Some of the work was carried out with chemically prepared calcium fluoride powder (B.D.H. extra pure grade). This material had a specific surface area of 8.5 sq.m/g with an equivalent particle diameter of 0.22μ .*

* These measurements were kindly carried out in the Department of Mineral Technology by Messrs. D. Codd and J. Armstrong.

Method of Flocculation.

The various powders were dispersed in distilled water by means of a small impeller stirrer running at 800 r.p.m. for five minutes. The flocculant solution was run in at this stage and stirring continued for a further five minutes before measurements of the state of the suspension were made. The above procedure provided a convenient routine for comparative testing of the degree of flocculation. The conditions required to achieve the largest possible change in a particular index of flocculation would be dependent on both the nature of the index and also the specific mineral-flocculant system studied.

The stirrer had a variable speed unit from 30 - 2000 r.p.m. A 5 cm diameter, double bladed, stainless steel, propeller agitator was used. The flocculant solution was diluted to 25 ml and added, by pipette, to the bottom of the liquid vortex. The running time of the pipette was approximately 32 seconds. The final volume of the suspension was 500 ml. The above, simple, procedure proved reproducible, giving good mixing and moderate shearing of the flocs. Larger flocs could probably have been obtained by slower addition and more gentle stirring, but there is no "perfect" procedure.

Degree of Flocculation.

An apparatus was developed so that the various parameters defining the degree of flocculation could be measured (see Fig. 2) (A similar apparatus was used first by La Mer et al (38).

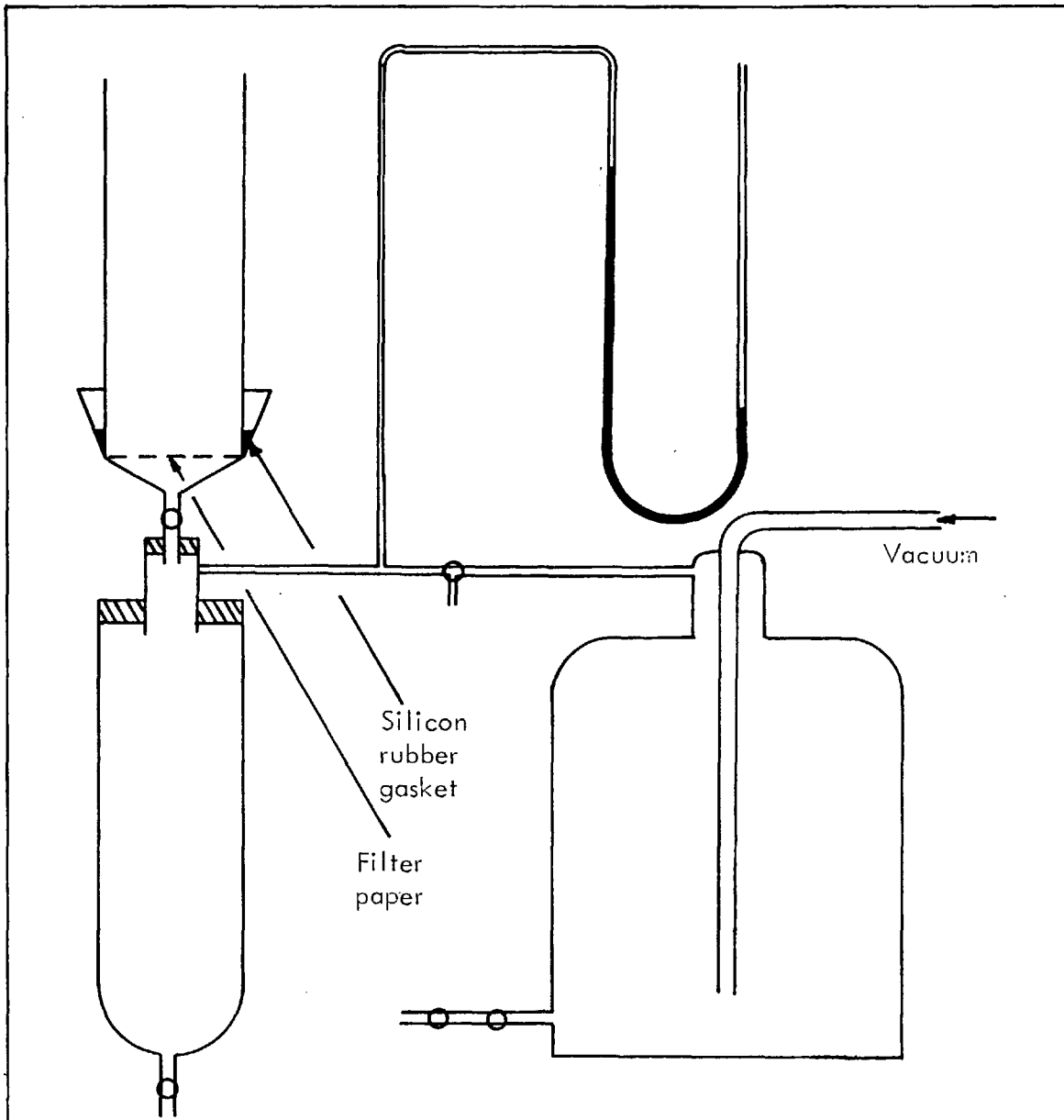


Fig. 2

Refiltration Apparatus (not to scale)

The parameters studied were the rate of fall of a floc line, the turbidity of the supernatant liquid, the volume of the settled flocs and the "refiltration rate" through the flocculated sediment.

After the mixing stage (described above), the flocculating suspension was rapidly transferred to the upper unit of the filtration apparatus. The settling rate was measured over the middle portion of the column. The turbidity of the supernatant liquid was determined on a sample drawn from the centre of the column after the flocs had settled for three minutes. The floc volume was also measured at this stage. A vacuum of 65cm Hg was then applied and filtration started. All but 100 ml of the liquid was filtered before the filtrate was returned to the upper unit. The vacuum was reapplied and the "refiltration time" for the middle portion, 300 ml, was measured. The vacuum was produced by a water pump working off the main supply and measured by a mercury manometer. A constant suction was obtained by using a large reservoir with a bleed-off tap.

The suspension or the filtrate were poured into the upper unit through a "J-tube". This ensured constant mixing conditions and also prevented any disturbance of the compacted bed. For the same reason, the bed was never sucked dry, as this can lead to cracking. This procedure was necessary for reproducible results.

During the first filtration, consolidation of the bed occurred and any material suspended in the supernatant liquid was trapped in

the bed, giving a clear filtrate. Thereafter, the refiltration rate was constant and the filtrate could be recirculated several times and still gave a constant flow rate.

Preliminary Results.

Flocculation is generally sensitive to both the duration and intensity of agitation (see Page 13). This was investigated to set the limits for secondary agitation i.e. after the addition of polymer. The time of secondary agitation was set at five minutes: the influence of the intensity of agitation (r.p.m.) is shown in Fig. 3. Similar results were obtained at higher dosages for the polyacrylamide (P 250) — hematite system and also for the calcium phosphate— and fluorite — P 250 systems.

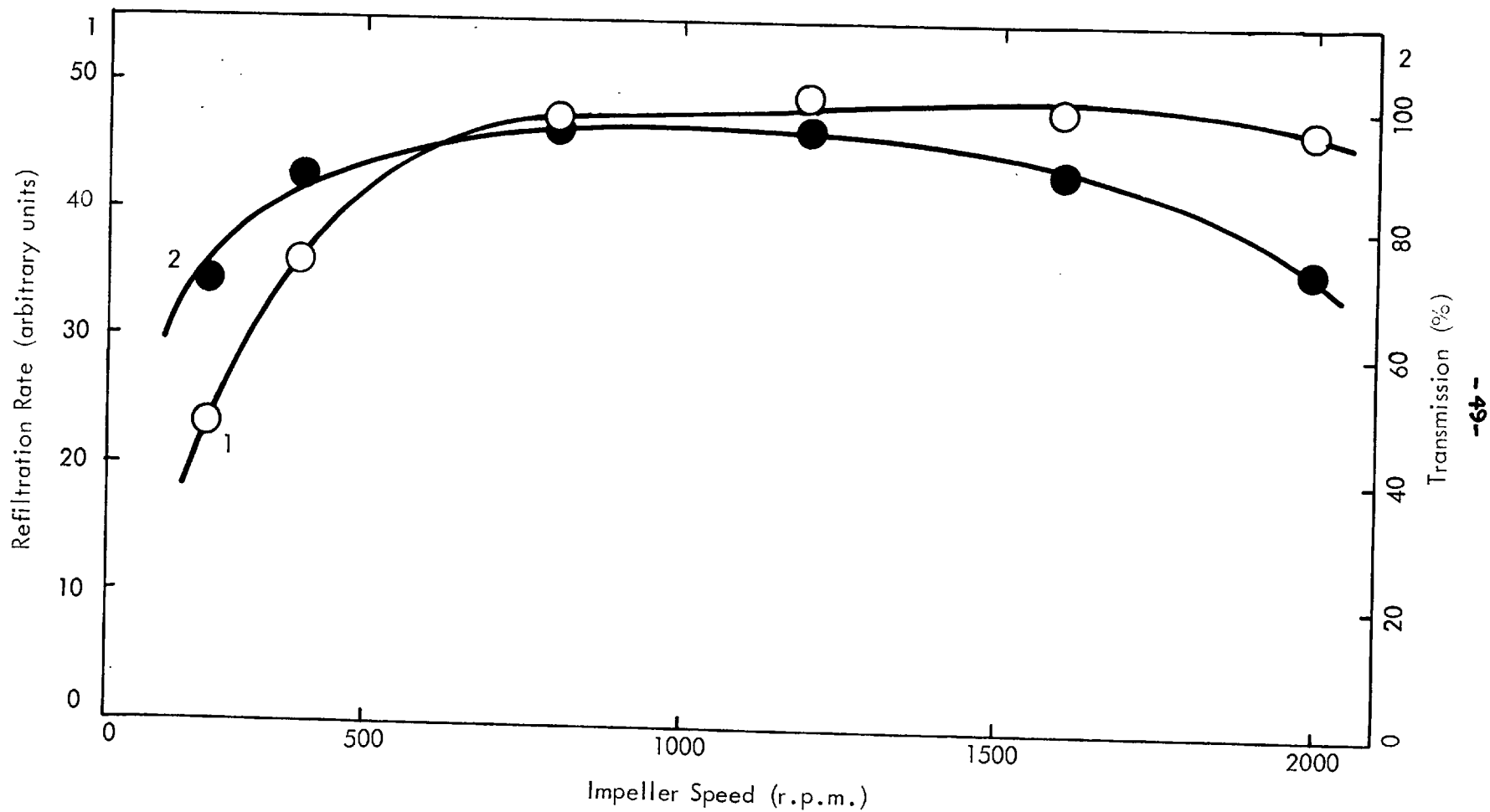
It can be seen that five minutes of secondary agitation at a speed of 800 r.p.m. provided suitable standard conditions for measuring comparative flocculation.

Determination of trace quantities of flocculant.

The quantity of flocculant left in solution after a suspension has been flocculated is an important characteristic. However, it has rarely been measured with any accuracy because of the difficulty in analysing quantitatively for very low concentrations of flocculant in aqueous solution. Consideration has therefore been given to possible methods of determination. Various properties of the polymers have been used or considered in attempts to determine trace quantities. Analytical techniques have been concerned almost exclusively with polyacrylamide-based polymers owing to their

Fig. 3

Influence of agitation on refiltration rate and transmission of the supernatant liquid
(2% hematite suspensions with 3 p.p.m. polyacrylamide - P 250)



predominance as flocculants.

Chemical methods considered.

1) Nitrogen content. Most methods incorporate a Kjeldahl distillation and Nesslerisation of the nitrogen in the sample. The accuracy is limited by the reproducibility, especially at low concentrations, and the necessity to determine blank nitrogen concentrations (73).

2) Oxidation of carbon content (74). With only a few p.p.m. of organic matter, the accuracy of this technique is very limited for the same reasons as above.

The main objection to the above methods is that they are not specific. The techniques depend on the chemical analysis of constituents which are likely to be present in the solvent as well as the polymer.

3) Nephelometric method. Polyanions can react with suitable cations to produce insoluble complexes. In the presence of excess surface-active cations the insoluble material remains suspended and this gives rise to a turbidity which can be used as a measure of the polyanion concentration. Crummet and Hummel (73) developed this technique by reacting "Hyamine 1622" (p-diisbutylphenoxyethoxyethyl dimethylbenzyl ammonium chloride) with hydrolysed polyacrylamide. They converted non- or partially hydrolysed-polyacrylamide to a largely anionic character by alkali hydrolysis. In later work, Griot (75) experienced considerable difficulty in getting the degree

of hydrolysis reproducible. He also discovered that small quantities of silica interfered with the determination.

It was found that an adequate precipitate could be formed directly by reaction between Hyamine 1622 and a partially hydrolysed polyacrylamide (such as "AP30" - a 30% hydrolysed polyacrylamide, molecular weight three million, made by American Cyanamid). This had the advantage that the irreproducible hydrolysis stage was not required. A technique was developed to determine AP30 in concentrations of less than 10 p.p.m., as follows:-

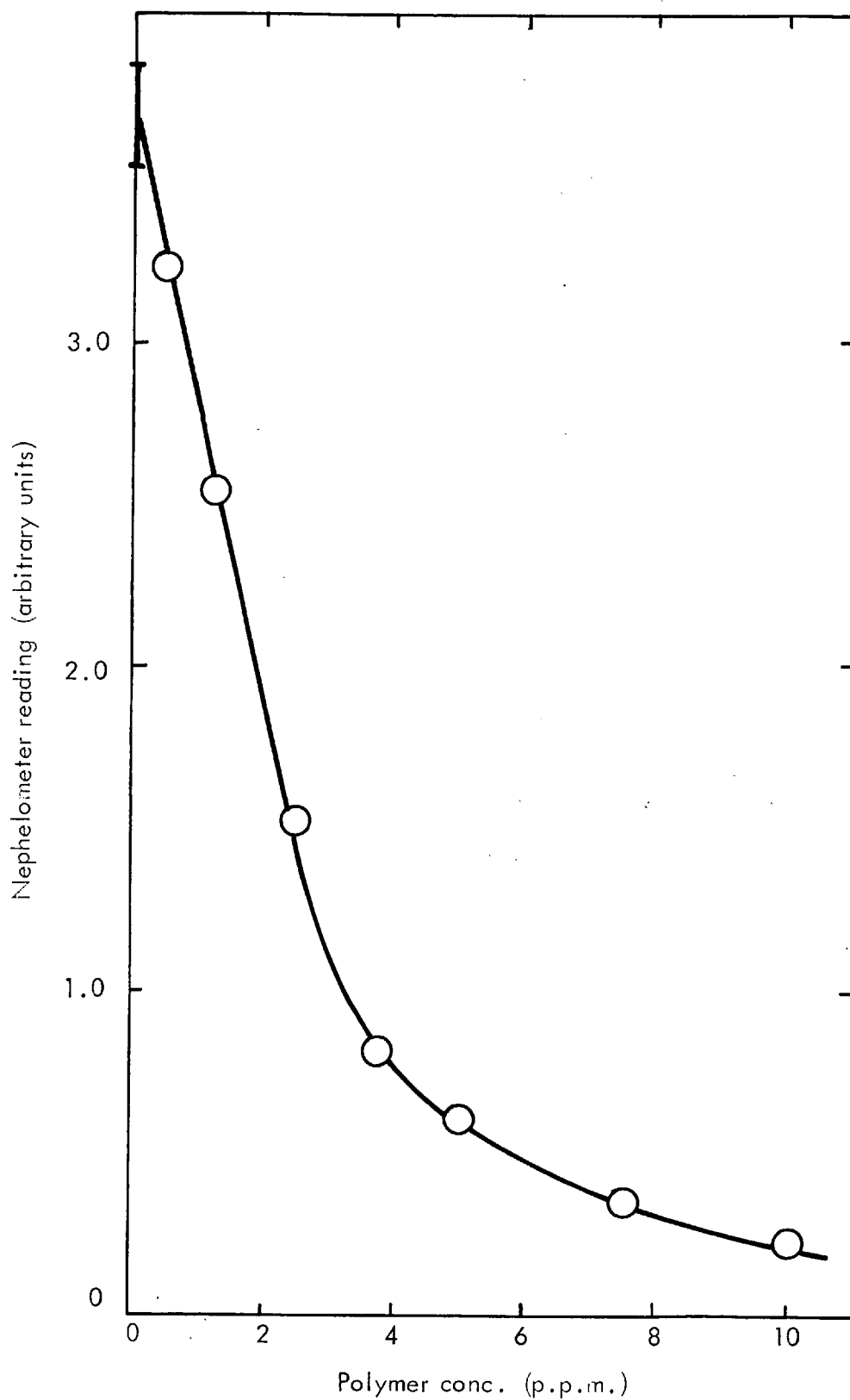
1 ml of a 4% solution of Hyamine 1622 was fed continuously over a period of 64 sec to 25 ml of polymer solution, the mixture being vigorously agitated by a magnetic stirrer. Careful standardization of these conditions was essential for the formation of reproducible turbidities, determined with a simple photoelectric nephelometer. A calibration graph is shown in Fig.4.

When the amount of AP30 adsorbed by calcium fluoride was to be estimated, the solutions were first centrifuged for 20 minutes at 3600 r.p.m. before the addition of Hyamine. This resulted in excellent clarification except when the initial polymer concentration was high enough to stabilise some particles. Then polymer concentration could still satisfactorily be estimated by the difference in turbidity before and after addition of the Hyamine.

When the effect of pH was investigated, the solutions were centrifuged and the pH adjusted to 5.3 ± 0.1 before the Hyamine was added.

Fig. 4

Calibration curve for a hydrolysed polyacrylamide (AP 30)



Contrary to the findings of Crummet and Hummel (73), it was found that a polymer solution in N/2 NaCl gave a markedly increased turbidity with Hyamine (presumably due to "salting out"). Therefore it was possible to investigate the influence of NaCl concentration on the adsorption only within a certain range. The centrifuged solutions were adjusted to N/100 NaCl and the polymer concentration estimated from a slightly modified calibration graph.

Although the above technique proved suitable, it could not be readily extended to any other range of commercial flocculants. Other properties were also investigated.

Ultra-violet absorption spectrometry.

Jankovics (76) claimed to have analysed for non-ionic polyacrylamide by measuring u.v. absorption at 212 m μ wavelength where strong absorption was recorded, but attempts to repeat this work were unsuccessful. Although polyacrylamides of different molecular weight and from various manufacturers were tested, all showed an absorption peak at about 191 m μ and very little absorption at 212 m μ . Light-scattering due to the presence of colloidal mineral particles made the method insensitive to slight variations in polymer concentration, and centrifugation at 12,000 r.p.m. did not give sufficient clarification. Passing the suspension through a membrane filter introduced organic impurities into the filtrate which absorbed strongly in the far ultra-violet. The method was therefore abandoned.

Infra-red absorption spectrometry.

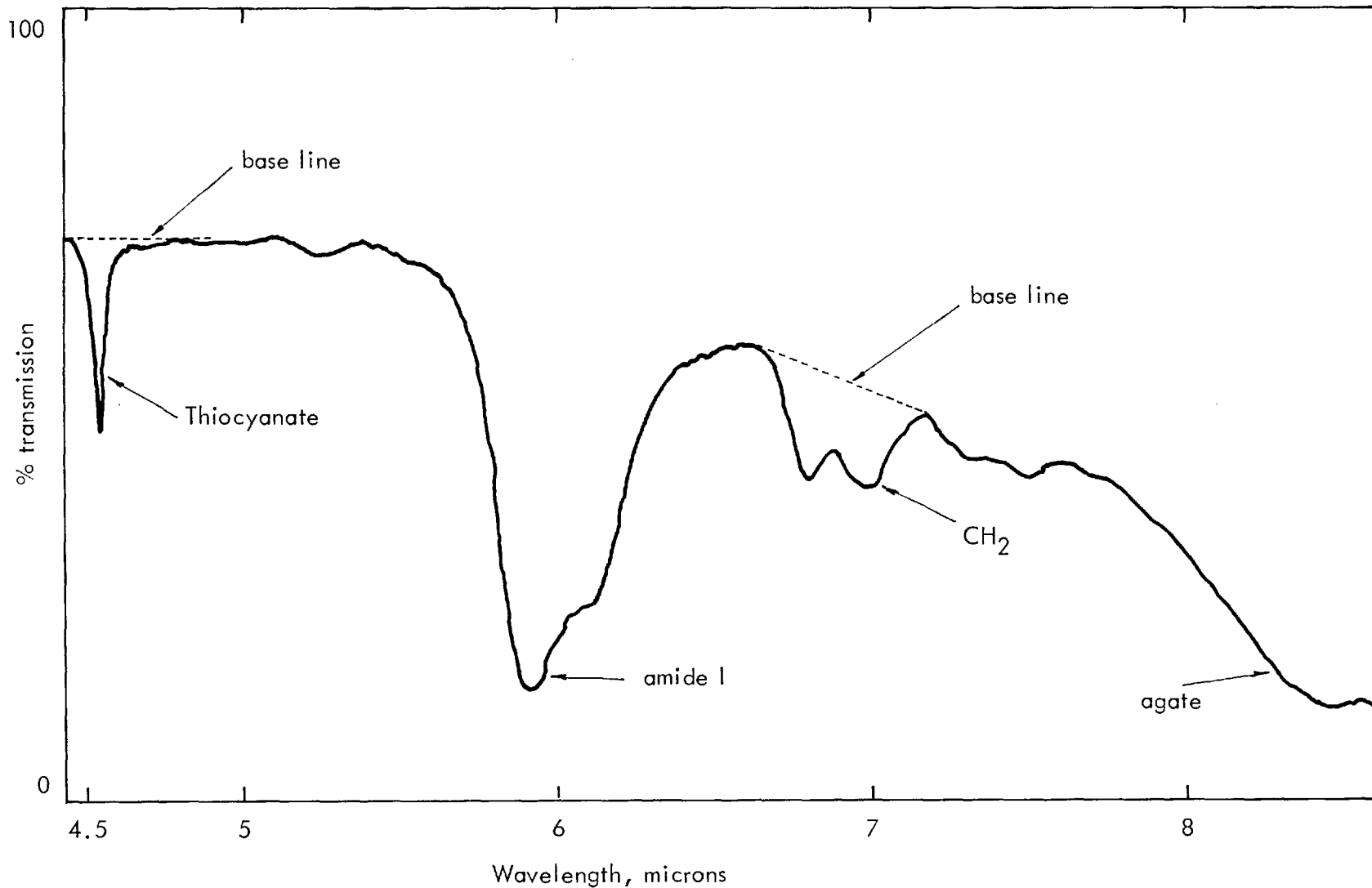
The infra-red spectrum of polyacrylamide indicates two peaks which might be used for its determination (77). A primary amide bond absorbs strongly at a wavelength of 6.15μ and further absorption at 7.1μ is derived from the CH_2 bond. The latter has a peak height of about 40% of that of the amide bond.

Polyacrylamide is not soluble in any of the standard organic solvents suitable for infra-red analysis. Consequently the sample was prepared in a KBr disc. Quantative analysis using this technique is not simple and a method incorporating an internal standard has been developed by Wiberley et al (78). The use of the internal standard is to compensate for the variable geometry of the disc, i.e. it eliminates need to measure the thickness of the disc. The internal standard is chosen so that it has a well defined absorption peak which does not interfere with the spectrum of the test material.

By Beer's law, the absorbance (optical density) of the known material to be assayed at λ_k will be given by $A_k = a_k b c_k$: where a_k is a constant for the material, b is the disc thickness and c_k is the concentration of the material in the disc. The absorbance of the internal standard at a wavelength λ_s is similarly given by $A_s = a_s b c_s$; dividing these equations gives $A_k/A_s = a_k b c_k / a_s b c_s$. The b 's cancel, a_k and a_s are constants for the conditions under which the measurements are made, and c_s , the concentration of the internal standard, remains effectively constant. These constants

Fig. 5

Spectrum of a polyacrylamide calibration sample. Polyacrylamide in potassium bromide containing cuprous thiocyanate and ground in an agate capsule.



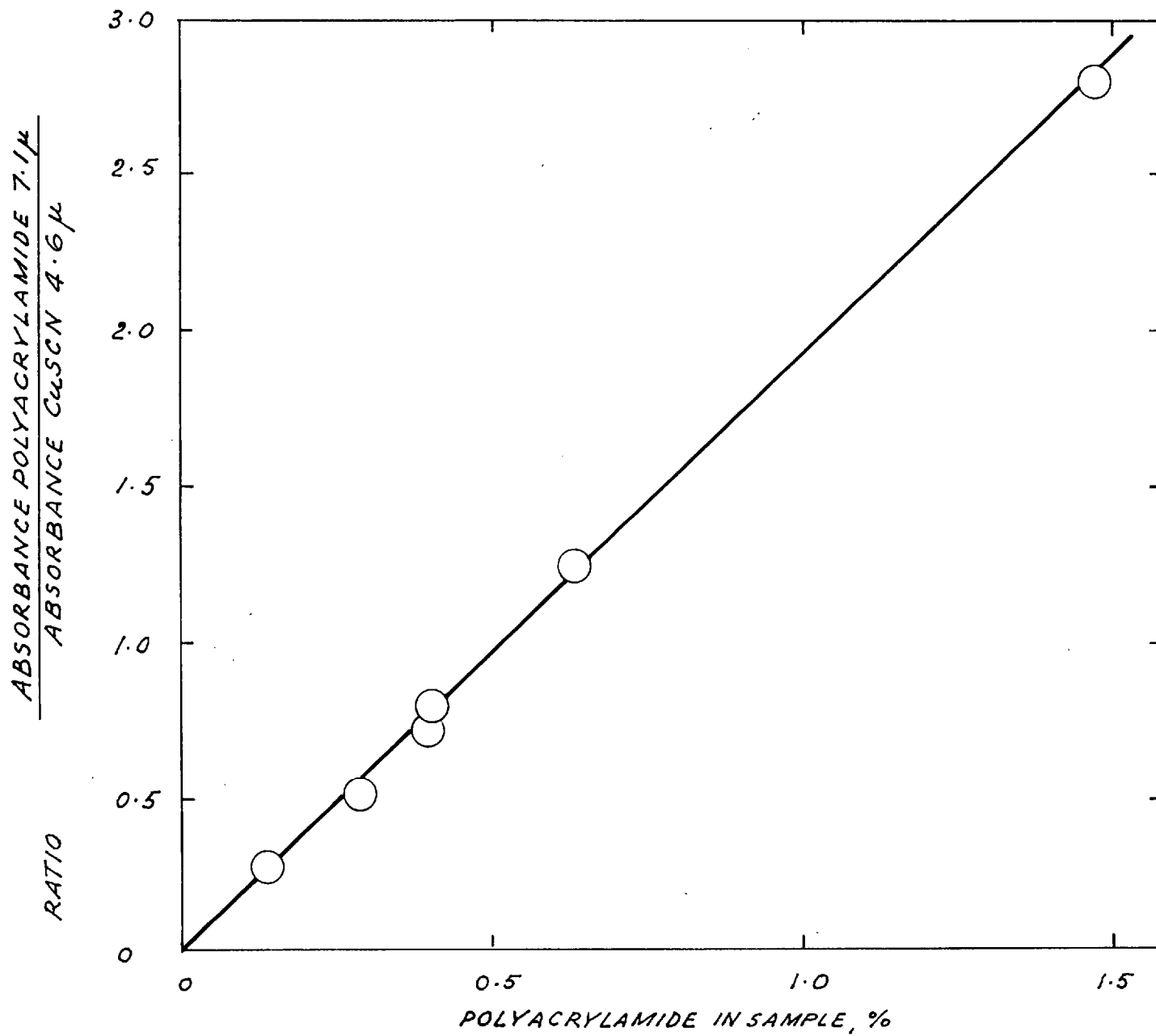
can be accumulated into an overall constant K, such that $A_k/A_s = Kc_k$. Hence a plot of A_k/A_s against c_k should give a straight line and such a graph would be available as a calibration curve.

The thiocyanate peak at 4.6μ is suitably placed for determination by either of the absorption peaks of polyacrylamide (see Fig.5). Cuprous thiocyanate was found to be far less hygroscopic than the potassium thiocyanate used by Wiberley (78) and was preferred. Even so, an absorption band at 6μ from absorbed water precluded the use of the amide I peak at 6.15μ . Hence the less sensitive CH_2 bond at 7.1μ was used for polyacrylamide determination. Figure 5 shows the combined infra-red spectrum of the internal standard and polyacrylamide. Figure 6 shows the calibration graph derived from it and similar spectra.

More detailed theoretical and practical details are available in the paper by Wiberley et al (78). The samples were mixed in a Grindex colloid mill with agate grinding capsules and an agate ball charge. The spectrum in Figure 5 indicates that some agate was transferred to the sample and an interpolated base-line had to be drawn. It is interesting to note that the calibration curve could be determined in the presence of significant quantities of at least one mineral. This contamination was later avoided by grinding in stainless steel capsules. Infra-red measurements were made on a Grubb-Parsons "Spectromaster" spectrophotometer.

This method was suitable for determining small quantities of solid polyacrylamide. An evaporation procedure is necessary to

FIGURE 6. CALIBRATION GRAPH FOR
NON-IONIC POLYACRYLAMIDE (CYANAMER P.250)



prepare solid polyacrylamide from the dilute flocculant solutions encountered, as water absorbs strongly in the infra-red. Although many different techniques were tried none were acceptable. Irreproducibility was introduced by "splash" losses and adsorption of the polymer on to the containers. Also, polyacrylamide is difficult to dehydrate by heating without causing chemical changes. This was unfortunate as this technique is theoretically suitable for most polymers, and is potentially important because of the problem of determining trace amounts of flocculant that, in the future, may be present in drinking water.

Radio-tracers. Polymers tagged with C_{14} have been prepared and their concentration determined by scintillation counting (12). Although excellent for this purpose, they are not commercially available and the high cost involved in producing a tagged, well characterised flocculant, especially was beyond the scope of this study. It would be essential to control closely the molecular weight etc. of the product. Similarly, the tagging of a non-active flocculant with tritium is possible in principle, but some reliable method of purification would be needed to remove tagged decomposition products which would otherwise give misleading indications.

Filtration through membrane filters. Veitser and Kolobova (79) proposed that the reduction in permeability of a membrane filter when a dilute solution of polyacrylamide was filtered through it could be quantitatively related to the concentration. This method would be highly dependent on the presence of any suspended material or

incompletely dispersed polymer.

Conclusion.

Of the various analytical methods tried or considered, only the nephelometric method with anionic polyacrylamide proved thoroughly satisfactory. Therefore adsorption studies were made with this material.

Chapter III

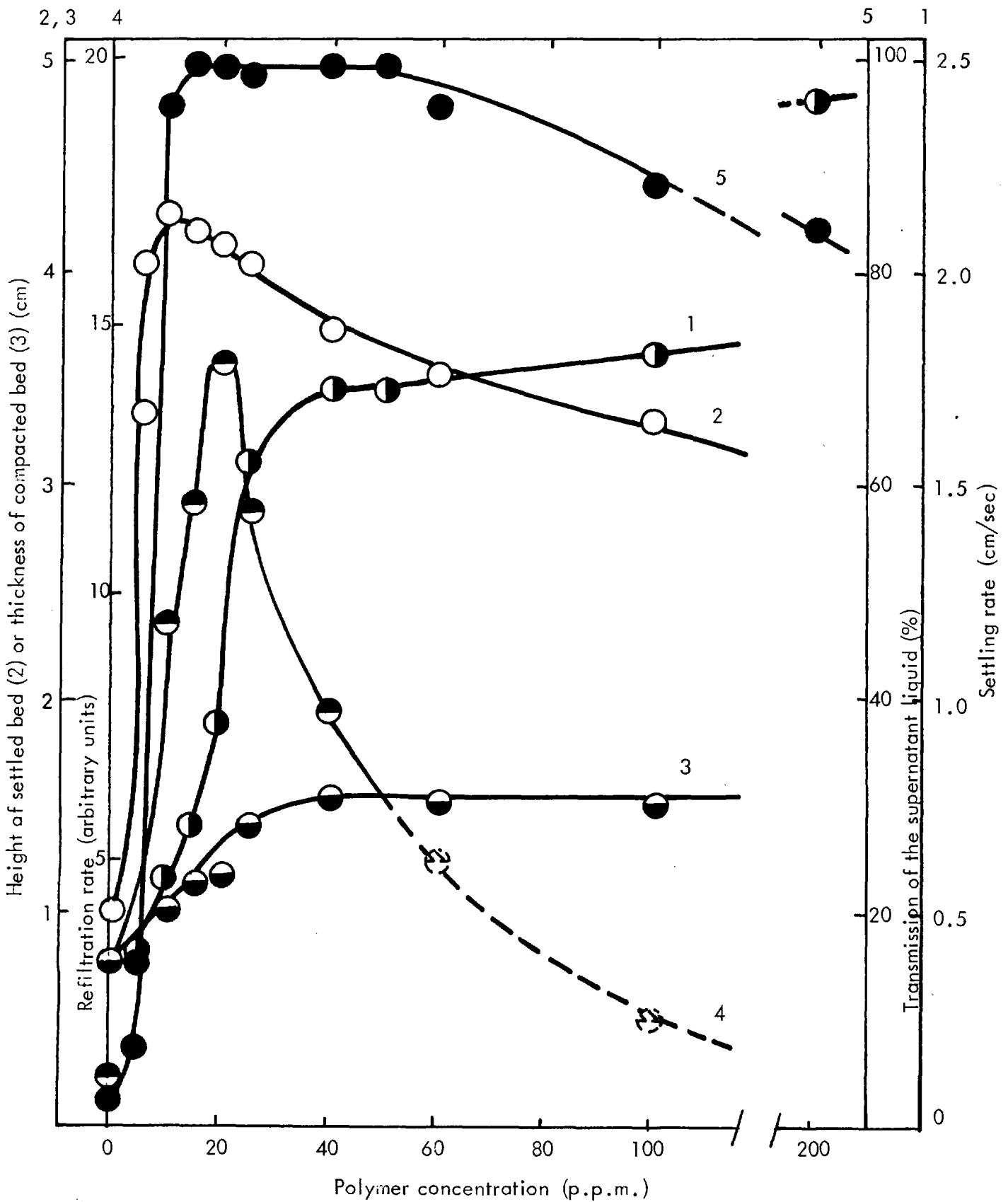
PHYSICAL ASPECTS OF FLOCCULATION

Indices of flocculation. A series of tests was carried out to measure the different properties which have been used to estimate the degree of flocculation of suspensions. The following parameters were measured on the same suspensions: (i) optical transmission of the supernatant liquid- (ii) permeability of the filter-cake- (iii) the rate of sedimentation of the floc boundary- (iv) height of the settled bed- (v) thickness of the filter-cake after consolidation by filtration under suction. The results are collected in Fig. 7. In the low concentration region (0-15 p.p.m.) all five parameters are in agreement in registering a progressive improvement in flocculation with increasing dosage of flocculant. But the permeability curve differs from the others in showing a sharp "optimum dosage" at 20 p.p.m.

This figure also shows that the conditions necessary to optimise one parameter do not necessarily apply to other parameters. There appears never to have been an attempt to correlate the various parameters. As they refer to essentially different properties of the suspension and are also variously dependent on the kinetics of mixing, flocculant addition etc. a mathematical analysis would be extremely difficult if not impossible. It has also been reported that the chemical nature of the flocculant (polyelectrolyte or non-ionic) can effect the conditions necessary to optimise a single parameter (6).

Fig. 7

Flocculation characteristics of an 8% by weight suspension of fluoride flocculated by polyacrylamide (P 250)



All the parameters, however, are suitable measures of comparative flocculation. A floc boundary is formed only in suspensions of high solids content and so has limited application. The height of the settled bed is reproducible only under equilibrium conditions: as this takes about 24 hours (9), this parameter is often impractical. The transmission of the supernatant liquid and the permeability of the filter-cake were extensively used. Doubts arose as to the significance of the filtration maxima and this is considered in Chapter IV.

The origin of "haze". Haze is the suspended material left in the supernatant liquid in a system exhibiting otherwise good flocculation. With a controlled mixing regime, the amount of haze goes through a minimum as the polymer concentration is increased (see Fig. 7). Linke and Booth (9) proved by chemical analysis that at high concentrations (greater than optimum) the haze carries a disproportionately high dosage of flocculant and for this reason it passes into the stabilised state. The results of the present tests collected in Table 1 show that the haze was formed during the addition of the flocculant and not through degradation by stirring. The haze resulted from the rapid adsorption of large quantities of polymer by particles that encountered high local concentrations during the addition of the flocculant. This initial adsorption is rapid and once the flocs have been formed they are not degraded in the presence of excess polymer (Test No.4) i.e. equilibrium is not attained with ten minutes subsequent stirring.

Table I

Conditions of tests: fluorite suspensions stirred for 5 minutes, then addition of polyacrylamide ("Cyanamer P250") made, and stirring continued for a further period, as shown. Table I gives T, % optical transmission of supernatant liquid after the floc has settled for 3 min.

TEST NO.	FLOCCULANT DOSAGE AND STIRRING TIME	T(%)
1.	5 p.p.m. and 5 min. (optimum)	99-100
2.	45 p.p.m. and 5 min. (large excess)	67
3.	45 p.p.m. and 10 min.	67
4.	5 p.p.m. for 5 min., then 40 p.p.m. for further 5 min.	100
5.	45 p.p.m. added in 32 sec. then 5 min. stirring	67
6.	45 p.p.m. added in 3½ min., then 5 min. stirring	88
7.	45 p.p.m. of more dilute solution (32 sec.), then 5 min.	72

The gradual addition of a dilute flocculant solution reduces the possibility of high local concentration and reduces the amount of haze formed (Test Nos. 6 and 7). This should have direct industrial application where the formation of haze can be detrimental to the quality of the product (e.g. treatment of potable water). In all processes its presence indicates an inefficient distribution of flocculant. The fact that any haze formed cannot subsequently be removed by adding some fresh dispersed solid proves that redistribution of polymer does not readily occur.

Solid concentration. A non-ionic polyacrylamide (Cyanamer P250) fluorite system was investigated to determine the influence of solids content on "optimum dosage" and on maximum permeability of the filter-cake. The results are collected in Fig.8. The permeability and "transmission" maxima were measured for a number of suspensions of different solids content (e.g. Fig.7). In this system the optimum polymer concentration for the two parameters coincided. Therefore the "optimum specific dosage curve" represents data obtained for both parameters.

These results show that at higher solids content there is an improvement in flocculation. Not only is a more permeable filter-cake formed but the optimum dosage per g of solid is reduced. Similar results were obtained for the hematite - "Nalco - D 1782" system ("high molecular weight anionic polyacrylamide" (80)). (cf. Fig.9). In this case there is no clear correlation between the parameters: the polymer concentration for optimum permeability is consistently less than that required for optimum clarity of the supernatant liquid. In Fig. 9 curve (2) refers to the per cent transmission at the polymer concentration for the optimum permeability. These data also show improved flocculation at higher solids content although with this system the optimum polymer dosage /g was constant at 0.09 mg/g between 0.5 and 2 % solids. The improvement in flocculation is in agreement with the general findings of previous workers (9,10).

Fig. 8

Influence of solids content on "optimum dosage" and on maximum permeability of filter-cake

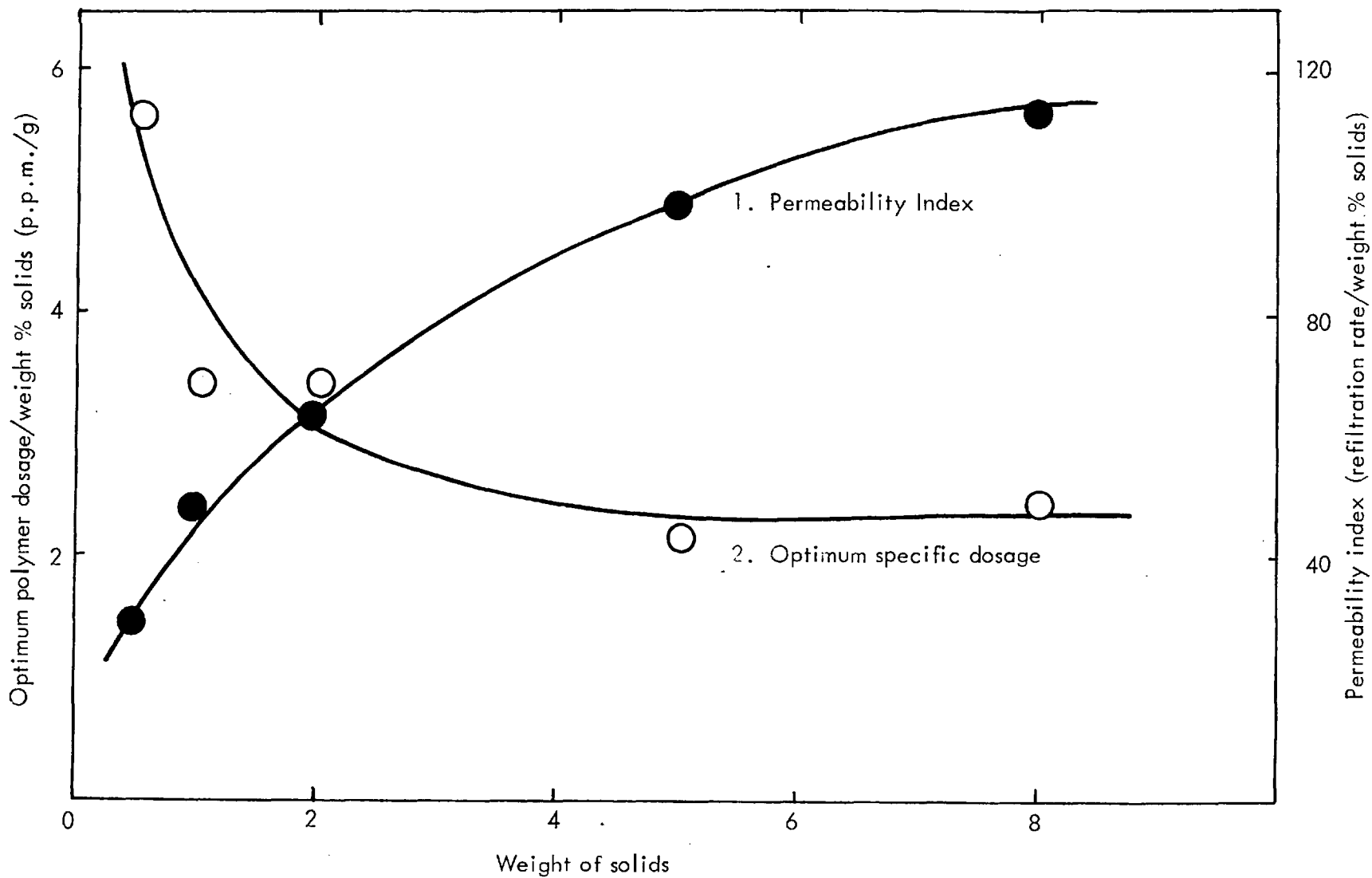
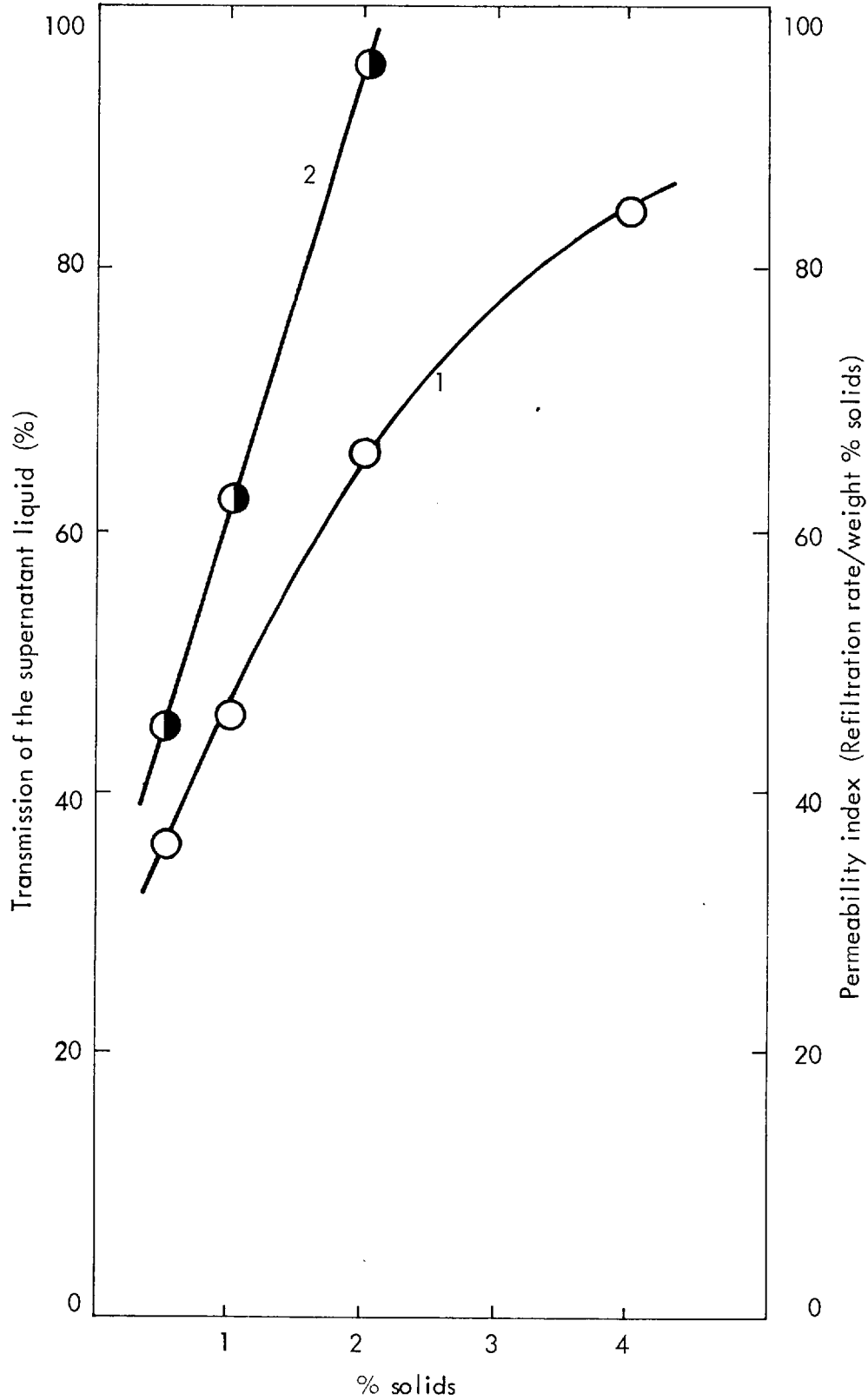


Fig. 9

Influence of solids content on the flocculation of hematite suspensions with an anionic polyacrylamide (Nalco D - 1782)



In low per cent solids dispersions orthokinetic flocculation can be important in bringing particles together so that bridging can occur. In suspensions with high particle concentrations this is of secondary importance as the average interparticular distance is much reduced and there is a consequent increase in the frequency of inter-particle collisions. On the basis of the bridging theory this should improve flocculation. It has been shown that when the length of the flocculant molecule is equal to or greater than the average distance between the particles a rapid improvement in flocculation occurs (11). The results, therefore, are in agreement with the bridging theory of flocculation.

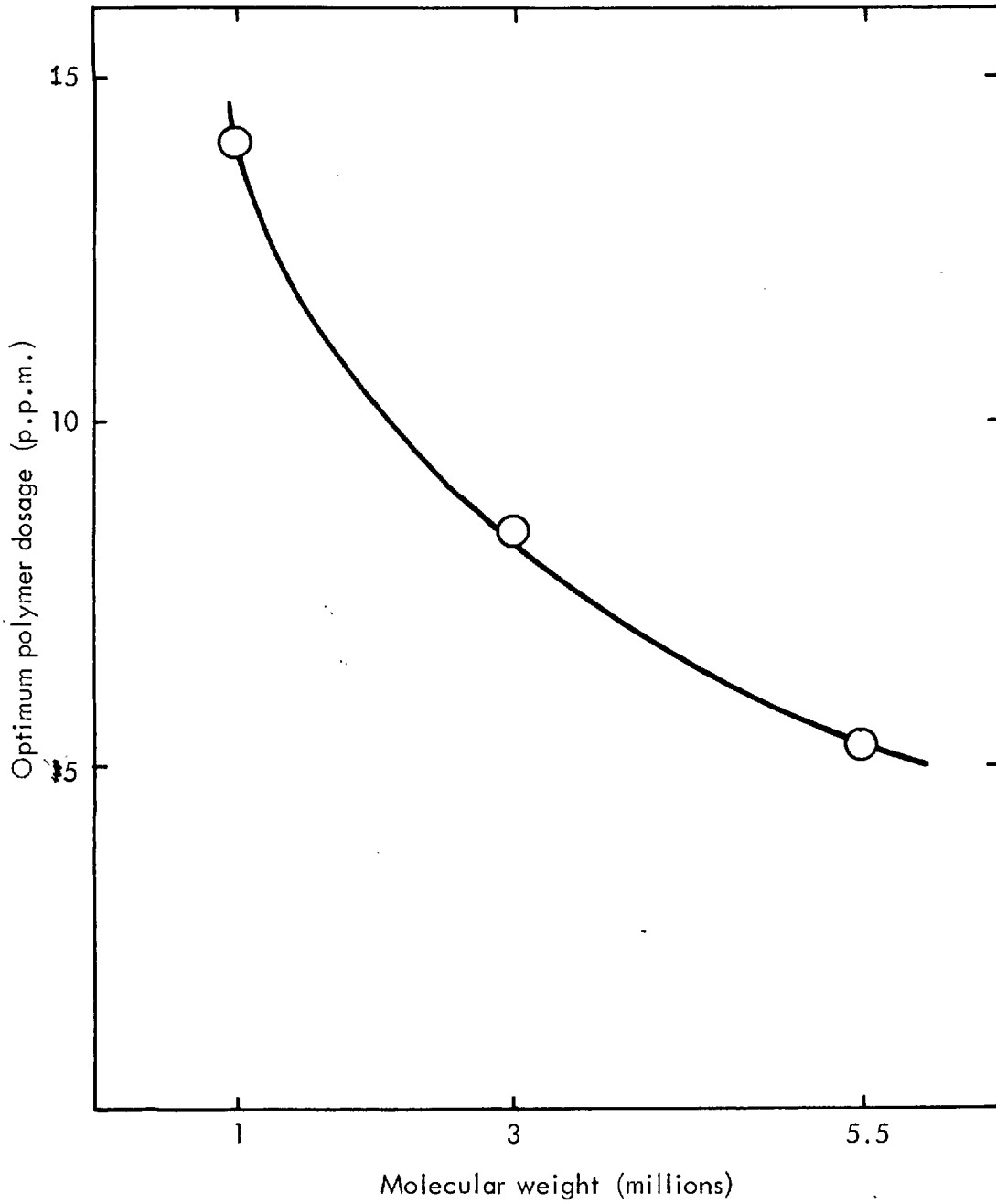
Molecular weight of the flocculant. Suspensions of fluorite were flocculated by non-ionic polyacrylamides of different molecular weight. The results are collected in Fig.10 and Table 2. As above, the polymer concentration required for maximum permeability is the same^{as} for optimum transmission of the supernatant liquid.

Table 2. The optimum flocculation (permeability and transmission parameters) produced by non-ionic polyacrylamides of different molecular weight.

Nominal Molecular Weight (millions)	Optimum refiltration rate (arbitrary units)	Optimum transmission of the supernatant liquid (%)
1	39.2	96
2	37.8	97
3	42.5	97.5
5-6	34.5	98

Fig. 10

Influence of molecular weight on optimum polymer dosage
(polyacrylamide - fluorite system)



The data show that although the maximum degree of flocculation is essentially independent of molecular weight, the optimum polymer concentration is reduced at high molecular weights. This suggests that, within the range of molecular weights tested, the same mechanism was operative i.e. the bridging mechanism. The greater efficiency of the higher molecular weight flocculants can be explained on this basis. An adsorbed macromolecule extends further into solution with increasing molecular weight (44) and this increases its ability to form polymer bridges which is reflected in its higher efficiency as a flocculant.

It was found that the high molecular weight flocculant P250 was completely dissolved only after 14 days in contact with water. The permeability parameter was found to be sensitive to the presence of incompletely dispersed lyophilic agglomerates and a highly solvated polymer solution was necessary for reproducible results. It has been suggested that the industrial use of very high molecular weight non-ionic polyacrylamides is determined by the difficulty of dissolution (81).

Conclusion. It has been shown that a suspension is more efficiently flocculated when it has a high solids concentration and the flocculant is of high molecular weight. These results provide further support for the bridging theory of flocculation.

CHAPTER IV

THE THEORY OF REFILTRATION THROUGH FLOCCULATED
SEDIMENTS ACCORDING TO LA MER, SMELLIE AND HEALY

It has long been known that flocculants improve both the efficiency of filtration and the handling properties of the product (113). Therefore the permeability of the filter-cake is a parameter of industrial importance. In a series of papers, La Mer and Smellie (5,22-25) have developed a relationship between the permeability of the filter-cake and the concentration of the flocculant.

The original derivation of the theoretical equation was subsequently modified by Healy (82): it leads to the following equations:

$$P_m = (1 + bk/\beta)^2/b \quad \dots (1)$$

$$\text{and } P_o^{1/2}/(Q-Q_o)^{1/2} = A_m + \beta_m P_o \quad \dots (2)$$

$$\text{where } A_m = c(1 + bk/\beta)^{1/2}/b^{1/2} \quad \dots (3)$$

$$\text{and } \beta_m = Cb^{1/2}/(1 + bk/\beta)^{3/2} \quad \dots (4)$$

P_m = concentration of polymer required to give optimum refiltration rate (i.e. highest permeability).

P_o = initial polymer concentration.

Q = refiltration rate through the flocculated sediment.

Q_o = refiltration rate with no polymer addition.

β = number of segments of the polymer adsorbed at the surface.

b = affinity factor derived from the Langmuir adsorption isotherm.

K = constant.

c was also referred to as a constant but is in fact equal to β^2/k^4

The theoretical equation No.2 predicts curves of the shape shown in Fig.11. The originators of the theory have shown that many experimental permeability results can be fitted to the equation, at least to the region round the maximum. The shape is similar to the experimental curves in Fig.12.

The assumptions made in developing this theory also define the physical model of flocculation on which it is based. These are:

1) Adsorption of flocculant. It was assumed that when flocculation occurs equilibrium adsorption conditions exist which conform to the Langmuir adsorption isotherm.

Actually, equilibrium conditions are difficult to justify in all rapidly flocculating systems. Initial adsorption is very rapid but equilibration slow. Even the system polyacrylamide-calcium phosphate, studied extensively by La Mer et al, can require hours rather than seconds to come to "equilibrium" (76).

The adsorption of polymers from solution at liquid-solid interfaces exhibits isotherms which clearly resemble Langmuirs. Eirich et al (83) gave an explanation for this finding; if adsorbed polymers have a tendency to repel one another within the surface layer, this results in an isotherm similar in shape to the Langmuirian type but of greater capacity. Forseman and Hughes (84) also

Theoretical form of the refiltration rate against dosage curve, according to the theory of La Mer and Smellie

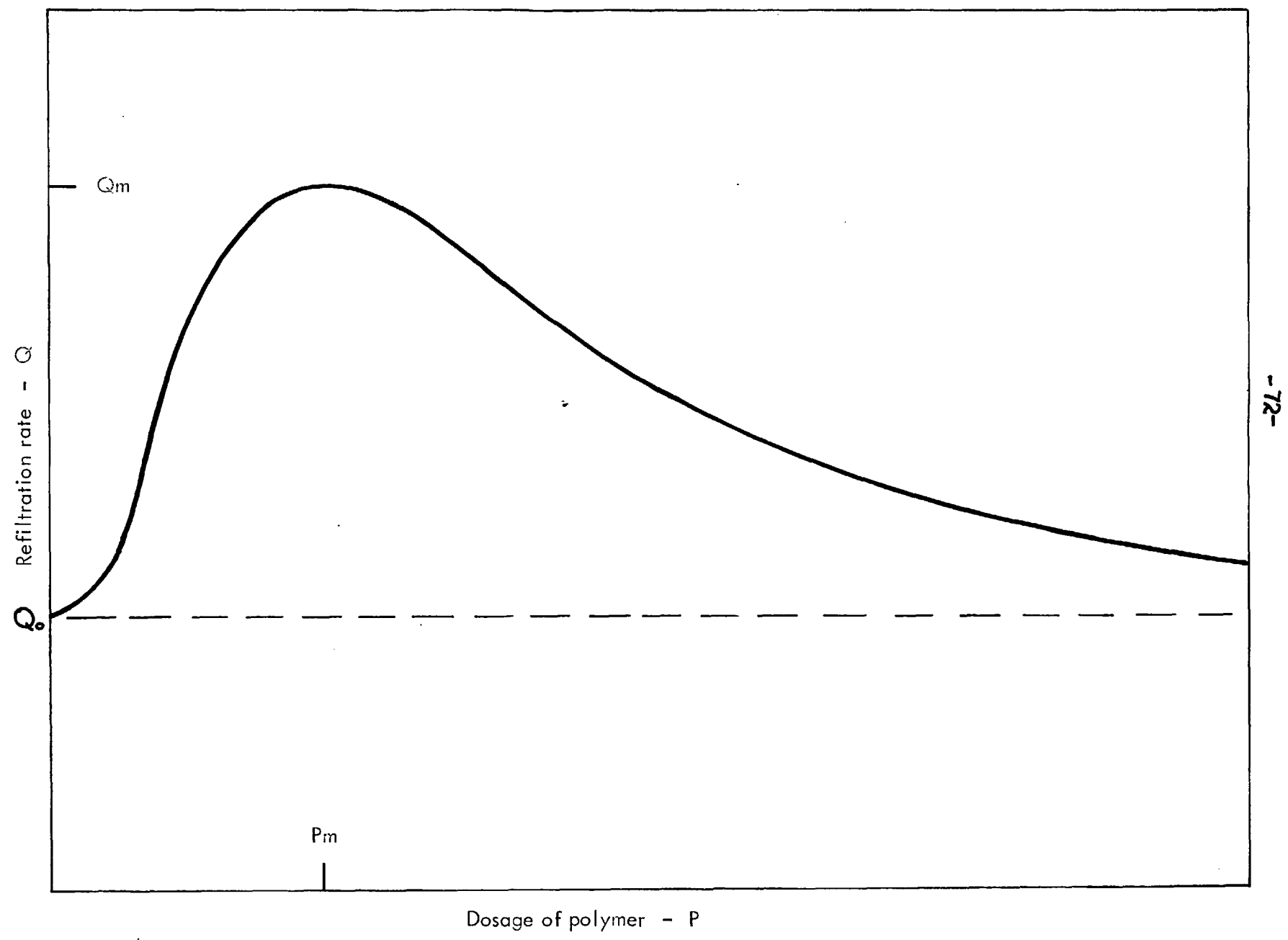
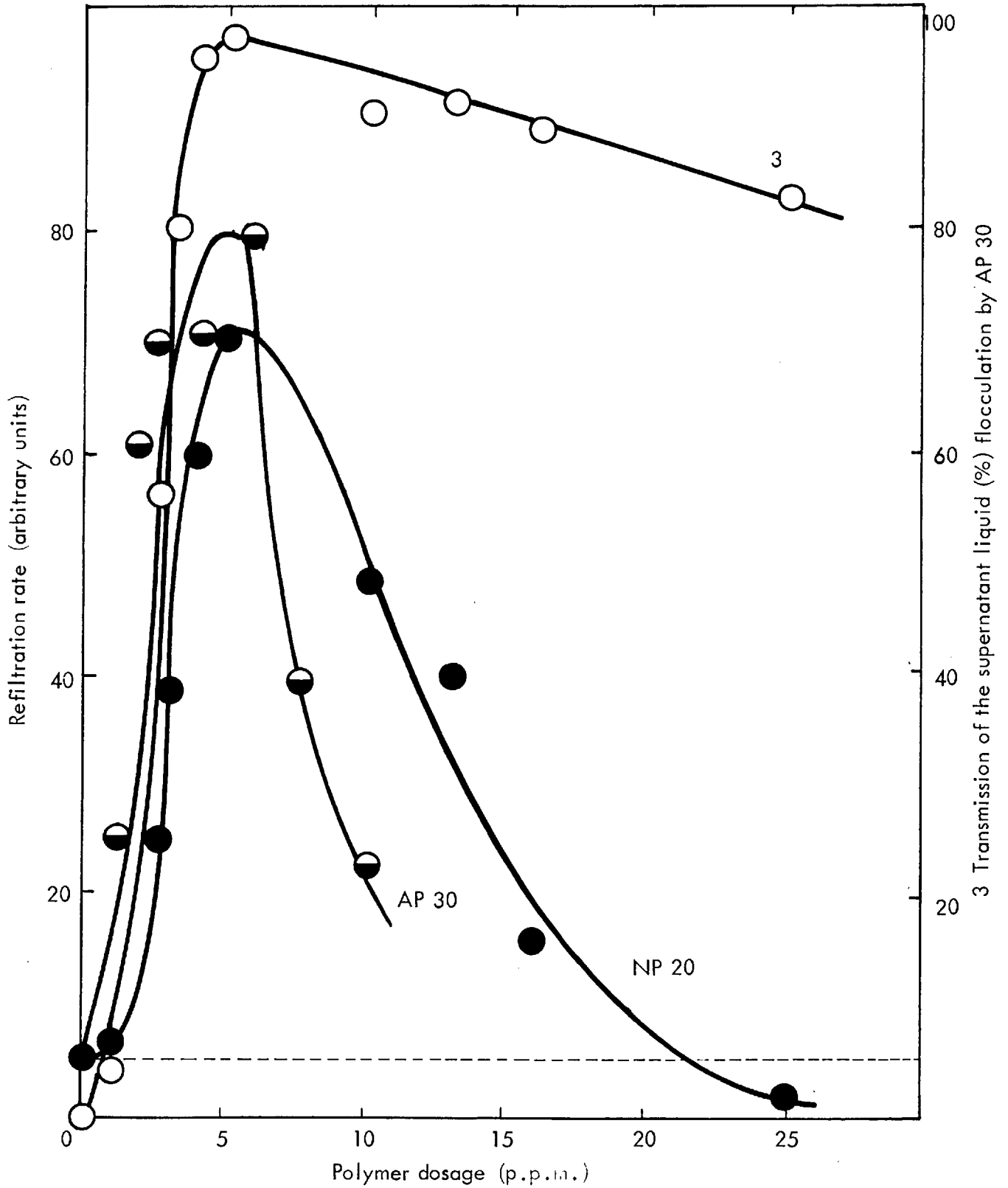


Fig. 12

Typical "refiltration curves" showing rate of refiltration as a function of polymer dosage; for a non-ionic (NP 20) and an anionic (AP 30) polyacrylamide of similar molecular weight (3 million). Suspensions: 1% by weight fluorite. Also associated transmission curve for AP 30.



suggested that when there is little interpenetration of the adsorbed polymer coils isotherms superficially of the Langmuir type will be produced. Eirich (83) went still further to suggest that any adsorption process which yields a monolayer will have an initial linear slope proportional to affinity multiplied by concentration and will show saturation or a plateau. Therefore, at least the high and low concentration sections of any such isotherm could be characterised by two constants as if it were a Langmuir isotherm.

Healy (82) justified the use of the Langmuir isotherm by considering the adsorption at the individual segment-surface site. He suggested that as only a fraction of the available segments are adsorbed (he cites "less than a third") and that as they are not adjacent along the polymer chain then they can be considered as being equivalent to "small molecules" in their adsorption behaviour. This concept is inadmissible as it implies that the monomer unit of a macromolecule has as many degrees of freedom as a simple molecule in solution. Healy has attempted to provide a physical model of flocculation based on the parameters describing the Langmuirian isotherm.

2) Floc formation. The rate of the floc formation was assumed to follow the classical Smoluchowski coagulation rate theory, i.e. to be dependent on the square of the number of primary particles (n_0). This was modified by the function $\theta(1-\theta)$, where θ = fraction of

surface covered by polymer. Therefore $(1-\theta)$ = fraction of surface still available for bridging.

The rate of floc formation was given by

$$-\frac{dn_o}{dt} = K_1 n_o^2 \theta (1-\theta) \quad \dots(5)$$

This expression has a maximum value when $\theta = 0.5$ and it is an integral part of the theory that optimum flocculation should be associated with $\frac{1}{2}$ surface coverage. In fact the "surface coverage" associated with optimum flocculation has been determined experimentally as being between 10 and 33% (5, 7, 8) and is dependent on the system.

It has been found (84) that the Smoluchowski equation is applicable only to very dilute suspensions (volume fraction $10^{-4} \text{ cm}^3/\text{cm}^3$)(85). Therefore it is doubtful whether it should be used for comparatively concentrated suspensions.

3) Floc disintegration. An empirical equation was proposed to describe the disintegration of a floc which occurs on stirring

$$\frac{dn_o}{dt} = \frac{k_2 R}{\theta(1-\theta)} \quad \dots(6)$$

where R = radius of the floc

This expression was supposed to satisfy certain limiting conditions:-

- a) When the surface is fully covered ($\theta=1$) polymer bridges cannot form. Therefore, $dn_o/dt = \infty$ i.e. spontaneous disintegration.

- b) At half surface coverage the theory predicts that the rate of floc formation is a maximum; therefore, $\frac{dn_o}{dt}$ should have a minimum value at $\theta = 0.5$.
- c) When no polymer is adsorbed ($\theta=0$), $\frac{dn_o}{dt} = \infty$. This is the condition for spontaneous disintegration of a floc. However, when no flocculant is present (i.e. $\theta=0$) no flocs exist; therefore it is impossible to apply the above limit. The relationship does not satisfy its own limiting conditions. When $\theta=0$, $\frac{dn_o}{dt}$ should equal 0; this is not satisfied by equation 6.

Equations 5 and 6 imply that the kinetics of flocculation are controlled by the number of discrete primary particles present in the suspension. This suggests that flocs are formed by these primary particles becoming attached to a major floc structure. Vold (36) tried unsuccessfully to account for floc structure on this theory. In subsequent work Sutherland (37) showed that the low solids content of flocs could be accounted for only by postulating that major flocs were formed from aggregates of minor flocs. In a computer calculation, the adhesion of randomly moving discrete single particles gave porosities which were far too low.

Furthermore, deflocculation under controlled agitation does not necessarily produce primary particles but a whole spectrum of floc sizes. Therefore equation 6 is inadequate on this basis too.

4) It was assumed that "the volume density of solid was at any instant the same throughout the whole subsiding column". This was disputed by Tozy and Shannon (68) who presented a theoretical argument to show that the maximum density is formed at the base of the settling column.

5) The equilibrium value of the floc radius (R) under any given set of conditions was obtained by combining equations 5 and 6.

$$R = \frac{k_1 n_0^2}{k_2} \theta^2 (1-\theta)^2 \quad \dots(7)$$

When no flocculant is present, $\theta = 0$, R from the above expression also equals 0. In fact R should equal R_0 , the average radius of the untreated primary particles. To provide an internally consistent expression equation 7 was modified to:

$$R^2 - R_0^2 = \frac{k_1^2}{k_2} n_0^2 \theta^4 (1-\theta)^4 \quad (\text{see equation 18 of ref.25}).$$

This was a totally unjustifiable, wholly arbitrary, mathematical "correction."

The structure of the filter-cake.

The surface area associated with the flocs was introduced into the Kozeny-Carman equation to estimate filtration rates.

La Mer and Smellie assumed that the flocs are essentially spherical in shape and made up of closely packed primary particles —

also, that the porosity and the thickness of the filter-cake remained constant for the suspension in different degrees of flocculation. It is also implicit in the derivation that the floc size is the same in the stirred suspension as in the filter-cake and also that they remain coherent in the cake. It is not clear how any of these assumptions can be justified. A series of tests were carried out during the present work on the fluorite — polyacrylamide system to check the theory of La Mer and Smellie. The results are collected in Fig.7 (see Page 61).

La Mer and Smellie assumed that the optimum permeability of the filter-cake reflects a maximum degree of flocculation. (The impairment of flocculation at high surface coverage is associated with the reduced bridging capacity of the adsorbed polymer). They therefore ascribed the right hand branch of the curve in Fig.11 to a decreasing floc size. This would increase the surface area of the flocs composing the filter-cake and reduce its permeability according to the Kozeny-Carmen equation.

Fig.7 shows that this is incorrect for the system mentioned. Floc size and strength continued to increase smoothly at dosages well beyond the permeability optimum and substantial stabilisation did not occur until much larger dosages were applied. Furthermore, curve 3 in Fig.7 shows that the reduction in permeability beyond the optimum was actually accompanied by continued expansion of the bed with

increasing dosage. The sharp fall of permeability beyond the optimum was not due to a reduction in the average floc size and the tests recorded in Table 3 show that the phenomenon was not simple.

Table 3

Filter-cakes were formed from 1% by weight suspensions of fluorite flocculated by a non-ionic polyacrylamide (NP20) under the stated conditions. Refiltration rates were measured according to the standardised procedure.

Test No. (A)	Direct "refiltration rates"	filtration rates (arbitrary units)
1	no flocculant added	5.2
2	5 p.p.m. ("optimum dosage")	68.5
3	16 p.p.m. (well beyond optimum)	16.7
4	25 p.p.m. (very large excess)	2.2
5	25 p.p.m. but before filtration supernatant liquid twice syphoned off and replaced by distilled water.	55.5
(B) Filtration of stated liquid through filter cake prepared with 5 p.p.m. (Optimum)		
6	distilled water	66.7
7	filtrate from test 3 (16 p.p.m.)	61.3
8	ditto + 1 p.p.m. more flocculant	40.0
9	supernatant liquid from 16 p.p.m. test	31.7
10	ditto, but clarified by centrifugation	39.2
11	supernatant liquid from 25 p.p.m. test	8

Comparing the results from tests Nos. 2, 4 and 5 in Table 3 indicates that the flocculated bed formed at 5 times the optimum polymer concentration is essentially the same as that formed

at the optimum. This is in accord with the results shown in Fig.7. It also agrees with the work of Weitser and Paskutskaja (20) (see page 16) who found that the floc strength was not reduced at concentrations greater than optimum.

The influence of the supernatant liquid on the filtration rate through the filter cake can be seen in tests 6 - 11. Test no. 8 shows that the permeability is markedly reduced by trace quantities of polymer and tests nos. 9 and 10 show that this index is also sensitive to a small amount of stabilised material (haze).

Hence, at least two parameters are involved. The suspended material is drawn into the bed and blocks the pores through which the liquid is drawn, thereby reducing the permeability. The second effect is associated with the adsorption of polymer from the supernatant liquid on to the walls of the pores during filtration. This leads to a reduction in the effective pore diameter and a consequent decrease in the filtration rate. The phenomenon is well known. (cf. Eirich et al 44).

At polymer concentrations well in excess of optimum, the filtration rate can be reduced to below that of the untreated suspension, even though good flocculation occurred at the high polymer dosage (see Fig.12) The above hypothesis explains this. According to the theory of La Mer and Smellie the low filtration rate at high

polymer concentration would have been associated with stabilisation of the suspension and a higher state of dispersity than in the untreated suspension.

Conclusion

These data show that the quantitative theory developed by La Mer, Smellie and Healy is invalid. It is based on an erroneous assumption as to the origin of the permeability maximum and an incorrect physical model of flocculation.

The permeability of the filter cake may, however, still be employed as a comparative index of flocculation, as it provides a sensitive, non-subjective measurement and the maximum is a good indication of the optimum dosage for a given system.

Chapter V

CHEMICAL ASPECTS OF FLOCCULATION

The flocculation of minerals of ionic lattice structure has been rarely studied, previous workers being almost exclusively concerned with oxide and clay minerals.

The surface chemistry of fluorite has been studied to elucidate the flocculation characteristics of the polyacrylamide-fluorite system.

Zeta-Potential and Stability Studies.

Micro-electrophoresis measurements were made on a demountable cell developed for mineral suspensions in these laboratories by Marshall (89) and Shergold (90). The fluorite suspensions were dispersed for five minutes (the same as for the flocculation testing procedure) and the coarse particles allowed to settle. With the suspensions mainly studied, the fluorite particles were found to be positively charged with a zeta-potential around + 40 mV; the pH was about 6.0 (because of CO₂ in the distilled water). Similar results were obtained with suspensions of chemically precipitated calcium fluoride (Hopkin and Williams, extra pure grade). These suspensions were, however, not at equilibrium, for fluorite is appreciably soluble but slow to reach saturation.

Some streaming-potential measurements were made on the apparatus of Joy, Watson and Botten (91) (which these authors kindly made

available), and these showed that many hours or days were required before steady readings were obtained. Furthermore the apparent zero point of charge was then as low as pH 4.7. The measurements were made on a de-slimed sample of - 100 + 72 mesh fluorite mineral.

The above observations may explain why the literature on the zeta-potential of fluorite is very discordant, even as regards sign (31,92-95). One consequence is that probably non-uniformity of potential exists in a ground fluorite suspension until recrystallisation has had time to occur. The flocculation data obtained certainly refer to non-equilibrium suspensions, as in many mineral treatment processes.

A further possible complication results from the use of glass components in these measuring devices. Davies and Holliday (96) have shown that F^{-} ions can form soluble complexes with glass which could give rise to anomalous results if adsorbed by the fluorite, and, conversely, glass removes fluoride ions from solution, thus shifting the equilibrium composition.

The charge on particles in the presence of polymer was not measured owing to the considerable experimental problem posed by slowly settling flocs and also to difficulty in interpreting results of zeta-potential measurements when polymers are present (115)(see Page 40).

Although Ca^{++} and F^{-} are, presumably, the primary potential-determining ions for fluorite, pH has an effect through the

dissociation equilibrium of HF and HF_2^- . Figs. 13 and 14 show the influence of pH and MgSO_4 (as an "indifferent" electrolyte) on the stability of fluorite in water. "Rapid coagulation" by indifferent salt leads to relatively permeable filter cakes (Curve 2, Fig. 14) and there is a plateau rather than a maximum in the refiltration against concentration curve. This is because excess coagulant over and above that required to eliminate electrical double layer repulsion does not cause redispersion nor does it adsorb within the pores of the filter cake reducing its permeability (see Chapter 4). It is interesting to note that the maximum permeability of the coagulated suspension shows a good correlation with the maximum instability of that suspension. But this permeability falls far short of that produced by a good flocculant (see Fig. 15) showing that the flocs formed by polymers retain during filtration a more open structure than those formed by electrolytic coagulation.

Influence of pH and Electrolytes on Flocculation.

It is common industrial practice^c to combine coagulation (induced by a change in pH or salt concentration) with polymer flocculation to economise in flocculant. The chemical action involved is not fully understood; this has already been discussed in Chapter 1 (see page 36).

The influence of electrolytes and pH on the flocculation of a fluorite suspension is shown in Fig. 15 and 16 respectively.

Fig. 13

Influence of pH on the coagulation of 1% fluorite suspensions

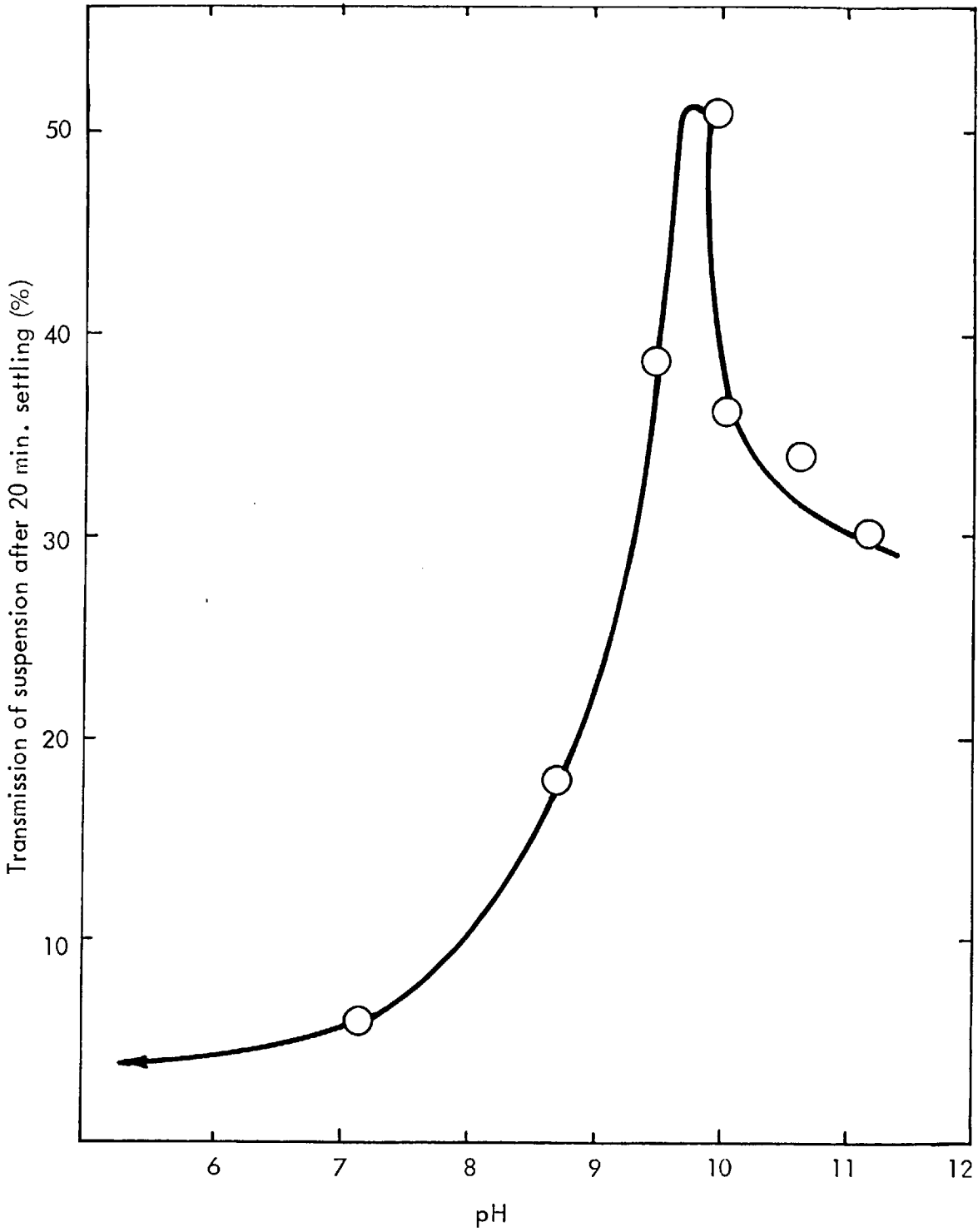
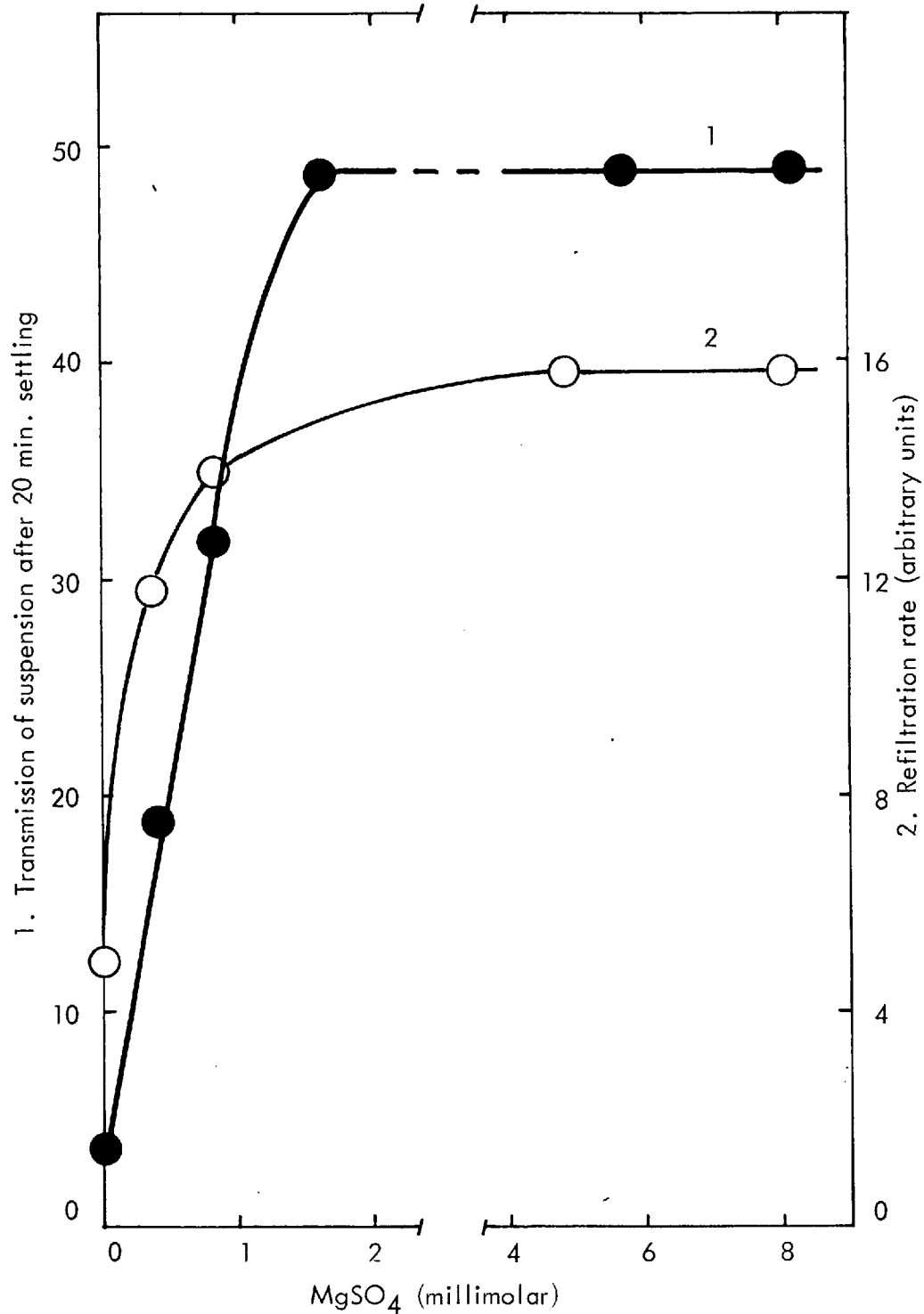


Fig. 14

Influence of $MgSO_4$ on the stability of fluorite suspensions



Influence of electrolytes on the flocculation of fluorite suspensions with constant dosage of polyacrylamide. 1. CaCl_2 , 2. NaF , 3. MgSO_4 .

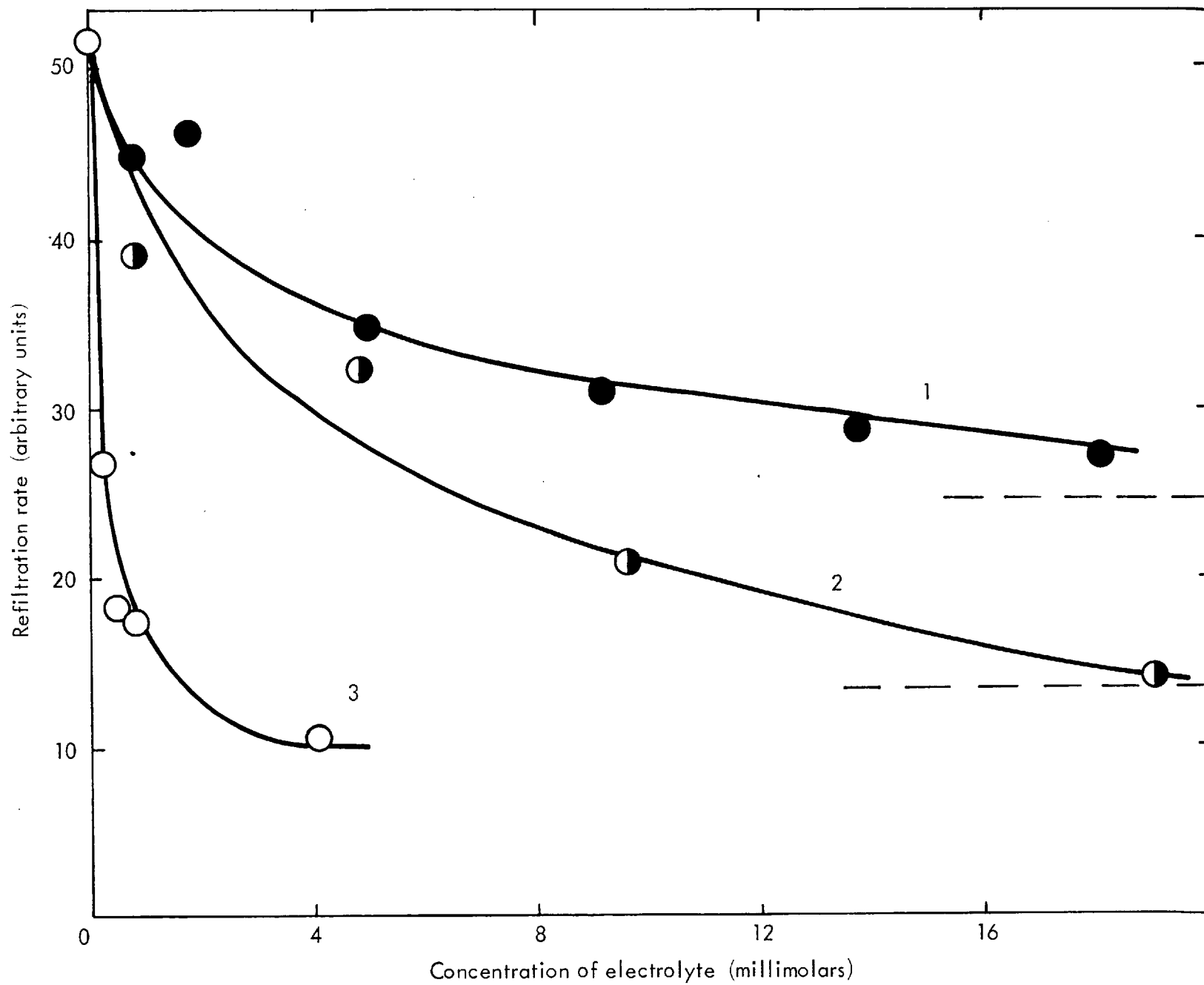
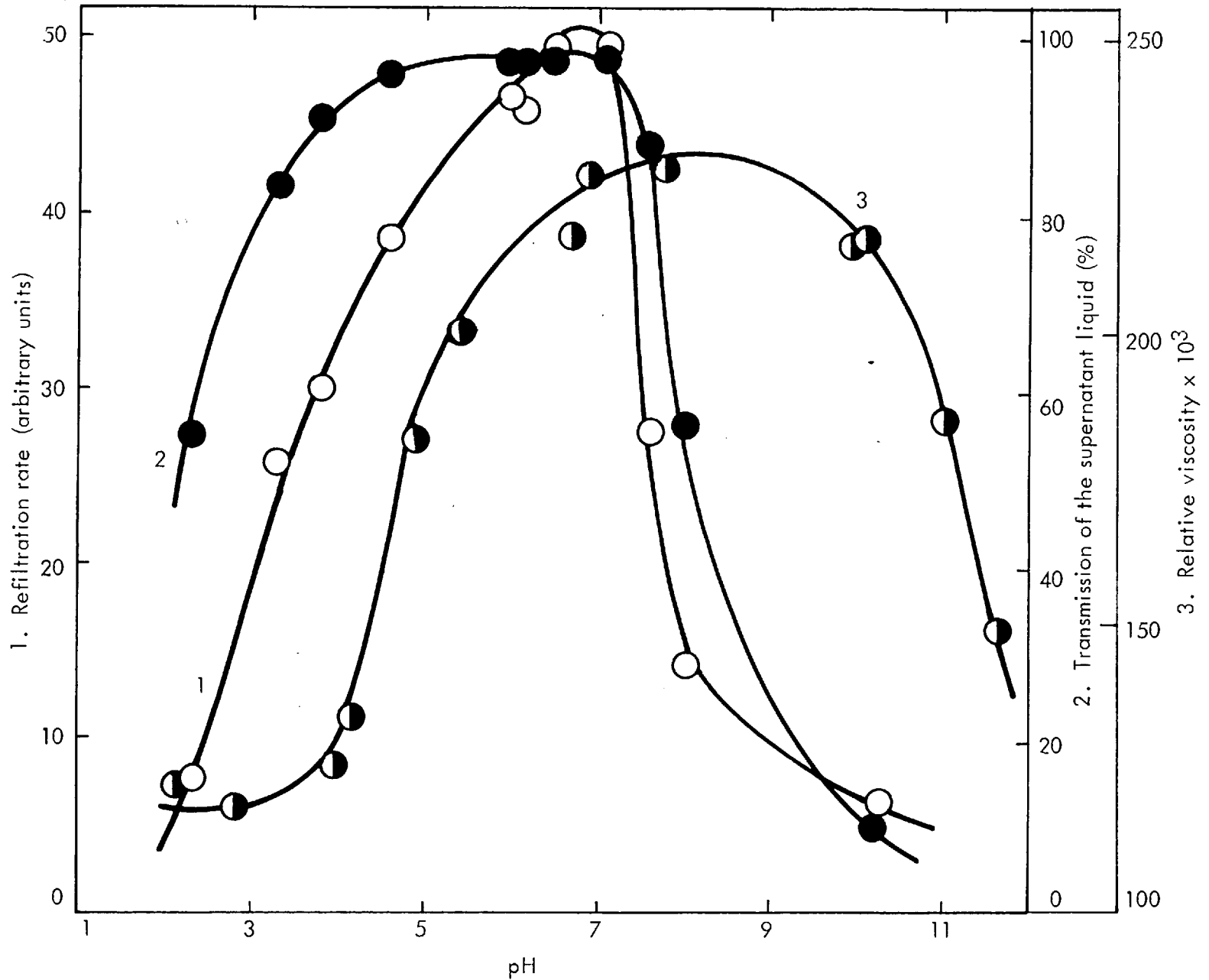


Fig. 16

Influence of pH on the flocculation of fluorite by a non-ionic polyacrylamide (Cyanamer P 250)



These data indicate that both indifferent electrolytes and electrolytes containing potential-determining ions are detrimental to flocculation. They also show that flocculation is most effective within a certain pH range. These factors may influence flocculation in two ways (see Pages 36-40).

- 1) Preliminary destabilisation can be induced by reducing the surface potential or collapsing the double layer.
- 2) The effective length of polyelectrolyte molecules is sensitive to both salt concentration and pH. The degree of ionization of the small number of carboxyl groups (1%) in the nominally non-ionic polyacrylamide, Cyanamer P250 is dependent on pH. This is important in determining its configuration which can be estimated by viscosity measurements of moderately concentrated solutions (see Fig. 16). Similar measurements showed a considerable reduction on addition of electrolytes, indicating coiling of the polymer molecules.

However, no good correlation is apparent between the degree of flocculation and either the effective length of the macromolecules or the stability of the suspensions in water. A more thorough examination of this system was excluded because a suitable analysis technique for non-ionic polyacrylamide could not be devised.

Therefore, the hydrolysed polyacrylamide-calcium fluoride system was studied. Chemically precipitated calcium fluoride was used in these tests.

An "adsorption isotherm" for the AP30-calcium fluoride system is presented in Fig. 17. The amount of unadsorbed polymer was estimated after the flocculant had been stirred with the suspension for five minutes and then the flocculated material allowed to settle for a further three minutes; i.e. the same procedure was adopted as in the standard flocculation test. The adsorption data do not refer to equilibrium conditions. In fact after 24 hours of stirring, 96% of the polymer was adsorbed by a suspension at an initial dosage of 20 p.p.m. (optimum concentration of AP30), whereas under standard flocculation conditions less than 50% was adsorbed. The rate of adsorption was found to be dependent on the stirring conditions, increasing with more vigorous agitation. It is important to emphasize that flocculation data definitely refer to non-equilibrium adsorption conditions.

The effect of pH on flocculation can be seen in Fig. 18. The following parameters were measured: i) The degree of flocculation (as indicated by optical transmission of the supernatant liquid); ii) the amount of polymer adsorbed; iii) the degree of ionization of the polymer; iv) its relative viscosity in a solution containing 0.01% by weight. The pH of the suspension was

Fig. 17

"Adsorption Isotherm" for AP 30 on calcium fluoride (1% by weight suspensions) under flocculation conditions.

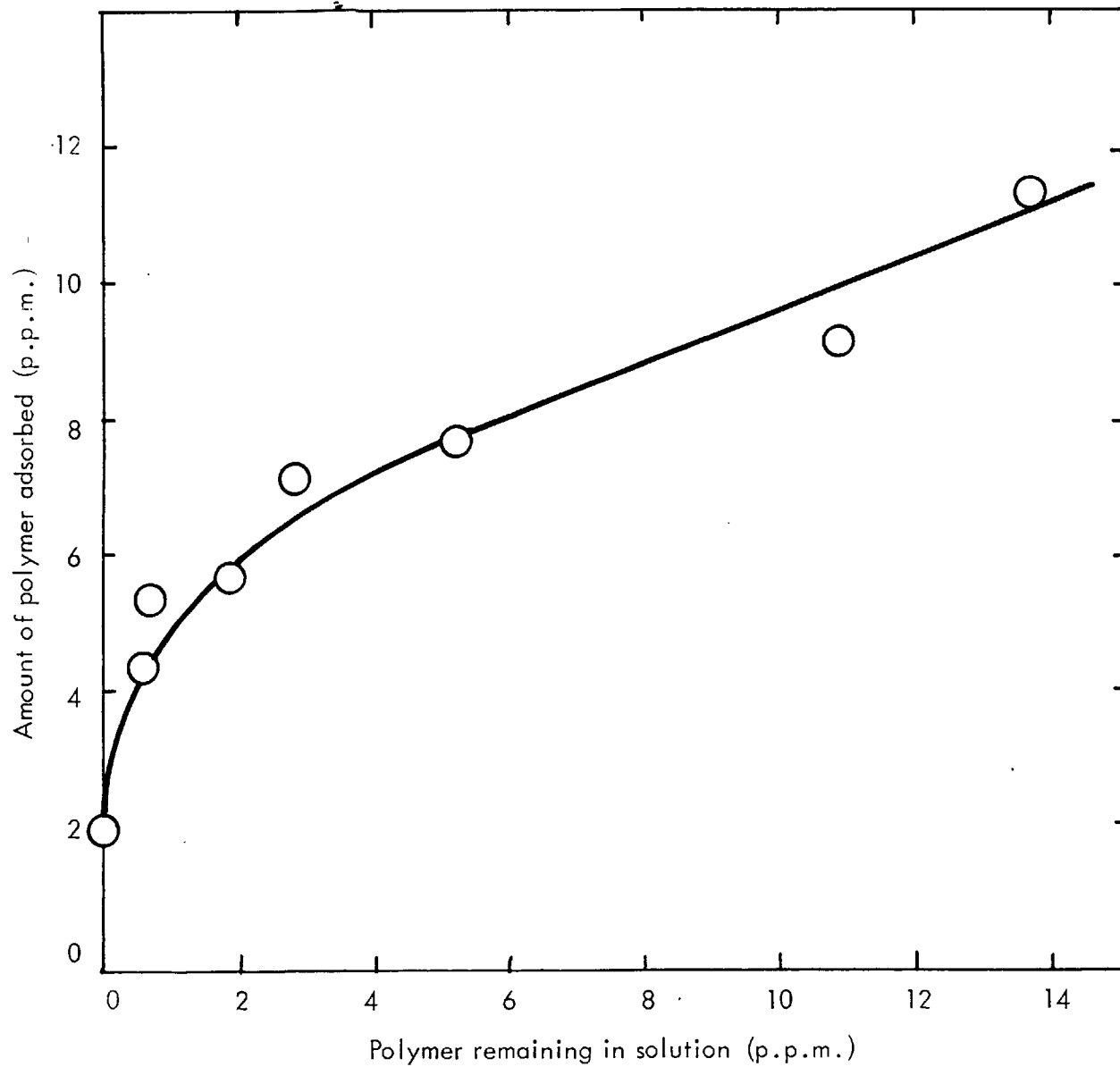
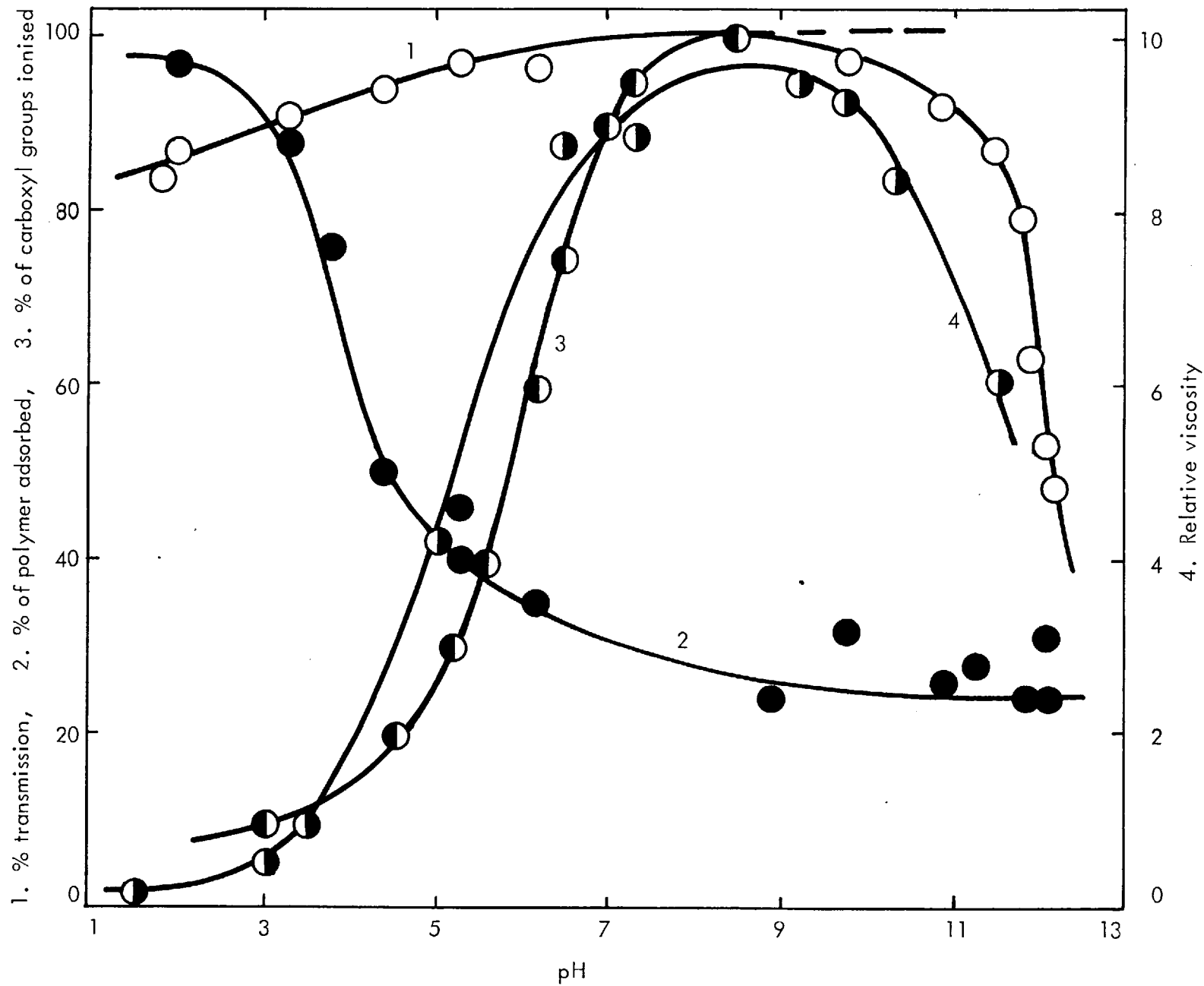


Fig. 18

Influence of pH on the calcium fluoride - hydrolysed polyacrylamide (AP 30) system.
 Constant polymer dosage (20 p.p.m.) to 1% by weight suspensions.



adjusted by the addition of HCl or NaOH three minutes before the polymer was added.

The significance of the adsorption data was subject to three initial reservations:

1) The analysis technique is dependent on the turbidity produced by reacting a polyanion with a cation (see Page 50). Synthetic flocculants frequently contain a wide range of molecular weights and are characterised commercially by their average value. The possibility that the method of analysis might be biased towards a particular range of molecular weights was investigated. An anionic polyacrylamide (similar to AP30) was prepared and mechanically degraded to give three products of identical chemical type but of different average molecular weights. (These were kindly provided by Mr. E.A. Gill of B.T.I. Limited (Bradford)). Solutions of 3 and 5 p.p.m. by weight of polymer were prepared and analysed with the nephelometric technique. The results fitted the calibration curve, Fig. 4, within 5%. It was concluded that the analysis technique was not strongly dependent on the molecular weight of the polymer.

2) The adsorption characteristics of a polymer solution exhibiting a range of molecular weights is not simple. Initial adsorption of the low molecular weight fraction is preferred, because of the higher diffusion coefficient of the smaller molecules (35). With systems showing strong irreversibility e.g. poly(dimethyl siloxane) on glass or iron (114), this initial

situation is preserved under "equilibrium" conditions. The thermodynamic equilibrium conditions, however, are present only in reversible systems e.g. polystyrene-butadiene copolymers (97) and polystyrene (98) on carbon black. Then there is a preferential adsorption of high molecular weight polymers under the final, true equilibrium conditions (97,98).

Any significant fractionation of the molecular weight of a polymer by adsorption should have a marked effect on its efficiency as a flocculant (by analogy with the effect of different molecular weight polymers in flocculation : Page 14). A flocculation test was completed at pH 12. Curve 2, Fig. 18, indicates that about 75% (i.e. 15 p.p.m.) of the polymer, AP30, was unadsorbed. Therefore 250 ml of the supernatant liquid from this test was decanted and the pH adjusted to 5.3; it was then used to flocculate 5 g of fluorite dispersed in 250 ml of distilled water. 250 ml of a 15 p.p.m. solution of AP30 was prepared, the pH increased to 12 and then brought back to 5.3. It was then used to flocculate a similar suspension of fluorite. The results of the two tests were identical, viz. 74% transmission in the supernatant liquid. They therefore suggest that there was no significant fractionation of this polymer under flocculation conditions.

3) It has been suggested that the amount of polymer adsorbed might be dependent on the rate of floc formation (99). Accordingly,

when the primary particles are rapidly aggregated into flocs the surface area available for subsequent polymer adsorption would be markedly reduced, and hence could give rise to low adsorption values. Conversely, with slower floc formation the primary particles would be available to unadsorbed polymer molecules for a longer time so that a higher degree of adsorption could be expected.

This hypothesis was tested by using a new mixing technique which was designed to give a more uniform and immediate distribution of polymer than the standard mixing conditions, (see Page 45). A comparison of the amount of polymer adsorbed under the two mixing conditions should then indicate whether the rate of floc formation has a significant effect. "Flash mixing" involves the simultaneous addition of equal volumes of polymer solution and suspension to a measuring cylinder. (3% by weight suspensions of calcium fluoride were used at an AP30 dosage of 20 p.p.m.). The cylinder was then gently inverted for five minutes before the settling rate of the floc boundary was measured. The settling rates were compared with flocs formed under "standard" mixing conditions. The amount of polymer adsorbed was estimated by decanting 250 ml of the clear supernatant liquid above the flocs and "flash mixing" it with a new suspension of calcium fluoride. Although the "flash mixing" technique gave slightly higher settling rates the amount of polymer left in the supernatant liquid (as

judged by the second flocculation test) was independent of mixing conditions over the pH range 3 - 12. This was confirmed by nephelometric analysis at pH 6.5 when it was shown that 95.5% and 96% of the initial polymer dosage was adsorbed under standard and flash mixing conditions respectively.

Hence, in the present system, the amount of polymer adsorbed and the degree of flocculation were largely unaffected by the different mixing conditions. Presumably, the inner surfaces of the high porosity flocs were still accessible to polymer molecules. The degree of adsorption would probably be significantly effected only when the pores in the adsorbent were comparable in size with the polymer molecules, by analogy with the adsorption of polymers on to activated charcoal. This situation is unlikely to arise with the porosity of initially formed free flocs approaching 93% (100). It would, however, probably be important in pre-coagulated suspensions or with an incompletely dispersed powder containing aggregates.

With the significance of the adsorption data confirmed, the flocculation results were interpreted as being dependent on both the adsorption and the effective length of the polymer molecules (as indicated by the relative viscosity of the solution).

Below pH 6 electrostatic forces enhance adsorption, as the fluorite is positively charged and the polymer partially ionized as an anion. This effect is probably supplemented by the reduced

solubility (hence, high activity coefficient) of the polymer at low degrees of ionization; at pH 1.7 a 0.01% solution of AP30 produces a precipitate of insoluble polymer. Above pH 8 the amount of polymer adsorbed is almost independent of pH. Under these conditions both polymer and particles are negatively charged, indicating a non-ionic mechanism of adsorption, as with pure polyacrylamide. There is a close relationship between the degree of ionization of the carboxyl groups in AP30 and its relative viscosity (curves 3 and 4, Fig. 18). In the unionised (hydrogen) form the molecule is a fairly compact "random coil." With increasing ionization, mutual repulsion between the similarly charged carboxyl groups leads to considerable chain extension. "Tangling" of these chains gives rise to increased viscosities and a maximum value is observed at pH 9. At still higher pH values the increased ionic strength partially collapses the electrical double layer in the vicinity of the chains and hence weakens the electrostatic expansion.

The viscosities of the polymer solutions were measured in an 0.01% by weight solution in a standard Ostwald viscometer. The degree of ionization of the carboxyl groups was calculated from a potentiometric titration of 0.1% AP30 solution with N/10 HCl (the assumption being made that the ionization of a weak poly-electrolyte is independent of its concentration and controlled mainly by pH).

The results collected in Fig. 18 show that while adsorption is, of course, indispensable, optimum flocculation is obtained with maximum extension of the polymer chain. This hypothesis assumes that the bridging theory of flocculation is operative and also that the configuration of the solvated macromolecule is similar to that of the adsorbed molecule. The work of Eirich and Rowland (44) is in accord with this latter concept (see Page **35**)

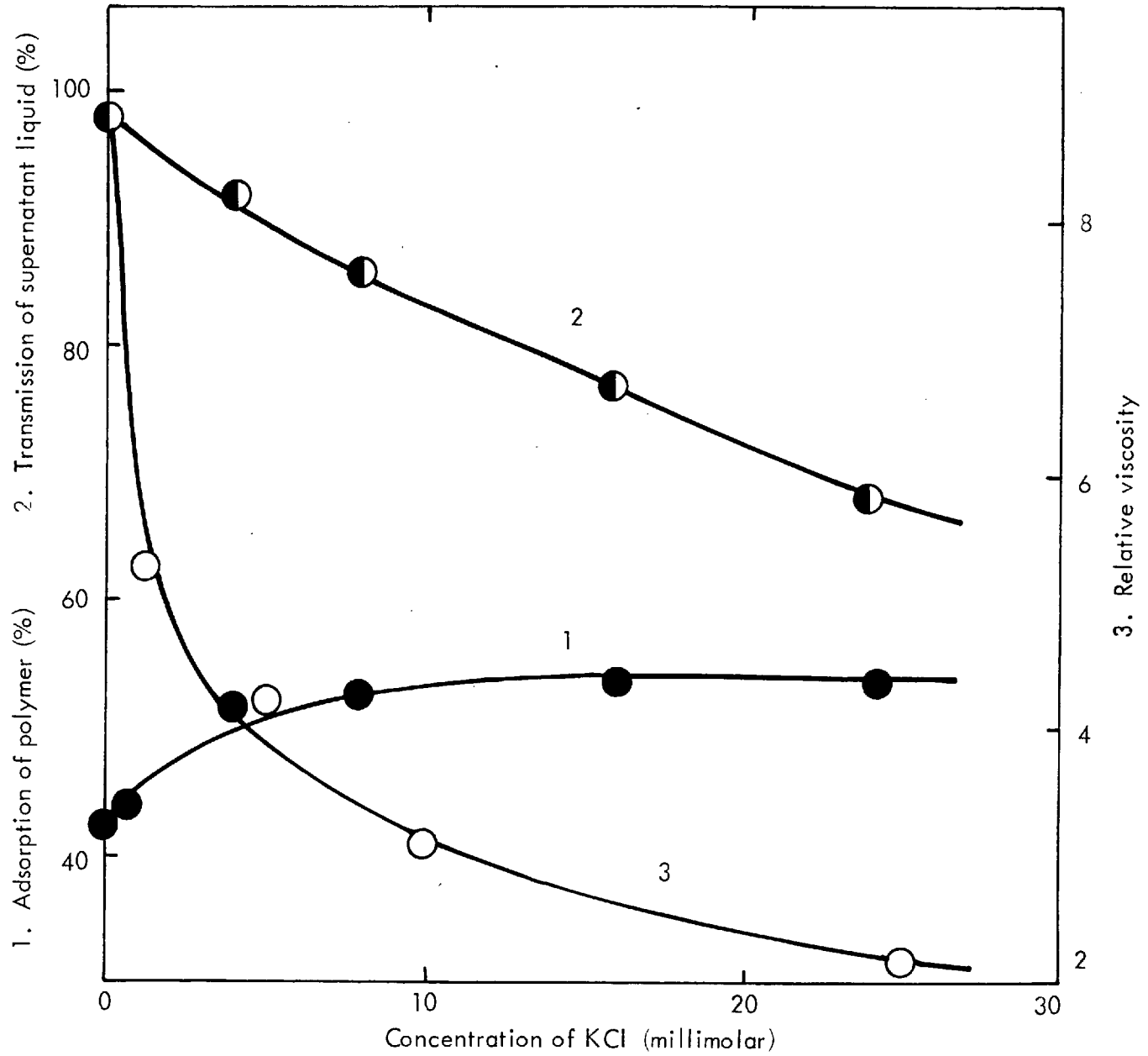
The effect of reduced chain extension below pH 9 is partly off set by increasing adsorption. Above pH 9 a progressive coiling of the polymer chain leads to poorer flocculation.

A further consequence of the good correlation between the relative viscosity and degree of ionization of AP30 is that there is no indication of any significant intra-molecular interaction (H-bonding). In the case of polypeptides the viscosity does not increase very much until there is about 40% ionization (102). Up to this value the intra-molecular repulsive force introduced by the ionized groups is insufficient to overcome the majority of the intra-molecular H-bonds and the molecule remains in the coiled state. With carboxyl groups only, intra-molecular H-bonding is comparatively weak and the polymer coil expansion is directly related to the proportion of ionized groups.

The effect of a neutral salt on the flocculation can be seen in Fig. 19. With increasing ionic strength the relative

Fig. 19

Influence of KCl on the flocculation of fluorite by AP 30



viscosity is reduced, indicating a progressive coiling of the polymer chain due to the collapse of the double layer in the vicinity of the macromolecule. This again reduces the bridging capacity of the polymer and is detrimental to flocculation. The slight increase in adsorption is probably due to a "salting out" mechanism (51) but is insufficient to overcome the dominant effect of chain coiling.

The Mechanism of Adsorption of Polyacrylamide on to Fluorite.

Kuz'kin and Nebera (56) have suggested that polyelectrolytes containing carboxyl groups, e.g. AP30, are adsorbed by minerals containing calcium through the formation of an insoluble calcium-polyacid salt.

Mortensen (68,69) and Jones et al (14) have suggested a similar mechanism whereby calcium ions are adsorbed on to the surface of mineral particles which then act as "key points" for the adsorption of polymers containing carboxyl groups, again through the formation of a calcium-polyacid salt.

However, the suggestion of Kuz'kin and Nebera has never been proved and alternative explanations have been given for the findings of the other authors (see Page 36) which does not involve the formation of such a salt.

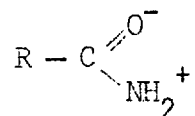
The amount of AP30 adsorbed was not dependent on the proportion of ionized groups (see curve 3, Fig.18). This indicates that, over at least part of the pH range, a non-ionic

mechanism of adsorption operates. Also, there was little difference in the efficiency of flocculation of two polymers of similar molecular weight, one being nominally non-ionic (NP20) and the other (AP30) with 30% carboxyl groups (see Fig. 12). If adsorption was mainly through the formation of a calcium salt a much larger difference would be expected. The slightly better flocculation obtained with AP30 is probably due to the greater effective length of the molecule, resulting from the higher density of mutually repelling ionic groups along the polymer chain. (Nevertheless, attempts were made to convert any carboxyl groups in NP20 into the amide (103). Unfortunately the reaction, suitable for the monomer, was not directly applicable to the polymer and a certain amount of insoluble (presumably cross-linked) material was also formed. The soluble material was a suitable flocculant although considerably higher concentrations were required to provide flocculation equivalent to NP20).

A high molecular weight copolymer of acrylamide and a quaternary ammonium compound has recently been made available as a flocculant (Cl10, B.T.I. Limited Bradford). This is reputed to contain no carboxyl groups but was found to flocculate fluorite. On the other hand, fluorite was not susceptible to flocculation with a completely cationic polyelectrolyte, namely polyethyleneimine (which does flocculate negative suspensions such as precipitated silica).

It follows, therefore, that adsorption is not of the general electrostatic type nor through the formation of an insoluble polyacid salt. It seems likely that there is a non-ionic adsorption mechanism through the amide group. The mechanism is evidently not specific to fluorite as non-ionic polyacrylamide can flocculate many ionic minerals (CaCO_3 , PbS , BaSO_4 , etc.). The problem is to explain how amides are linked to ionic crystal lattices. One possibility, by analogy with oxides, is that some of the surface groups on these ionic solids in water are replaced by hydroxyl groups, and adsorption of amide groups occurs by hydrogen-bonding (51). Hydrolytic anion exchange doubtless occurs to some extent, and as F^- and OH^- are of about the same size, the surface reaction, $\text{Ca}^{2+}\text{F}_2^- + \text{OH}^- (\text{aq}) \rightleftharpoons \text{Ca}^{2+}\text{F}^-\text{OH}^- + \text{F}^- (\text{aq})$ is particularly plausible with fluorite. In support of this theory, infra-red spectra were taken by the KBr - disc technique on chemically precipitated calcium fluoride powder and these showed the -OH bond at c.2.9 μ , which was not removed by prolonged drying at 250°C. On the other hand, flocculation of fluorite has found to be unaffected by "hydrogen-bond competitors" e.g. bis (2 - (2 - methoxyethoxy) ethyl)ether which inhibit adsorption on "isolated" hydroxyl groups on silica (51). Also, a high molecular weight polyethylene oxide (presumably a good hydrogen bonding agent) which was a successful flocculant for silica and alumina was ineffective with fluorite suspensions.

A second possibility is that adsorption could occur through the dipolar nature of the amide group. Although it has not been completely proved, it is generally accepted that the amide group does possess a dipole (104).



This could interact with the electrostatic field on the surface of the ionic crystals to provide an adsorption mechanism. The recent work of Tahaun and Mortland(58,59) on the adsorption of amide monomers on to Cu, Ca and Na forms of montmorillonite appears to support this possibility. They viewed adsorption as occurring by a dipole-ion interaction, the ion (Cu, Ca or Na) being incorporated in the lattice of the clay platelets. Their evidence was based on the interpretation of infra-red spectra.

Attempts were made to study the adsorption of polyacrylamide on to fluorite with the aid of infra-red spectra from KBr discs. Although fluorite does not absorb over a wide range in the infra-red, the amount of light scattered by the small particles of fluorite reduced the transmission so much that the spectrum of the adsorbed material could not be adequately resolved. The success of Griot and Kitchener (51) using a similar disc technique to study the adsorption of polyacrylamide on to silica was favoured by two factors - firstly, the very high surface area of the silica (380 sq.m/g) would have a comparatively high adsorption

capacity and, secondly, it was possible to prepare transparent, self-supporting discs of the silica which did not cause much scattering.

Attempts to analyse the fluorite system by the multiple internal reflectance technique were also unsuccessful. (These measurements were kindly made by Techmation, London).

Influence of Divalent Cations on Flocculation.

Several authors refer to the beneficial effect of salts of divalent cations on flocculation (6,14,23,31). There are probably two completely different modes of action:

- 1) If the pH of the medium is sufficiently high, polynuclear hydrated species of Cu^{++} , Ni^{++} , Co^{++} etc. are formed and can themselves act as flocculants. The mechanism involved is probably similar to the well documented cases of Fe^{3+} and Al^{3+} (67) (which are widely used for clarifying water).
- 2) The system, however, may be at a pH where the cations are fully ionised and the action of these is not completely understood (see Page 36)

The systems which have been previously studied have been negative particles, silica (14,31) and clay minerals (6), flocculated by an anionic polyacrylamide. Such systems are subject to two opposing forces. Firstly, the effective length of the polymer molecule can be increased by introducing similarly charged ionic groups along the chain; therefore, the adsorbed molecule can extend further into solution and exhibit a higher bridging

capacity. Secondly, if the adsorption is due to non-ionic hydrogen-bonding, increasing the negative charge of the polymer increases the electrostatic repulsion between the polymer molecule and the charged particle. This could reduce the amount of adsorption.

The influence of Ba^{2+} on the silica - AP30 system was investigated. Suspensions of 0.25% "Aerosil" (Degussa, Germany) in water were used as the experimental dispersion. (Aerosil is a high purity silica (99.9% SiO_2) with a specific surface area of 380 sq. m/g. It is made by the combustion of $SiCl_4$ with another combustible gas such as hydrogen, the SiO_2 being collected directly from the flame on a cooled surface). Ba^{2+} alone had no immediate effect on the settling characteristics of suspensions at pH values below 9.6. Above this value, immediate, massive flocculation took place $BaCl_2$. This effect has been reported previously (105). Amorphous silica is slightly soluble in water above pH 9 (106). Under such conditions, and in the presence of Ba^+ , the precipitation of $BaSiO_3$ would be expected. A reticular structure of insoluble $BaSiO_3$ would probably be an effective flocculant acting as a binder, like the hydrolysed species of multivalent cations.

The system was also investigated at a pH of 4.3 ± 0.2 ; at this value the Ba^{++} should be completely ionised. Two forms of silica suspension were used - fresh and "aged." (cf. Griot and Kitchener (51), Page 32).

AP30 is only a marginally effective flocculant with fresh silica. However, at a BaCl_2 concentration of $4 \times 10^{-4}\text{M}$, AP30 was effective at a dosage of 5 p.p.m. At an equivalent ionic strength, ($1.2 \times 10^{-3}\text{M}$), KCl produced only a slight improvement in flocculation. The aged silica suspensions were unaffected by Ba^{2+} up to a concentration of 0.1M in the presence of AP30.

Divalent cations are adsorbed on to silica surfaces and this does not appear to be dependent on whether the surface has been "aged" or not (107,108,109).

Several possible mechanisms are suggested by the results and, together with the hypotheses of previous authors, they are discussed below.

1) The adsorption of a divalent cation on to the surface of silica could act as a "key point" for the attachment of a functional group, by analogy with the formation of an insoluble polyacid salt (14,31). If this were applicable to the above system then "aged" silica should be equally susceptible to flocculation by AP30 in the presence of Ba^{2+} .

Similarly no difference between "aged" and fresh silica would be expected if (2) or (3) below were applicable:-

2) An increase in the ionic strength might enhance adsorption by a "salting-out" mechanism, without any specific salt formation.

3) The cations could associate with the polymer in solution to form a hydrated polyacid-ion complex (110). It is well known that

measurements of the rigidity of surface films of fatty acids in the presence of various cations have indicated that association can occur prior to precipitation (111). If such a complex were formed it would probably be more likely to be adsorbed than the untreated polymer.

4) The increased ionic strength could reduce the zeta potential below a threshold value which might then allow adsorption forces to predominate over electrostatic repulsive forces. If this were the mechanism, then there should be no difference between the effects of KCl and BaCl₂ on the AP30 — (fresh silica) system.

5) Alternatively, the cation, acting as a potential-determining ion, might adsorb on to the silica surface and thereby reduce the surface potential. The repulsion between polymer and particle would then be reduced and adsorption could occur by hydrogen-bonding (as in (4)). This would explain the effect of Ba²⁺ on fresh and "aged" silica, as in "aged" silica there are no surface sites available for hydrogen-bonding.

This hypothesis was further investigated by a study of an alumina suspension flocculated by two cationic polyacrylamides in the presence of (NH₄)₂ HPO₄. 0.5% by weight suspensions of Degussa alumina were used at pH 6, where both the alumina and the polymer are positively charged. (The alumina is a high purity (99%)

Al₂O₃ made by Degussa, Germany. This material has a specific surface area of 100 ± 10 sq.m/g and a particle size of 5-30m μ).

Alumina is flocculated by non-ionic polyacrylamide, adsorption occurring by hydrogen-bonding (51) also HPO_4^{--} and HPO_4^- are specifically adsorbed on the alumina surface by complex formation. This system, therefore, is analogous to the AP30 — silica — Ba^{2+} system, but of opposite charge.

C100 and C110 were the cationic polyacrylamides used; the former has a lower proportion of the quaternary ammonium compound copolymer but they are reported to be of similar molecular weight. Therefore, C110 has a higher charge than C100.

Up to a concentration of $(\text{NH}_4)_2\text{HPO}_4$ of $1.3 \times 10^{-5}\text{M}$ there was no immediate effect on the stability of the alumina suspensions. At $1.6 \times 10^{-5}\text{M}$ there was incipient coagulation and at higher concentrations rapid coagulation was observed.

C100 alone caused marginal flocculation of alumina and its effectiveness increased in the presence of $(\text{NH}_4)_2\text{HPO}_4$. On the other hand C110 was ineffective alone and did not have a significant effect until a concentration of $1.6 \times 10^{-5}\text{M}$ $(\text{NH}_4)_2\text{HPO}_4$ was reached. At a concentration of $2 \times 10^{-5}\text{M}$ massive, immediate flocculation with C110 occurred. However, still higher concentrations were detrimental to flocculation, although causing rapid coagulation in the absence of polymer.

These results can be interpreted on the basis of the hypothesis developed above for the silica system. The electrostatic forces of repulsion between the alumina and the C100 macromolecule are insufficient to prevent adsorption, but it is weak. With C110 the

higher repulsive force has to be reduced, by lowering the surface potential of alumina through the adsorption of phosphate ions, before adsorption of the polymer can occur. In this system the threshold surface potential for adsorption would appear to be associated with the zeta potential at which slow coagulation occurs, i.e. about +30mV. At high ionic strengths the collapse of the double layer around the polycation would lead to a reduction in its effective length (cf. AP30/fluorite in the presence of KCl — Fig. 19). It is assumed that no association complexes between the polycations and the phosphate ions are formed and that the adsorption occurs through hydrogen-bonding.

Conclusions

(1) From the investigations that have been made into the chemical factors effecting the flocculation of fluorite suspensions by polymers based on polyacrylamide, data have been obtained which show a clearly marked influence of pH and of a neutral salt on the hydrolysed polyacrylamide (AP30) and fluorite system - namely on (a) the flocculation characteristics, (b) the adsorption characteristics and (c) the viscosity of the polymer in solution. These results indicate that, while adsorption is indispensable optimum flocculation is obtained only with maximum extension of the polymer molecules, and this property is itself strongly dependent on the pH and the ionic strength of the medium.

(2) The mechanism of adsorption of polyacrylamide on to ionic crystals such as calcium fluoride has been considered. Adsorption by hydrogen bonding appears unlikely to occur and the possibility of dipole interaction of amide groups with the electrostatic field of the crystal lattice is suggested.

(3) The influence of divalent cations on the adsorption of hydrolysed polyacrylamides on to silica has also been investigated. The possibility of adsorption occurring through the formation of an insoluble polyacid salt is discounted. A more likely mechanism is that the cation might adsorb on to the silica surface and thereby reduce the effective double-layer potential. The electrostatic repulsion between polymer and particle would then be reduced and adsorption could occur by hydrogen-bonding (as between non-ionic polyacrylamide and fresh silica (51)). This hypothesis was tested by investigating a similar system but of opposite charge -- the alumina -- cationic polyacrylamide -- ammonium hydrogen phosphate system. This system provided confirmatory evidence for the hypothesis.

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APPENDIX 1 - A LIST OF THE POLYMERS USED IN THIS STUDY

1) Polyacrylamide and its derivatives.

a. Nominally non-ionic.

<u>Trade Name</u>	<u>Molecular Wt. (millions)</u>	<u>Manufacturer</u>
NP10	1	Dow Chemical Company
N20	3	Dow Chemical Company
Polyflok PX	2	Yorkshire Dyeware Co.
Cyanamer P250	5 - 6	American Cyanamid

b. Anionic derivatives produced by alkali hydrolysis of polyacrylamide.

<u>Trade Name</u>	<u>Molecular Wt. (millions)</u>	<u>Manufacturer</u>
AP30	3	American Cyanamid
A100	several millions	B.T.I. Ltd., Bradford
A110	several millions	B.T.I. Ltd., Bradford
A130	several millions	B.T.I. Ltd., Bradford
A150	several millions	B.T.I. Ltd., Bradford
The anionic character is reported to increase in the order A100 to A150		
Nalco D-1782	several millions	Nalco Limited

c. Cationic derivatives formed by the copolymerisation of acrylamide monomer with quaternary ammonium compounds.

<u>Trade Name</u>	<u>Molecular Weight</u>	<u>Manufacturer</u>
C100	several millions	B.T.I. Ltd., Bradford
C110	several millions	B.T.I. Ltd., Bradford

C110 is reported to have a higher proportion of cationic groups than C100

2) Flocculants not derived from acrylamide.

a. Non-ionic.

<u>Trade Name</u>	<u>Chemical Type</u>	<u>Manufacturer</u>
Polyox	a polyethylene oxide of several million molecular weight	Union Carbide Corp.

b. Cationic.

<u>Trade Name</u>	<u>Chemical Type</u>	<u>Manufacturer</u>
C120	polyethyleneimine of molecular weight 50,000	Dow Chemical Company
Polyethyleneimine	Molecular weight 50,000	B.D.H.

APPENDIX 2 - TABLES OF RESULTS

TABLE I

The effect of the intensity of agitation on the refiltration rate and turbidity of the supernatant liquid when stirred for five minutes after the addition of the flocculant. (2% by weight suspension of hematite flocculated by 3 p.p.m. of Cyanamer P250).

Speed of impeller (r.p.m.)	Refiltration rate (arbitrary units)	Transmission of the supernatant liquid (%)
250	23.5	69
400	36.2	83
800	47.6	94
1200	49.8	94
1600	48.8	88
2000	47.6	73

These results are presented graphically in Fig. 3.

TABLE II

Calibration results for determining small quantities of anionic polyacrylamide (AP30) by a nephelometric technique.

Polymer concentration (p.p.m.)	Nephelometer reading (arbitrary units)
0.	3.53-3.84
0.5	3.22
1.25	2.55
2.5	1.55
3.75	0.82
5.0	0.62
7.5	0.36
10	0.23

These results are presented graphically in Fig. 4.

TABLE III

The effect of polymer concentration on a number of indices of flocculation. (The suspensions were 8% by weight fluorite and the flocculant was non-ionic polyacrylamide — ^aCynamer P250).

Polymer dosage (p.p.m.)	Settling rate (cm/sec)	Settled height (cm)	Transmission of supernatant liquid (%)	Refiltration rate (arbitrary units)	Thickness of the compacted bed (cm)
0	-	1.0	2	0.9	0.8
5	0.41	3.3	15	-	-
10	0.58	4.5	95	9.4	1.0
15	0.69	4.3	99	11.6	1.1
20	0.94	4.1	99	14.3	1.15
25	1.6	4.0	98	11.5	1.4
40	1.7	3.7	99	7.7	1.55
50	1.7	-	99	-	-
60	-	3.5	95	<5	1.5
100	1.8	3.3	88	<2	1.5
200	2.4	-	84	-	-

These results are presented graphically in Fig. 7.

TABLE IV

The influence of solids concentration on the flocculation of
of fluorite suspensions by non-ionic polyacrylamide (Cyanamer P250)

Percent solids by weight (%)	Optimum polymer dosage (mg/g)	Permeability index (Refiltration rate/ wt. % solids)	Transmission of supernatant liquid at optimum polymer dosage (%)
0.5	5.6	29	95
1	3.4	47.6	98
2	3.4	62.6	99
5	2.2	98	100
8	2.5	113.6	99

These results are presented graphically in Fig. 8.

TABLE V

The influence of solids concentration on the flocculation of hematite suspensions by an anionic polyacrylamide (Nalco D-1782).

Percent solids by weight (%)	Optimum polymer dosage (mg/g)	Permeability index (Refiltration rate/wt. % solids)	Transmission of the supernatant liquid at optimum polymer dosage for refiltration rate (%)
0.5	0.09	45.0	37
1	0.09	62.3	46
2	0.09	95.4	64
4	-	-	84 [±] 3

These results are presented graphically in Fig. 9.

TABLE VI

Effect of the molecular weight of polyacrylamide flocculants on the efficiency of flocculation. The polymer dosage reported was that required to achieve the highest permeability of the filter-cake produced from 3% by weight suspensions of fluorite.

Optimum polymer dosage (p.p.m.)	Nominal mol. wt. of polymer (millions)
14	1
8.4	3
5.4	5-6

These results are presented graphically in Fig. 10.

TABLE VII

The influence of polymer concentration on two flocculation characteristics for the AP30 — fluorite and NP10 — fluorite systems. (Suspension 3% by weight).

NP20			AP30	
Polymer dosage (p.p.m.)	Transmission of the supernatant liquid (%)	Refiltration rate (arbitrary units)	Polymer dosage (p.p.m.)	Refiltration rate (arbitrary units)
0	0	5.2	0	5.2
1	4	7.0	0.5	25.5
2.5	56	25.5	1.9	60.6
3	80	38.7	2.5	69.7
4	95	59.7	4.0	70.7
5	97	70.2	6.0	79.3
10	90	48.2	7.5	39.9
12.5	91	40.4	10	23.0
16.0	89	16.4		
25	83	2.2		

These results are presented graphically in Fig. 12.

TABLE VIII

Effect of pH on the stability of a 1% suspension of fluorite. The transmission of the supernatant liquid was measured at half the height of the liquid column after 20 minutes settling.

pH	Transmission (%)
2 - 6.2	4
7.2	6
8.7	18
9.5	39
9.9	51
10.1	36
10.6	34
11.1	30

These results are presented graphically in Fig. 13.

TABLE IX

Effect of MgSO_4 on stability and filterability of 1% suspension of fluorite. The transmission of the supernatant liquid was measured at half the height of the liquid column after 20 minutes settling. The refiltration rate was determined as in the standardised procedure for flocculated suspensions. pH of the suspensions was 5.5 ± 0.2 .

Conc. of MgSO_4 (millimolar)	Transmission (%)	Refiltration rate (arbitrary units)
0	4	5.1
0.4	19	11.9
0.8	32	14.1
1.6	49	-
4.1	-	15.8
5.6	49	-
8.1	49	15.4

These results are presented graphically in Fig. 14.

TABLE X

The influence of electrolytes on the flocculation of fluorite suspensions with a constant dosage of polyacrylamide (NP20). 1% by weight suspensions were used and the polymer dosage of 5 p.p.m. the optimum dosage established in the absence of electrolytes.

Conc. NaF (milli-molar)	Refiltration rates (arbitrary units)	Conc. CaCl ₂ (milli-molar)	Refiltration rates (arbitrary units)	Conc. MgSO ₄ (milli-molar)	Refiltration rates (arbitrary units)
0	51.8	0	51.8	0	51.8
0.95	38.7	0.9	44.9	0.16	26.7
4.8	32.2	1.8	46.4	0.41	18.4
9.5	20.6	4.6	34.8	0.81	17.3
19.0	14.3	9.1	31.2	4.1	10.9
28.6	14.5	13.6	29.1		
		18.2	27.4		
		36.5	24.9		
		45.6	24.7		

These results are presented graphically in Fig. 15.

TABLE XI

The influence of pH on the flocculation characteristics of the Cyanamer P250 — fluorite system.

pH	Transmission of the supernatant liquid (%)	Refiltration rate (arbitrary units)
2.3	55	7.8
3.3	83	25.7
3.8	91	30.0
4.6	96	38.6
6.0	96	46.8
6.15	96	46.0
6.5	97	49.6
7.1	97	49.4
7.6	88	27.6
8.0	56	14.2
10.2	10	6.7

These results are presented graphically in Fig. 16.

TABLE XII

Adsorption data for the AP30 — calcium fluoride system established under the standardised flocculation test conditions. 1% by weight suspensions were employed.

Amount of polymer adsorbed (p.p.m.)	Polymer remaining in solution (p.p.m.)
2.0	0
4.4	0.6
5.4	0.7
5.7	1.9
7.2	2.8
7.7	5.2
9.2	10.8
11.4	13.6

These results are presented graphically in Fig. 17.

TABLE XIII

The influence of pH on the transmission of the supernatant liquid and the amount of polymer adsorbed on the AP30 — calcium fluoride system. (1% by weight suspension at a constant polymer dosage of 20 p.p.m.).

pH	Transmission of the supernatant liquid (%)	Percentage of polymer adsorbed (%)
1.8	83	-
2.0	87	95.5
3.3	91	87.5
3.8	-	76.0
4.4	94	50.0
5.3	98	40, 46
6.2	96	35
8.9	-	24
9.8	97	32
10.9	92	26
11.3	83	28
11.5	87	-
11.8	79	-
11.9	63	24
12.1	53	32
12.2	48	24

These results are presented graphically in Fig. 18.

TABLE XIV

The influence of the concentration of KCl on various characteristics of the AP30 — calcium fluoride system. 1% by weight suspensions were employed at a constant polymer dosage of 20 p.p.m. and at pH 5.3 \pm 0.2.

Conc. of KCl (milli-molar)	Transmission of the supernatant liquid (%)	Conc. of KCl (milli-molar)	Amount of polymer adsorbed (%)	Conc. of KCl (milli-molar)	Relative viscosity of 0.01% soln. of AP30 (arbitrary units)
0	98	0	42	0	8.8
0.8	97	0.8	44	1.0	5.3
4.0	92	4.0	52	5.0	4.2
8.0	86	8.0	52	10.0	3.1
16.0	77	16.0	54	25.0	2.2
24.0	68	24.0	54		

These results are presented graphically in Fig. 19.