

**Allied Colloids**



# **FLOCCULATION: THEORY AND APPLICATION**

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The efficiency of solid/liquid separation may be greatly improved by the application of synthetic polymeric flocculants, particularly in coal preparation where sedimentation, filtration and centrifugation processes are extensively used. This improvement is achieved by bringing dispersed particles together increasing the effective particle size of the solid phase. The stability of the suspension is broken and the liquid phase is released.

Most flocculants and filter aids in use today are synthetic polymers based on repeating units of acrylamide and its derivatives, which may contain either cationic or anionic charges and are available in a wide range of molecular weights and ionic charge.

The term flocculation is often confused with coagulation, although the two refer to quite different processes. Coagulation is basically electrostatic in that it is brought about by a reduction of the repulsive potential of the electrical double layer. The term flocculation is derived from the Latin, "flocculus", literally a small tuft of wool, or a loosely fibrous structure. Flocculation is brought about by the action of high molecular weight materials such as starch or polyelectrolytes, where the material physically forms a bridge between two or more particles, uniting the solid particles into a random, three-dimensional structure which is loose and porous.

## THEORY OF FLOCCULATION

### (i) Why flocculation is necessary

Coagulation/flocculation would be spontaneous if not for factors which impart stability to suspensions. All particles exert mutual attraction forces, effective only at short distances of separation. When surfaces are brought very close together, these forces, known as London-Van der Waals forces, predominate. This results in overall attraction and natural coagulation takes place. However, suspensions are rendered stable by repulsion forces which prevent particles from coming close enough for these attraction forces to take effect. See Fig. 1.

There are two main sources of these repulsion forces:

(a) Water is adsorbed from the surroundings onto the surface of the particles, forming solvation layers which repel one another.

(b) Electrical charges — all particles carry an electrical charge on their surfaces, the sign and intensity of which depend on the nature of the surface and on the chemistry of the aqueous suspending medium. In general, aqueous suspensions at pH 4 and above carry a negative charge.

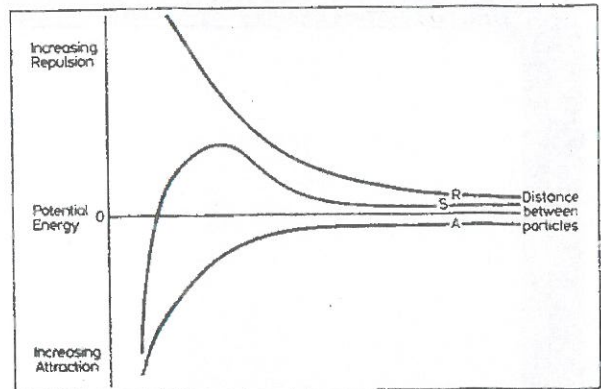


Figure 1: Curve A shows the attraction forces; curve R shows the repulsion forces; curve S is the summation of curves A and R and is the actual potential energy curve followed by two particles approaching each other

Positively charged suspensions occur in particular in strong acid. Charges may originate in several ways. There may be surface discontinuities in the crystal lattice, leaving an excess of positive or negative constituent ions on the surface. Alternatively, ions may be lost from the surface into the aqueous phase, leaving an unsatisfied charge on the surface, or charged ions such as  $H^+$ ,  $Al^{+++}$ ,  $SO_4^{---}$  may be adsorbed from the aqueous phase. See Fig. 2.

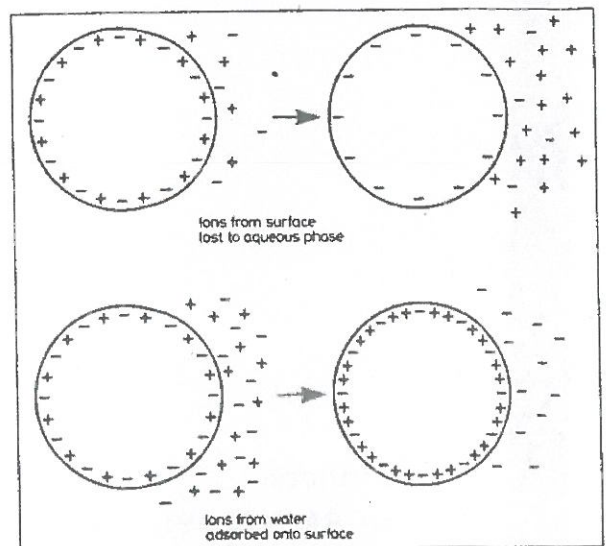


Figure 2: All particles carry an electrical charge on their surfaces, the sign and intensity of which depend on the nature of the surface and on the chemistry of the aqueous suspending medium



Not only does repulsion prevent particles from coming together, but it also retards settlement by keeping the particles in constant motion. Charge repulsion effects are most noticeable with very small particles since the ratio of surface area/mass, and hence charge/mass, is greatest.

## (ii) General mechanisms of flocculation

Flocculation may be brought about by a number of different processes:

### (a) Inter-particle collision

When solid surfaces are brought close enough together (eg 0.01 microns or less) the London-Van der Waals forces overpower the repulsion forces. Agitation of a suspension causes particles to come close or even collide, allowing natural flocculation (coagulation) to occur. Excessive agitation will cause floc breakdown since the bonding forces are relatively weak, and a compromise on the extent of agitation is necessary. Obviously this only gives a limited degree of flocculation.

### (b) Reduction of electrical charge

Charge reduction lessens electrical repulsion and enables coagulation to proceed to a further degree. Charge is neutralised by the addition of reagents giving rise to charged ions opposite in charge to that carried by the particles, eg in organic salts such as NaCl,  $\text{CaCl}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$ , etc. which give rise to  $\text{Na}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Al}^{+++}$ . The most highly charged cations are very much more effective, and in practice  $\text{Al}^{+++}$  and  $\text{Fe}^{+++}$  salts are mainly used. Most pronounced coagulation corresponds to minimum stability, when the suspended particle does not carry a charge in relation to the suspending medium. This occurs when the zeta potential is zero.

**Definition of Zeta Potential:** If the surface has a negative charge, positive ions will be attracted to it, forming a bound layer of positive ions. From this layer, a diffuse layer of counter ions extends outwards. When a particle moves in the liquid, the shear takes place in a plane outside the layer of bound ions, ie only the bound ions move with the particle. The potential which exists between the shear plane and the diffuse layer is the zeta potential. See Fig. 3.

There is always the possibility of overdosing with electrolyte and building up excess positive charge, hence optimum dosages are critical. Also different reagents have optimum pH ranges over which they are effective, eg pH 5.5 to 7.0 for  $\text{Al}^{+++}$ , 4.0 to 6.0 for  $\text{Fe}^{+++}$ .

Coagulation of this type is most suitable for the more finely divided suspensions. Flocs produced are generally small and compact, resulting in low sedimentation velocities. Again the flocs are weak and can be broken down under high shear conditions.

With either method (a) or (b), the flocculation may be further improved by the addition of a "bridging flocculant".

### (c) Synthetic bridging flocculants

These are synthetic water-soluble organic polymers of very high molecular weight. Requirements of

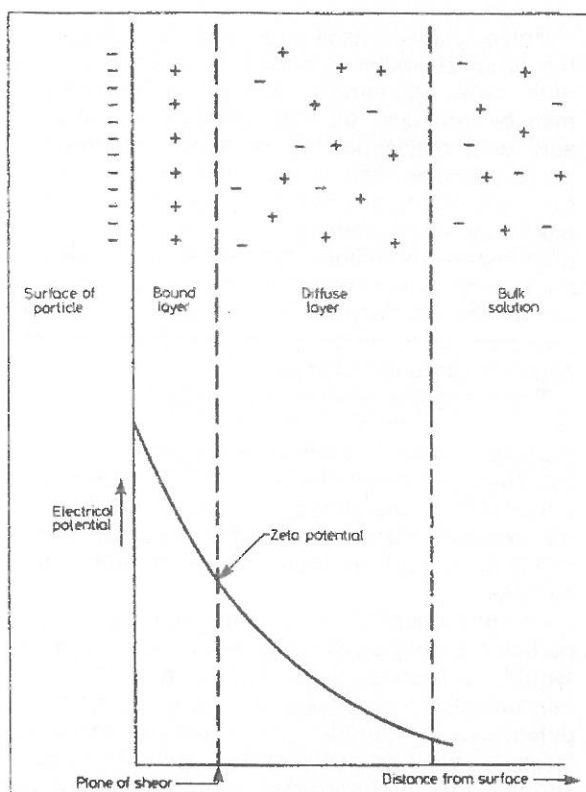


Figure 3: The Zeta Potential

bridging flocculants are that they be strongly adsorbed onto the particles, and that they are capable of spanning the gap between the particles. Synthetic polymers of high molecular weight are long enough for one end to adsorb onto one particle and the other end onto a second particle. Higher molecular weight polymers will adsorb on several particles at once, forming a three-dimensional matrix. With bridging polymers, generally the higher the molecular weight, the better the flocculant.

Most synthetic flocculants are based on polyacrylamide and its derivatives. See Fig. 4.

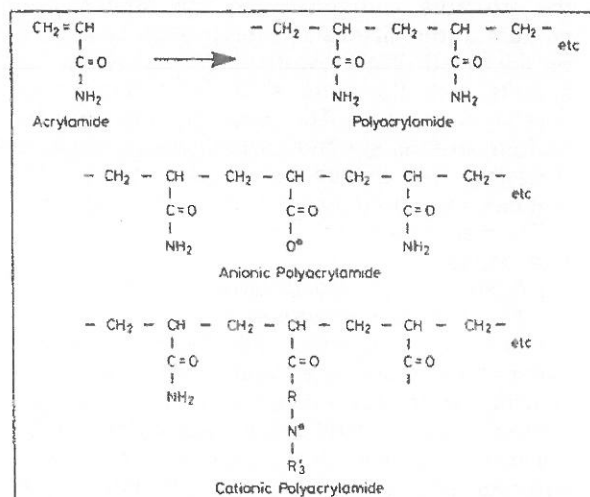


Figure 4: Most synthetic flocculants are based on polyacrylamide and its derivatives

Polyacrylamide itself is essentially nonionic and the ionic character is varied by copolymerisation with other monomers. Anionic polyacrylamides may be prepared by copolymerisation of acrylic acid with acrylamide, or by partial hydrolysis of polyacrylamide. This is the most common type of synthetic flocculant. Cationic polyacrylamides are made by copolymerisation of acrylamide with quaternary ammonium derivatives of acrylamide, the type of cationic material being variable depending on the application. Most bridging flocculants therefore, carry either a positive (cationic) or a negative (anionic) charge.

These charges serve two purposes:

- (a) They provide a means of adsorption onto the particle surface by electrostatic attraction and
- (b) They cause the polymer molecule to extend and uncoil due to charge repulsion along the length of the polymer chain, so that the molecule is more nearly linear and can therefore accommodate more particles.

As most suspensions contain negatively charged particles it is expected that cationic polyelectrolytes would be most suitable. This is true for charge neutralisation purposes, and attraction of the polymer to the particle surface, but not necessarily for bridging. For bridging the polymer must be strongly adsorbed, and adsorption can be promoted by chemical groups having good adsorption characteristics, eg amide groups. Either cationic or anionic groups may be used to extend the polymer chain as long as the polymer is of high enough molecular weight for bridging. The majority of commercially available bridging polyelectrolytes for minerals slurries are anionic, since these tend to be of higher molecular weight than the cationics, and are also less expensive than the cationics and therefore more cost effective overall.

In general, the higher the molecular weight, the better the flocculation and the faster the sedimentation rate, but in the case of filtration, particularly rotary vacuum filtration, the lower molecular weight products tend to be more effective. This is because the flocs formed with high molecular weight products are relatively large, trapping water within the structure and increasing the final moisture content of the filter cake, even though pick-up will be improved. With lower molecular weight flocculants, the flocs are small and have higher resistance to shear. The resulting filter cake is a uniform porous structure which allows rapid dewatering, yet prevents migration of the finer particles through the cake to the filter medium.

The mechanism of flocculation can be studied in two stages:

- (a) Adsorption of reagent onto the particles.
- (b) The formation of aggregates.

Adsorption is possible when the reagent and the surface are of opposite charge, resulting in non-specific electrostatic interaction. In theory, any positively charged mineral should adsorb any anionic polymer, and vice versa. With large amounts of adsorbed polymer, recharging of the particles and stabilisation should occur, and since the particle will then be of opposite charge to the initial charge, further adsorption of flocculant will cease.

Since surfaces are heterogenous with regard to charge, there can occur areas on the surface with higher, lower, or even opposite local zeta potential to the overall zeta potential. This means that if the greater part of the surface is negatively charged, there may be small areas of positive charge. Anionic polymer may then be adsorbed onto this relatively small area of positive charge, even though the net charge of the particle is of the same sign as the polymer. Since the area of positive charge will only be small, it is likely that the polymer molecules are attached by the ends, and not along any length of the chain. This type of bonding is specific electrostatic interaction. There is a threshold zeta potential at which adsorption at these centres becomes impossible. With this type of bonding there will still exist repulsion between the particles which are chemically bridged, and the resulting floc will be a loose open structure.

Hydrogen bonding is an important method of adsorption in the case of nonionic polymers such as polyacrylamide. The individual bond strength is relatively low, but an acrylamide polymer of molecular weight one million, for example, can form up to 15,000 of these bonds, and the overall bonding force is high. A feature of the hydrogen bond is the short distance between the atoms linked by the hydrogen, and the interacting atoms (ie, one atom on the polymer and one on the particle) must therefore approach closely by means of other methods before hydrogen bonding can take place.

Bonds can also form by the formation of insoluble salts, eg when polyacrylic acid is adsorbed on clay, limestone, and other calcium-containing minerals insoluble calcium polyacrylate is formed. Prolonged preliminary adsorption is necessary however, before the salt is formed.

There are several hypotheses for the mechanism of formation of the flocs, most of which remain unsupported by experimental evidence. One possibility, which must certainly play some part in floc formation, is the reduction of zeta potential by the adsorbed charged polymer molecules, allowing the particles to come together by Van der Waals attraction. A second possibility is that the polymer attaches simultaneously to two particles by its two ends. Further adsorption then occurs, and as the polymer molecule is contracted, the particles are drawn closer together. See Fig. 5.

This theory seems unlikely, and since the polymer

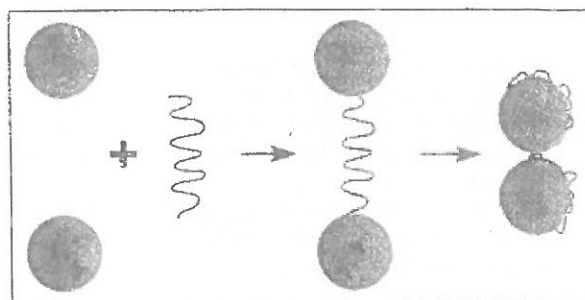


Figure 5: It is possible that the polymer attaches to two particles simultaneously by both ends

molecule is not linear, the ends will probably not be available for bonding.

A third theory assumes the polymer molecules to be well tangled so that one polymer molecule will adsorb at several points on the surface of a particle, leaving loops, which may be of varying length, projecting out from the surface. Collision of these partially covered particles, results in bridge formation. See Fig. 6.

Using this theory it is possible to postulate that the polymer molecules may completely adsorb on individual particles before bridge formation can occur. This is most likely to happen at high polymer concentrations and explains why flocculation is seen to decrease above a critical dosage. In this case, flocculation will be further hindered by repulsion of the charges on the polymer molecules. This would seem to be the more feasible theory since it better explains the observed effects.

*(d) Natural bridging polymers*

Natural polymers such as starch, gums, glues, alginates, etc., function as bridging flocculants but are of a much lower molecular weight than synthetics and are only capable of a much lower degree of flocculation. Polysaccharides (starch, dextrin, etc.) are effective in neutral and slightly alkaline conditions, and organic colloids (glue, gelatin, albumin, casein, etc.) which consists of aggregates of giant molecules, are effective in acid solution. These polymers have several disadvantages, such as the dosages required, unstable solutions, variable quality, and loss of floc strength on storage of sedimented slurries. Natural polymers are generally non-ionic, but may be rendered slightly anionic or cationic by chemical treatment. However, ionic character is of little importance since they have little effect on zeta potential and appear to function by hydrogen bonding.

**(iii) Factors affecting flocculation (using synthetic polymers)**

*(a) Effect of polymer dosage*

Flocculation in a given system cannot be increased beyond a certain optimum dosage of polyelectrolyte, and further additions result in decreased efficiency.

The optimum dosage is the maximum amount of polymer that the solid can utilise for flocculation under the conditions of the experiment and is directly related to the amount of multiparticle adsorption. It has been shown, for example with silica slimes, that up to a certain dosage, all added polymer is adsorbed on the solid. The point beyond which the polymer is not completely adsorbed corresponds to the optimum dosage determined from settling rates. However, the total amount adsorbed continues to increase with increasing concentration.

Optimum dosages (ie the dosage required for maximum settling rate) cannot be easily predicted since they are known to vary not only with ionic character and degree, but also with molecular weight. Optimum dosages increase with increasing molecular weight, but on the other hand the settling rates achieved will be higher.

*(b) Effect of shear on the flocs*

All flocs, whether formed by natural coagulation or bridging flocculation, are subject to breaking up with excessive agitation, and do not readily reform when the cause of agitation is removed. If flocs formed in the presence of excess polymer are agitated, they degrade faster than those formed with the optimum polymer ratio. The excess polymer is then adsorbed from solution, since as the flocs break apart, fresh adsorption sites are exposed. The flocs cannot then reform efficiently as the excess adsorbed polymer causes repulsion.

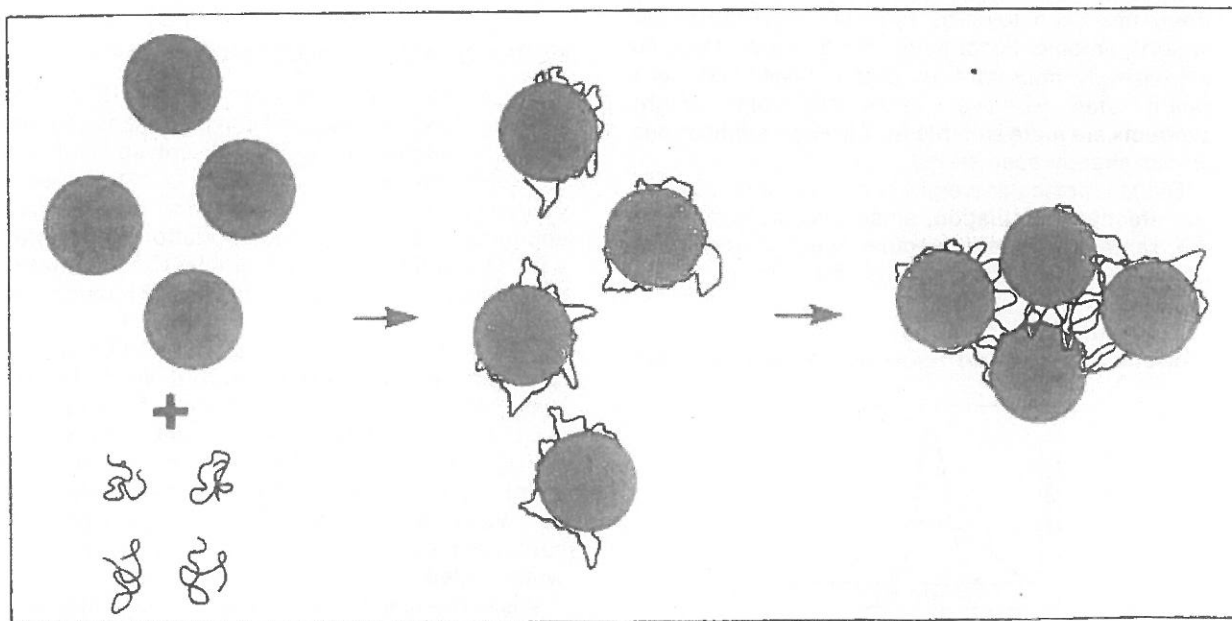


Figure 6: Another theory assumes that the polymer attaches at several points leaving loops projecting which attach to other particles



Hence optimum dosages for a polymer only hold for a particular degree of agitation.

*(c) Effect of particle size*

On fine silica particles, the optimum polymer/solid ratio has been found to be directly proportional to the surface area of the solid, therefore, a decrease in particle size means an increase in flocculant demand.

*(d) Effect of pulp density*

The pulp solids content should affect the optimum dosage since it determines the number of inter-particle collisions. However, although the optimum dosage decreases at very low pulp densities, the changes in optimum dosage over the range 4% to 50% have been shown to be negligible (using silica).

The rate at which aggregates form is proportional to the square of the concentration of the particles, and the "time of coagulation" (ie the time for the number of particles to be halved) is inversely proportional to the initial concentration.

Stability of flocs to agitation increases with increasing pulp density. After the flocs become torn apart by agitation, the probability of recombination of flocs depends on the time before collision with another particle. With low pulp densities, this time is relatively large and the polymer molecules will tend to adsorb on the same particle, reducing the amount of bridging in the system. With higher pulp densities there is a greater chance of collision with another particle before this happens.

*(e) Effect of molecular weight*

When a low molecular weight polymer is used there is a tendency for each polymer molecule to adsorb on to a single particle. The degree of flocculation is then lessened by further polymer addition. With a polymer of the same type but higher molecular weight, a greater amount can be adsorbed and utilised by the flocs. Optimum dosage and settling rate both increase with increasing molecular weight. In the treatment of coal-washery water, the trend has been towards the very high molecular weight anionic flocculants since it has become increasingly important to obtain faster sedimentation rates. However, lower molecular weight products are more suitable for filtration applications as has already been stated.

Overall molecular weight is not the only criterion for effective flocculation, since two products with the same apparent molecular weight may have different molecular weight distributions, as shown in Fig. 7.

Polymers A and B have the same average molecular weight and aqueous viscosity, but can

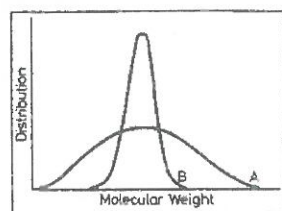
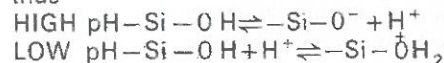


Figure 7. Two products with the same apparent molecular weight may have different molecular weight distributions

give considerably different performance. Polymer A has a wide molecular weight spread, containing considerable amounts of both high and low fractions, and polymer B has a narrower spread with more of the intermediate fractions than polymer A. The actual difference in performance in a given situation may depend on the nature of the slurry being treated as well as the properties of the polymer.

*(f) Effect of pH*

The pH of the pulp determines the surface charge, thus



The isoelectric point for silica is around pH3. With high charge at either extreme of pH, flocculation is more difficult, hence optimum dosage varies with pH. When the high surface charges keep particles apart, bridging is less frequent as more polymer is adsorbed on single particles.

The pH also controls the degree of ionisation of the polymer, and therefore varies the amount of charge on the polymer chain, and hence determines the degree of extension of the molecule. This in turn affects the degree of bridging and flocculants can therefore only function over a certain pH range, depending on the type.

*(g) Effect of temperature*

It is generally thought that increase in temperature improves flocculation, although this is not always the case, since a change in temperature will exert different effects in different systems. The rate of diffusion of flocculant and the rate of collision of particles must increase with rise in temperature but the adsorption step, which is exothermic, must be unfavourably affected by higher temperature. The linear extension of the polymer molecules may vary with changing temperature, depending on the nature of the solvent — solute interactions. Thus it is difficult to accurately predict the effect of temperature in a given system.

## FLOCCULANT APPLICATION

For a synthetic polyelectrolyte to function effectively, it must be released from its transported state to be available as a free dissolved and fully extended single molecule. Sophisticated modern polymers are supplied in solid form for reasons of economy and ease of transportation and storage with the solid having a particle size distribution around a centrally selected mean. Each particle is a hard packed tangle of long polymer chains similar to a ball of string. For the individual chains to be released they must firstly absorb water to begin to uncoil by hydrating and activating their repulsive ionic groups. Unfortunately, the wetted polymer on the outer surface of each particle forms initially into a highly viscous gel which resists the passage of the free water necessary for wetting the polymer in the centre of the particle. Thus, this initial absorption of water is dependent on the particle size.

It is at this stage that most problems with polymer dissolving occur. If the particles are not completely separated when their surface is wetted, the outside

surface of a cluster of particles wets out and forms a gel layer through which water has difficulty penetrating. This is effectively now one very large particle which will take several hours to wet and dissolve. Efficient dispersing equipment supplied by the flocculant manufacturers has largely eliminated this problem.

Once this initial absorption is complete and has rendered each particle into a lump of gel, flocculant molecules continue to uncoil and are lost from the outside of the gel available as single molecules in solution. The rate at which this occurs is again dependent on the particle size. Fig. 8 shows the rate of dissolution of the large and fine fractions of a high molecular weight flocculant. The fine fraction is almost completely dissolved within 15 to 30 minutes whereas the large particles may take up to 2 hours.

It would seem therefore, that as the two rate dependent steps of dissolution are longer with an increase in particle size that flocculants would best be supplied with as fine a particle size as possible. However, this has two important drawbacks. Firstly, it is very difficult to disperse a very fine particle size powder to be completely separate for dissolution and secondly, the fine particles can cause a safety problem and be unpleasant to handle. The fine particles are easily airborne and cause very slippery and dangerous surfaces around the make-up areas.

A recent innovation which achieves a reduction

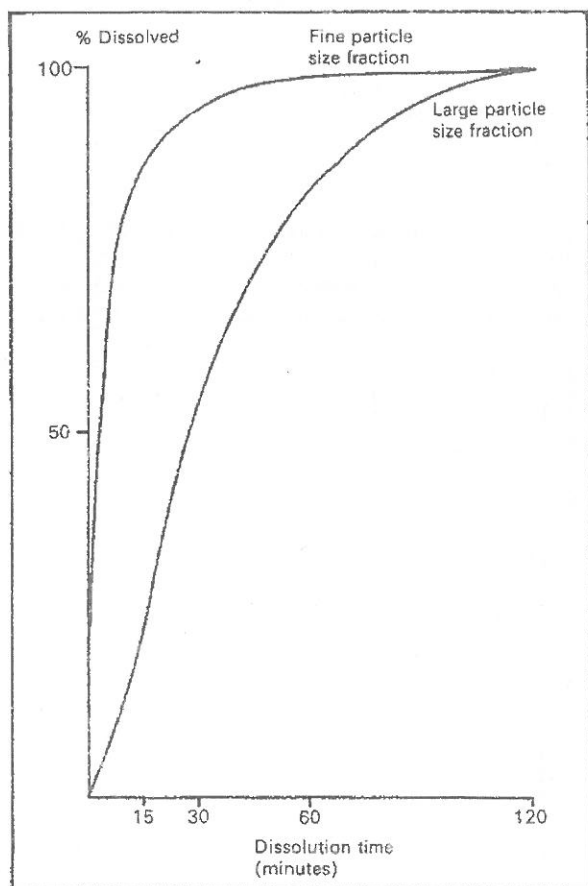


Figure 8.

in polymer particle size without the inclusion of unwanted ultrafines is the availability of flocculants in bead form. The manufacturing process enables the particle size to be set prior to polymerisation at a much lower average than conventional flocculants without including ultrafines. This therefore, achieves an improved rate of dissolution of bead form flocculants which adds to their advantages of storage and handling due to their excellent flow properties.

In order to speed up the rate at which the gelled particles dissolve into the body of the solution, a more highly concentrated solution can be prepared than that required for application. The high viscosity quickly built up in the body of the solution will help the applied agitation to tear the gel lumps apart giving a larger surface area, for dissolution. Other advantages of preparing a more highly concentrated solution are that fewer mixes are required and that each mix will be given a longer dissolution time. Also a larger reserve of fully prepared flocculant is available for use in periods of emergency conditions.

However, having described the role of particle size in dissolution, it must be noted that it is only with the least soluble polymers (ie very high molecular weight and/or low ionic polymers) that particle size becomes important. Lower molecular weight and/or higher ionic character products are so easily dissolved that many require far less dissolution times than indicated in Fig. 8.

During the dissolving process, agitation must be applied for the following reasons:

- (1) To maintain the particles in suspension in order to avoid settling into an immobile jelly layer at the bottom of the make-up tank.
- (2) To help the release of free polymer chains from the swollen gel particles.
- (3) To reduce the size of the gelled particles in order to increase the rate of release of free chains.

The type of agitation required must have sufficient force to achieve these requirements but have no centres of high shear conditions which would damage the flocculant molecules. Ideal mixing is given by a large paddle slow speed stirrer or by air agitation.

Once a polymer solution is prepared it must be transported to its point of addition to the suspension to be treated. Commonly it is initially transferred to the stock tank to enable a fresh solution to be prepared. From here, the solution can either be valve metred if above the addition points or pumped directly if below the addition point. However, these methods give problems of uneven dosing due to head variations in the solution tank. A common method to overcome this problem is to pump the solution to a small constant head box where the required volume of solution can be metred by valve control to the addition point while an excess of solution is returned to the stock tank. For flocculant delivery, high shear pumps should not be used. Figs. 9 and 10 show the effect a centrifugal pump has on the performance of a 0.1% solution of a high molecular weight polymer. The graphs show this product to give a lower molecular weight performance as the solution is harmed firstly



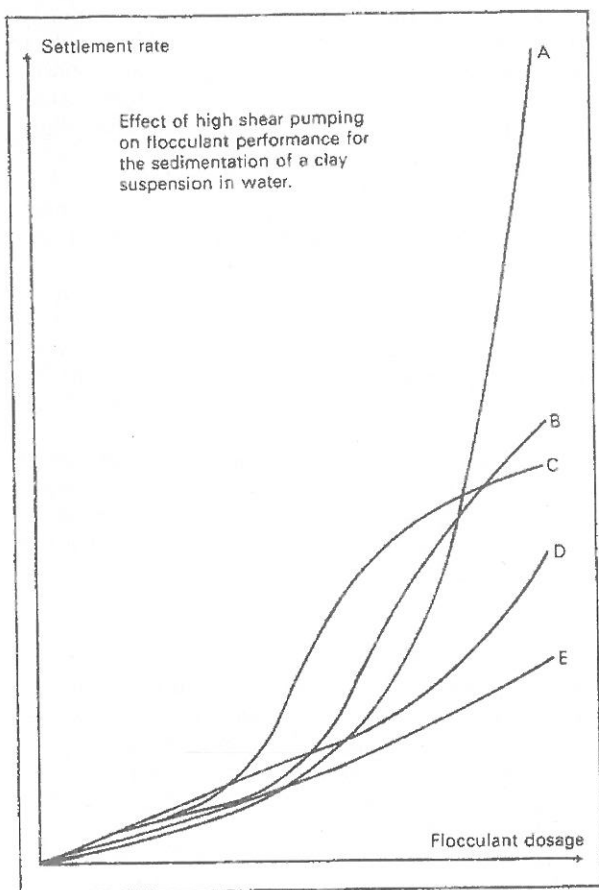


Figure 9.

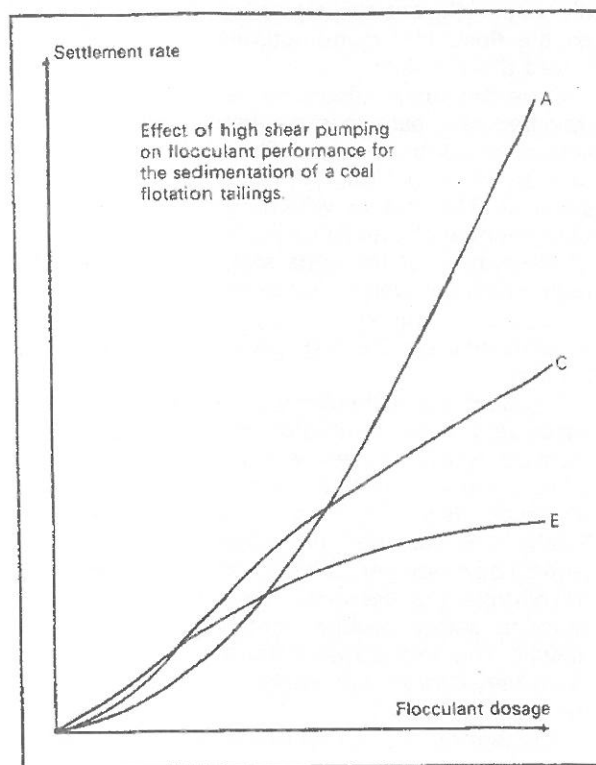


Figure 10.

Solution A— before pumping viscosity 600 cps.  
 Solution B— after one pass at full throughput, viscosity 540 cps.  
 Solution C— after fourteen passes at full throughput, viscosity 420 cps.  
 Solution D— after one pass at 10% of capacity, viscosity 330 cps.  
 Solution E— after one pass at 3% of capacity, viscosity 240 cps.

by passing at full throughput and further by throttling the pump back to a reduced throughput. This damage is clearly indicated by a reduction in the solution viscosity.

The application of the flocculant solution to the suspension is important enough to sometimes mean the success or failure of a flocculant treatment. The polymers by their very nature have very viscous solutions and to be distributed homogeneously throughout the suspension is sometimes a problem. The flocculants are designed to be very attractive towards particle surfaces and become irreversibly attached. Uneven distribution wastes flocculant in polymer-rich areas leaving insufficient for treatment of the bulk of the suspension. The overall result is a performance reflecting a low flocculant dosage which gives an ineffective solid/liquid separation. It is therefore necessary for the dosage to be stepped up until a satisfactory performance is achieved at the expense of a much higher cost than would otherwise be required.

The polymer solution should therefore be applied at a point of local turbulence (or one created) so that sufficient agitation is provided for complete and even distribution of the flocculant throughout the suspension but without giving an excess of

turbulence which would break down the delicate flocs formed. Fig. 11 shows the effect on the performance parameter due to floc size as the amount of mixing is increased. The performance

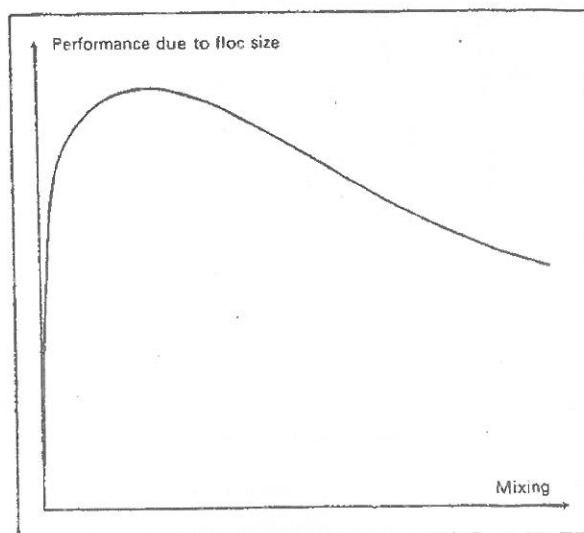


Figure 11.



risers to an optimum as distribution is improved but then falls gradually as floc breakdown occurs.

The need for good agitation to mix in the flocculant solution can be alleviated by the addition of as dilute a solution as possible. Fig. 12 shows the effect of the same dosage of flocculant applied at different solution concentrations. Of course, the more dilute the better for application conflicts with our previous requirements for the preparation of a solution at a high concentration. This can be overcome by means of in-line dilution of the metred flow of the concentrated solution.

Another important means of achieving improvements in treatment purely by varying the method of addition is by splitting the dosage into two or more streams and applying them at different points into the suspension to be treated. The improvements due to a two-stage addition are explained by reference to Fig. 13.

This is simply Fig. 11 with the effect that mixing has on the clarity (ie capture of fine solids) shown along with the effect of performance due to floc size. This shows that the capture of fine dispersed solid is increased with the extended mixing up to complete capture. However, this is invariably at the expense of floc size. With the two-stage addition, however, the initial floc size can be sacrificed by extended mixing in order to achieve maximum capture. The second addition then serves to re-build the floc size to the optimum level with controlled mixing. The total system therefore, gives maximum capture and maximum floc size and the effect of flocculating small flocs already formed generally achieves even larger flocs than the same single dosage would have given.

In conclusion, it is necessary to take full account of flocculant theory in order to select the optimum product for a particular system and equally important to obtain its maximum efficiency by correct dissolution and distribution.

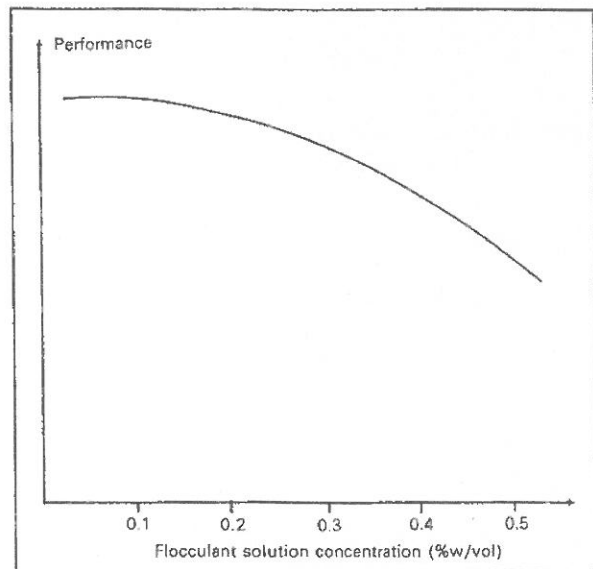


Figure 12.

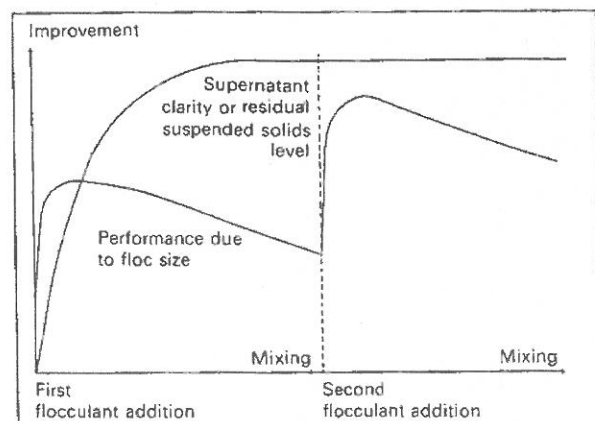


Figure 13.



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