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Theory of Flocculation

Reprint with Authorization by David L. Forbes

Introduction

The efficiency of most solid/liquid separation processes may be greatly improved by the application of synthetic polymeric flocculants. 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. These 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 different processes. Coagulation is basically electrostatic in nature. 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. These materials from a physical bridge between two or more particles, uniting the solid particles into a random, three-dimensional structure which is loose and porous. This structure is referred to as a "floc."

Why Flocculation is Necessary

Coagulation/flocculation would be spontaneous if not for factors which impart stability to suspensions. All particles exert forces of mutual attraction known as London-Van der Waals forces. These forces are effective only at short distances, but when surfaces are brought very close together, they predominate. This results in overall attraction and natural coagulation takes place. Stable suspensions occur when repulsion forces prevent particles from coming close enough for Van de Waals forces to take effect.

There are two main sources of these repulsion forces:

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

2. All articles carry an electrical charge on their surface, 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 pH4 and above carry a negative charge. 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 absorbed from the aqueous phase.

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.

General Mechanisms of Flocculation

Flocculation may be brought about by a number of different processes which are discussed in detail below:

1. Inter-particle collision

When solid surfaces are brought close enough together, London-Van der Waals forces over-power 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 break-down since the bonding forces are relatively weak, so a compromise on the extent of agitation is necessary. Obviously, this only gives a limited degree of flocculation.

2. Reduction of electrical charge

Charge reduction lessens electrical repulsion and enables coagulation to proceed to a greater degree. Charge is neutralized by the addition of reagents giving rise to charged ions opposite in charge to that carried by the particles. The most highly charged cations are the most commonly used. Pronounced coagulation corresponds to minimum stability,

i.e., when the suspended particle does not carry a charge in relation to the suspending medium. This occurs when the zeta potential is zero.

What is the 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, shear takes place in a plane outside the layer of bound ions, i.e. only the bound ions move with the particle. The potential which exists between the shear plane and the diffuse layer is the zeta potential.

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

Coagulation of this type is best suited to 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.

Whether using method 1 or 2, flocculation may be further improved by the addition of a "bridging flocculant."

3.   Synthetic bridging flocculants

These are synthetic, water-soluble, organic polymers of very high molecular weight. Requirements of 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 in general, the higher the molecular weight the better the flocculant. Most synthetic flocculants are based on polyacrylamide and its derivatives.

Polyacrylamide itself is essentially nonionic and the ionic character is varied by copolymerization with other polymers. Anionic polyacrylamides may be prepared by copolymerization 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 copolymerization 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: 1) they provide a means of adsorption onto the particle surface by electrostatic attraction and 2) they cause the polymer molecule to extend and uncoil due to charge repulsion along the length of the polymer chain. Thus, the molecule is more nearly linear and can accommodate more particles.

As most suspensions contain negatively charge particles, it is expected that cationic polyelectrolytes would be most suitable. This is true for charge neutralization 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, e.g. 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 mineral slurries are anionic, since these tend to be of higher molecular weight than the cationics and are also less expensive. Therefore, anionics tend to be more cost effective overall.

In general, the higher the molecular weight, the better the flocculation and the faster the sedimentation rate. In the case of filtration, however, 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 cake production is 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: 1) adsorbtion of polymer onto the particles and 2) the formation of aggregates.

Adsorption is possible when the polymer and the surface are of opposite charge, resulting in nonspecific 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 stabilization should occur. 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 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 centers 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 of one million, for example, can from 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 liked by the hydrogen. The interacting atoms, i.e. 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.

4.   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.

Factors Affecting Flocculation Using Synthetic Polymers

The degree of flocculation achieved in any system is affected by several factors which are discussed in detail below:

1.   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 utilize 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, i.e. 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.

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

3.   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.

4.   Effect of pulp density

The pulp solids content should affect the optimum dosage since it determines the number of interparticle 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. The "time of coagulation," i.e. 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.
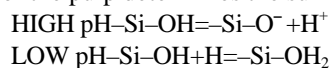
5. Effect of molecular weight

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 utilized by the flocs. Optimum dosage and settling rate both increase with increasing molecular weight. In the treatment of coal wash pant refuse, 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.

6. Effect of pH

The pH of the pulp determines the surface charge, thus
$$HIGH\ pH–Si–OH = –Si–O^- + H^+$$
$$LOW\ pH–Si–OH + H = –Si–OH_2$$

The isoelectric point for silica is around pH 3. With high charge at either extreme of pH, flocculation is more difficult, hence optimum dosage varies with pH. When the higher surface charges keep particles apart, bridging is less frequent as more polymer is adsorbed on single particles.

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

7. Effect of temperature

It is generally thought that an increase in temperature improves flocculation, although this is not always the case. A Change in temperature will exert different effects on different systems. The rate of diffusion of flocculant and the rate of collision of particles increases with a rise in temperature, but the adsorption step, which is exothermic, must be unfavorably affected by higher temperature. The linear extension of the polymer molecules may vary with changing temperatures, depending on the nature of the

solvent-solute interactions. Thus, it is difficult to accurately predict the effect of temperature in a given system.

Dissolution of the Flocculant

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. The solid particles have a 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 first adsorb 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 center of the particle. Thus, this initial adsorption 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 is wetted and forms a gel layer through which water has difficulty penetrating. This is now effectively only 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 adsorption 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 as single molecules to the solution. The rate at which this occurs is again dependent on the particle size, molecular weight, and charge.

It would seem, since 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. First, it is very difficult to disperse a fine particle size so as to be completely separate for dissolution. Second, 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 in polymer chemistry is the production of flocculants in a bead form. The manufacturing process enables the particle size to be set, before polymerization, at a much lower average than conventional flocculants and provides a product without the undesirable dusty ultra-fines.

The rate of dissolution of bead flocculants is much greater than conventional materials and handling is greatly improved due to the excellent flow properties of the beads.

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 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.

Having described the role of particle size in dissolution, it must be noted that it is only with the least soluble polymers, i.e. very high molecular weight and/or low ionic polymers, that particle size becomes important.

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 agitation must have sufficient force to achieve these requirements, but have no centers 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.

Delivering the Prepared Flocculant Solution

Once a polymer solution is prepared, it must be transported to its point of addition to the substrate to be treated. It is commonly transferred to a stock tank to enable a fresh solution to be prepared. From the stock tank, the solution can be valve metered if above the addition points, but this causes problems with uneven dosing due to head variations in the solution tank. This can be overcome by pumping the solution to a small constant head box where the required volume of solution can be metered by valve control to the addition point. The excess solution is returned to the stock tank. Alternatively, the flocculant solution can be pumped directly to the point of addition by means of a pump with a variable speed controller.
For flocculant delivery, high shear pumps should not be used. Tests have shown that when a 0.1% solution of a high molecular weight polymer is subjected to the high shear force of a centrifugal pump, solution viscosity is reduced. This reduction brings about a decrease in the rate of

flocculation, since the effective molecular weight of the polymer has been significantly reduced.

Point of Application for the Flocculant Solution

The application of the flocculant solution to a system is important enough to sometimes mean the success or failure of a flocculant treatment. By their nature, polymers generally have very viscous solutions and homogenous distribution throughout a system can be 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 an insufficient balance 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. Therefore, it is necessary for the dosage to be stepped up until a satisfactory performance is achieved. Expense of the treatment becomes much higher than would otherwise be required.

The polymer solution should 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. Beyond this amount, the excess turbulence breaks down the delicate flocs formed.

The need for good agitation to mix in the flocculant solution can be alleviated by the addition of as dilute a solution as possible. This maximum dilution conflicts with our previous suggestion for preparation of the solution at a high concentration. This can be overcome by means of in-line dilution of the metered flow of the concentration solution.

Another important means of achieving improvement in treatment by method of addition is to split the dosage into two or more streams and apply them at different points. With the two-stage addition, the initial floc size can be sacrificed by extended mixing in order to achieve maximum capture. The second addition then serves to rebuild the floc size to the optimum level with controlled mixing. The total system, therefore, gives maximum capture and maximum floc size. The effect of flocculating small flocs already formed generally achieves even larger flocs than the same single dosage would have given.

Conclusion

It is necessary to take full account of flocculant theory in order to select the optimum product for a particular system. It is equally important, to obtain the maximum benefit from the optimum product, that sound principles of dissolution and distribution be applied.