

COAGULATION AND FLOCCULATION

1. INTRODUCTION

Four factors influencing slurry dewatering, i.e., solid/liquid separation, are the properties of the particles (e.g., size), the properties of the liquid (e.g., viscosity), the concentration of solids, and the wettability of the particles. Many industrial and municipal slurries cannot be dewatered economically and efficiently without some sort of pretreatment to adjust one or more of these factors. Particle size is a factor commonly adjusted by means of pretreatment, namely enlargement of the particles through coagulation and flocculation. Although the two terms are often used interchangeably and although the processes may occur together or in rapid sequence, La Mer and Healy suggest they be regarded as two distinct processes.

1.1 COAGULATION

Small particles under 1μ are kept apart in colloidal solutions because the same electrical charge hovers above their surfaces. Same charges repel each other. When these hovering charges are neutralized by addition of a chemical with ions of the opposite charge, the particles then coagulate (adhere to each other) as they move randomly in the solution, bumping each other. The attracting energy is known as the London-van der Waals force. The more the particles move, the more they collide and adhere. An example of the chemical neutralization can be found in mineral oxide dewatering. Particles in nature, particularly oxide mineral particles, are predominantly negatively charged. When lime is added, the cations neutralize the negative charge and the particles then adhere to each other.

1.2 FLOCCULATION

This comes from the Latin word "flocculus" meaning "tuft of wool." Flocculation occurs when polymers (long chain-like molecules, macromolecules) act like bridges between the coagulated particles, resulting in still larger particles called flocs. Because the already-coagulated particles are larger than 1μ , they need mechanical assistance, such as mixers, to move them around so that they can make contact with the polymers. This is the generally-accepted mechanism whereby polyacrylamides, starches and Guar gums produce aggregation. Flocculated particles are more open aggregates than coagulated particles because of their polymer bridges.

1.3 GELATINOUS ENTRAPMENT OF PARTICLES

There is a third mechanism for enlarging particle size, that of entrapment of fine individual particles within a gelatinous metal hydroxide precipitate. This mechanism is typified by the addition of alum to systems causing aluminum hydroxide to precipitate. This precipitate then entraps fine solids.

2. BASIC AGGLOMERATION PROCESSES

There are two basic steps in the agglomeration process, whether it occurs by coagulation or flocculation. Purchas terms these steps "approach" and "adhesion."

2.1 APPROACH

Before the particles can adhere, they must come close enough, or "approach" each other.

Particles under 1μ are in continual random motion, Brownian movement, because of molecular collisions. The amount of Brownian movement depends on the degree of molecular excitation, which can be increased with heat.

On the other hand, particles that are larger than 1μ need assistance in order to move about. This assistance is a mechanical device such as a baffled tank, a paddle, a helicoidal mixer, a static

mixer, etc. These devices move the liquid, which induces shear motion and velocity gradients, bringing the particles into contact. Care must be taken because if the motion is too violent or the edges of the mixer too sharp, the floc might break apart.

2.2 ADHESION

The ways to induce particles to adhere are more complex than the ways to make them approach.

2.2.1 CHARGE NEUTRALIZATION

The charge that hovers around the outside of each suspended particle is the obstacle to adherence and must be neutralized for coagulation to take place. In a given colloidal suspension, all the particles will carry a similar surface charge (either positive or negative), thus repulsing particles from each other. The source of these surface charges may be ionization of soluble ionic crystals, lattice imperfections of crystal structures, or the adsorption of ions.

2.2.1.1 ZETA POTENTIAL

According to the D.L.V.O. theory on the behavior of the charges surrounding a particle, the surface charge of the solid is surrounded by a tightly-held layer of ions of opposite charge, beyond which is an outer layer through the depth of which the ionic concentration (and hence charge) decays with increasing distance until the equilibrium conditions of the bulk solution are attained (Figure 1). Under the influence of an external potential, the particles will move, a negatively-charged particle being attracted towards the cathode. As it moves, each particle carries with it the inner layer (i.e., of positive ions), separating from the outer layer at the plane of shear. The potential at the plane of shear is known as the zeta potential, usually denoted by the corresponding Greek letter.

The amount of the zeta potential is the degree that the colloidal particles repel each other. The greater that degree (and thus the zeta potential), the more stable the suspension.

2.2.1.2 LONDON-VAN DER WAALS FORCES

At the same time that the particles repel each other, they are attracted to each other by the London-van der Waals forces, an attractive force fundamental to all matter. The stability of the colloidal suspension depends on the balance between the two energies: the repulsive zeta potential and the attractive London-van der Waals force.

If the zeta potential is large enough, then repulsion (except for very small particles) will occur at all separation distances. If the zeta potential is small (say, less than 20 Mv) the London attractive forces will cause coagulation. The summation of the repulsive potential between particles, V_r , and the London-van der Waals attractive forces, V_a , yields the total interaction potential, V_t .

$$V_t = V_r + V_a$$

Figures 2 and 3 show these relationships.

Both forces lessen as the distance between the particles increases. Therefore, the zeta potential is influenced both by the concentration and the type of ions in solution which are present to form the double layer.

2.2.1.3 EXCEPTIONS

Unfortunately, there are many cases of coagulation which cannot be explained by simple application of D.L.V.O. theory.

These cases are normally associated with the use of hydrolyzable metal cations as coagulation aids and include the use of re-

FIGURE 1 THE ELECTRICAL DOUBLE LAYER MODEL AT A NEGATIVELY-CHARGED SOLID SURFACE; the Derjaguin and Landau, Vervey and Overbeek (D.L.V.O.) theory

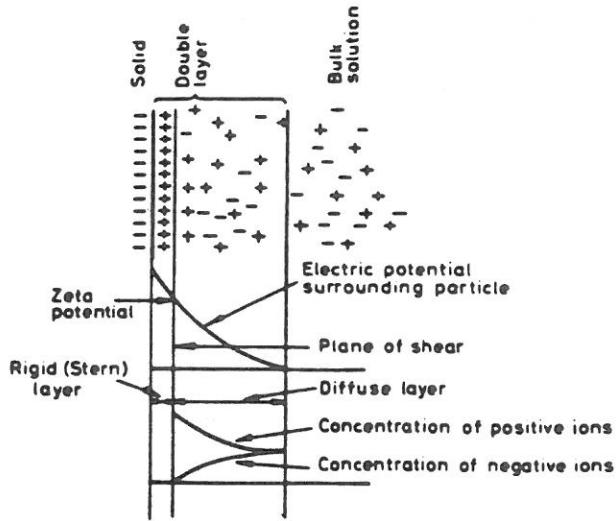


FIGURE 2 POTENTIAL ENERGY CURVES FOR A STABLE COLLOIDAL SUSPENSION

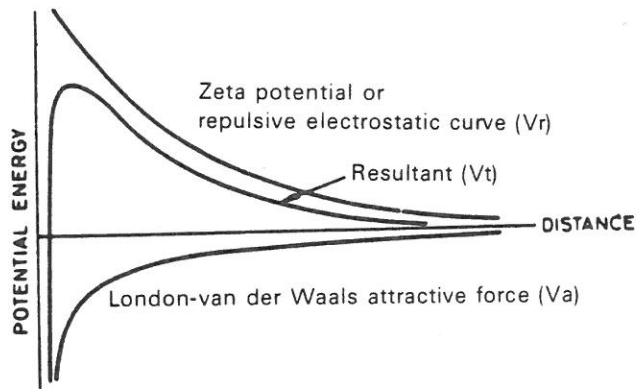
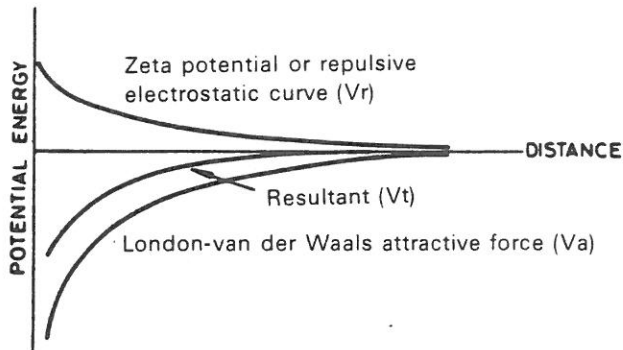


FIGURE 3 POTENTIAL ENERGY CURVES FOR AN UNSTABLE COLLOIDAL SUSPENSION



gents such as aluminum sulfate, zinc sulfate and ferric sulfate. Mechanisms which have been used to explain the lack of correlation between observed coagulation and electrokinetics or zeta potential data include: (1) heterocoagulation of positively-charged metal hydroxide precipitate and negatively-charged suspended particles; (2) flocculation, via polymer bridges, of the suspension by polymeric uncharged hydrolysis products; (3) cation exchange of silanol protons with hydrolyzed or non-hydrolyzed species producing dehydration and destabilization; (4) enmeshment of the suspension in the flocculated hydroxide of the coagulant.

2.214 SUPPRESSION OF ZETA POTENTIAL

2.2141 CONCENTRATION

Both the zeta potential force and the London-van der Waals force decrease as the particles get farther apart. Therefore, the concentration of the solids in the solution is a factor in zeta potential suppression.

2.2142 ADDITION OF SOLUBLE IONS

The addition of soluble ions in effect neutralizes the double layer charge. Charge neutralization (or reduction) is most frequently brought about by adding inorganic salts although polyelectrolytes can have that effect, as can pH adjustment by means of acid addition.

According to the Schulze-Hardy rule, the efficiency of an ion of electrolyte increases dramatically as the valency rises (e.g., SO_4^{2-} as compared with Cl^- , or Al^{+++} as compared with Na^+).

2.215 HYDROPHOBIC OR HYDROPHILIC

Colloidal suspensions may be either hydrophobic or hydrophilic, indicating the degree of affinity to water exhibited by the particles. Hydrophobic implies water repellant, while hydrophilic implies a strong affinity for water molecules in the surface layers of the particle, sometimes binding to a particle three to ten times its own dry mass. More generally, to include any liquid rather than only water, colloids can be categorized as lyophobic and lyophilic. An important difference between hydrophobic and hydrophilic colloids in the present context, is that the former can be precipitated by small quantities of electrolyte which have little if any effect on hydrophilic colloids.

2.2151 INDUSTRIAL EXAMPLES

Hydrophobic colloids (or sols, as they are sometimes called) are the more common industrially. Negatively-charged examples are metals, metallic sulfides, acidic hydroxides and acid dye-stuffs. Metallic oxides and hydroxides and basic dyestuffs are generally positively charged.

Hydrophilic colloids are natural organic materials and may have either positive or negative charges. Their colloidal charge is very sensitive to pH changes. Examples are starch, proteins, gelatin, viruses, and bacteria.

2.2152 MUNICIPAL EXAMPLES

In municipal water and waste water treatment, Bratby comments that, while colloidal material almost always has a net negative charge, it is usually difficult to classify a particular suspension as either hydrophilic or hydrophobic. Not only may both co-exist, but there may be a continuous transition from one to the other during treatment. An added complication is that sometimes both hydrophobic and hydrophilic zones may exist on the individual particles.

2.22 BRIDGING FLOCCULATION

The essence of the bridging mechanism is that two or more particles may become linked together as a consequence of each sepa-

rately becoming attached to some part of the same long chain polymeric molecule (such as starch or a synthetic polymer) or as a consequence of adhering to a gelatinous hydroxide precipitate.

2.221 HISTORY

Flocculation, as a process, occurred in nature long before commercial interests developed the range of reagents and the technology for their use which is available today. The geological deposition of sedimentary deposits in marine basins was undoubtedly influenced by aggregation caused by metal cations and it is entirely possible that vegetable-derived polymers were present in the river water which flowed into these basins and that these polymers also aided the formation of the sediments.

Mankind's use of high molecular weight soluble materials to destabilize suspensions is of great antiquity. For example, certain nuts have for centuries been used to clarify water in Egypt and India; for the same purpose, alum is known to have been in use in China in the seventeenth century and in England in the eighteenth century. The traditional industries of brewing and winemaking also have their long-established 'fining' agents, such as isinglass. The mineral treatment industry provides other examples, having for many decades been dependent on natural products such as starch, gelatine and guar gum.

While some of these traditional reagents (such as alum) continue to be widely used, since the early 1950s they have faced increasing competition from the ever-growing family of synthetic organic polymers commonly known as polyelectrolytes. During this period of time there have been substantial developments in the theory of flocculation and in the production and use of both synthetic and natural polymer flocculants. This development has been stimulated by factors such as: (1) environmental considerations which require that waste water and sewage disposal involve efficient solid-liquid separation; (2) the exploitation of lower grade mineral ones which require fine grinding and/or hydrometallurgical techniques; (3) the increase in the amount of fine coal processing.

2.222 POLYMER/POLYELECTROLYTE

The name polyelectrolyte arose from the structure of the long-chain polymer molecule which has many (poly) ionic groups (electrolytes) at regular intervals on the chain. Depending on whether the charges of the ionic groups are positive or negative, the polymer is termed anionic or cationic. Some being neither, are neutral.

Polymers change configuration and degree of ionization depending on the pH of the solution and the concentration of dissolved salts. In an acid solution a cationic polymer will be open and extended. In a base (alkaline) solution it will coil. In a solution with a high concentration of dissolved salts it will become compressed, and may even precipitate out.

2.2221 ANIONIC POLYELECTROLYTES

Most anionic polyelectrolytes (those generally used with chemical precipitates) are based upon polyacrylamide, and may have up to 25 percent of the amide groups hydrolyzed to carboxyl. Their molecular weight is in the range 1 to 7×10^6 , which corresponds with their being solids, but attention is being increasingly concentrated upon the development of liquid polymers of lower molecular weight, which are derived from other but similar materials.

2.2222 CATIONIC POLYELECTROLYTES

Cationic polymers, such as those that are used in water treatment, are normally in liquid form and are usually derivatives of amines. When they uncoil, e.g., in an acid solution, they increase the viscosity of the slurry.

2.2223 BRIDGING MECHANISMS USING POLYMERS

The polymer molecules are believed to attach themselves to the surface of individual particles at more than one point, so as to form a series of loops, as part of a three-stage process culminating in bridging flocculation, for which Akers proposed the pictorial model of Figure 4. The first stage, designated "1" in Figure 4, requires the polymer to be dispersed thoroughly in the liquid phase, to permit adsorption on to the surface of particles. There must be free adsorption sites on the particles for attaching the tails and loops of those polymers already adsorbed onto other particles. Either loops or tails of the adsorbed polymer must extend out from the surface.

The second stage ("2" in Figure 4) shows polymers adsorbed on the surface of the particles. In the third stage ("3b" in Figure 4), the free end of the attached polymer has formed a bridge with another particle. The alternate third stage ("3a"), which is to be avoided, shows the polymer wrapping around the particle, isolating it from the other particles instead of forming bridges. Purchas calls this "peptization."

2.2224 FACTORS AFFECTING FLOCCULATION WITH POLYMERS

2.22241 POLYMER STRUCTURE AND MOLECULAR WEIGHT
The function of ionic groups in the polymer chain to act as "chain-extenders" was probably the first indication that the actual molecular structure of the polymer could influence flocculation. Linear polymers are often more effective flocculants than highly branched compounds of comparable molecular weight. For example, synthetic polymers and guar gums can differ markedly in their flocculation characteristics.

Molecular weight, as well as structure, is a factor. If the polymer has too high a molecular weight and the settling rate is too fast, fines may remain dispersed. Adding more polymer will not help because the particles already are coated with polymer.

2.22242 ADSORPTION ENERGY

The configuration of the adsorbed polymer can vary with the specific adsorption energy of the polymer to the mineral surface. Polymers which are very strongly adsorbed, e.g., highly cationic polymers onto quartz at pH 7.0, can arrange themselves in a flat layer at the surface. This does not facilitate bridging (see Figure 4). In fact, this mechanism does not always produce large strong flocs. Polymers with a lower specific adsorption energy are more likely to have a large number of loops and tails extending outward into the solution. Therefore, the most strongly adsorbed polymer may not be the optimum flocculant. (It is obvious that a polymer exhibiting zero adsorption will produce no flocculation.)

2.22243 POLYMER DOSAGE/CONCENTRATION

Flocculation increases with the initial polymer concentration, reaches a maximum and then either plateaus or even decreases. This is a logical consequence of bridging. But if there are too many polymer molecules in the solution, they cover the coagulated particles so that bridges between them cannot form. This is called peptization (see above) and is shown in "3a" of Figure 4. On the other hand, if the polymer concentration (dosage) is too low, the flocs formed will be too small.

One polymer manufacturer has developed a control unit that uses a computer to optimize dosage. This control has sensors to detect the pH, solids concentration, and flow rate of the slurry. The sensors are monitored and the data fed into a computer. The computer then determines the optimum polymer dose needed. This kind of flexibility is needed because slurry characteristics can vary, even from day to day, particularly with organic slurry.

The optimum dosage for maximum flocculating effect varies with the size of the solid particles, and has been suggested to occur when half of the available surface sites are covered with polymer. Other important variables are the molecular weight of the polymer, the intensity of agitation and the time of constant agitation.

For a given solid/liquid suspension, the optimum dosage may vary widely from one reagent to another, as Figure 5 illustrates. This shows typical data for various reagents with uraniferous phosphate rock dispersion, expressed in terms of the time needed to collect a standard volume of filtrate. The optimum dosage to give maximum flocculating effect is not the same as the economic optimum; the latter often occurs at a much lower dosage rate since it depends upon many other factors such as the variation in equipment cost and in running costs.

2.22244 AGITATION

Flocculation is greatly influenced by agitation. Floc structures can be degraded, i.e., reduced in size, by agitation and this degradation is irreversible. However, agitation is essential to bring the particles and the flocculant into contact, because of the high molecular weights and low diffusion rates.

The decrease in particle size that results from too much agitation probably results from changes in polymer molecule configuration caused by the agitation. Increasing agitation possibly decreases the number of loops and tails extending from the particle surface and decreases the number of free adsorption sites available for bridging.

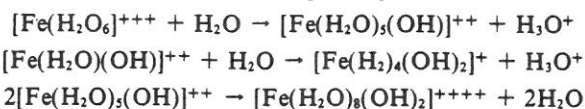
2.22245 AGEING

Purchas stresses the importance of ageing in solid/liquid separation, noting that it is not always true that ageing results in easier separation. Sometimes the converse is true. The relevant time scale also varies widely, from a matter of minutes to hours or even days. The effect may also be highly sensitive to numerous process variables, such as temperature, dynamic conditions, and the presence (or absence) of very small concentrations of impurities.

In the case of polymers, if the solution is aged too long the floc may deteriorate, if not long enough it may not floc completely.

2.223 INORGANIC FLOCCULANTS AND BRIDGING MECHANISMS

Inorganic salts of metals, such as aluminum and iron, are of major importance in water treatment. Their mode of operation is very complex, combining charge neutralization to reduce the zeta potential of colloidal particles, with a form of bridging mechanism whereby particles adhere to the gelatinous precipitates of the hydroxides. Underlying these mechanisms are a variety of hydrolysis and polymerization reactions which the trivalent cations Al^{+++} and Fe^{+++} undergo under appropriate pH conditions, illustrated by the following examples for Fe^{+++} :



Ageing is a factor in flocculation here too. Although many solid/liquid mixtures exhibit a change in separation characteristics with time, an obvious potential cause being crystal growth, which would tend to increase the ease of separation, it may not always be true. The same variables come into play as in the case of polymer flocculants.

FIGURE 4 MECHANISM OF BRIDGING FLOCCULATION (Akers)

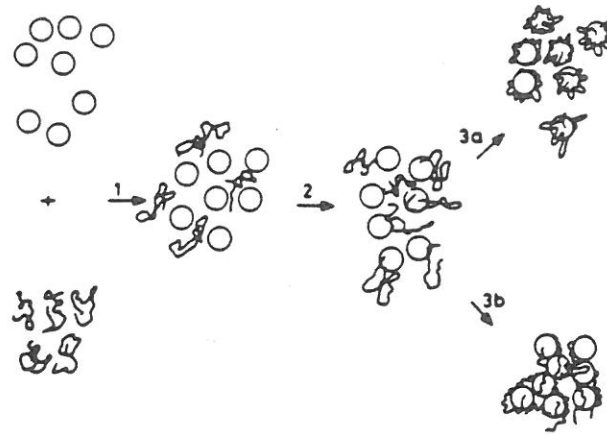
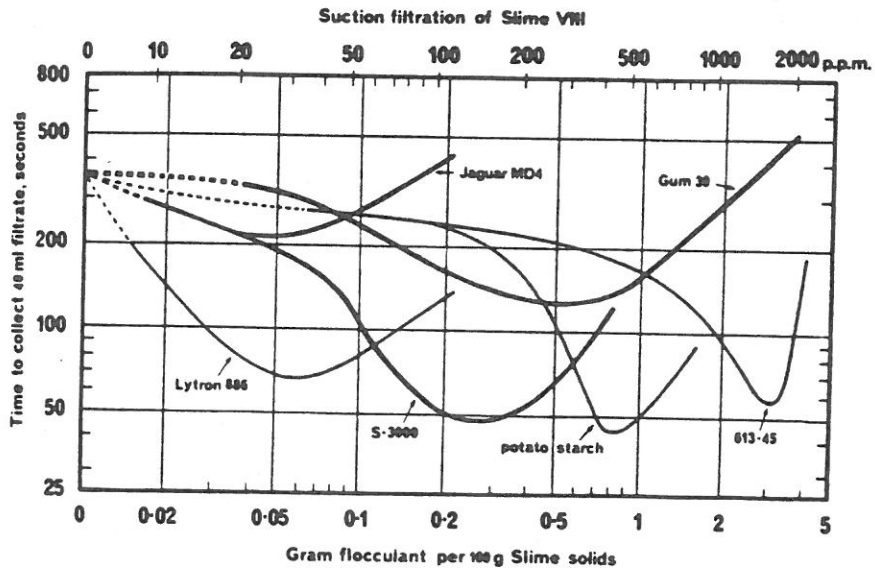


FIGURE 5 EFFECT OF DIFFERENT CONCENTRATIONS OF VARIOUS FLOCCULANTS ON THE EASE OF FILTRATION OF URANIFEROUS PHOSPHATE ROCK DISPERSIONS



3. COAGULANTS AND FLOCCULANTS

The wide variety of coagulation and flocculation reagents used may be conveniently divided into three major groups: inorganic chemicals, natural polymers, and synthetic polymers. Purchas prepared the following summary, based on the appendix in Akers' report.

3.1 INORGANIC CHEMICALS

Acids and alkalis. Common inorganic acids: H_2SO_4 , HCl , and alkalis: $NaOH$, $Ca(OH)_2$ may be used to adjust the pH.

Aluminum Chloride ($AlCl_3 \cdot 6H_2O$). Also known as aluminum chlorohydrate, this is a convenient source of aluminum ions. Solutions are corrosive, due to the release of HCl by hydrolysis, and must be stored in rubber, glass or plastic containers. Its composition is equivalent to a content of 20 percent Al_2O_3 .

Aluminum Sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$). Known commonly (though, in chemical terms incorrectly) as alum, this is available as powder or lumps and is slightly hygroscopic. In the dry state, it may be stored in concrete, iron or steel; solutions are corrosive and require containers of stainless steel, lead, rubber or epoxy resin-lined steel. Typical commercial material has an equivalent Al_2O_3 content of at least 17 percent.

Polyaluminum Chloride [$Al(OH)_{1.5}(SO_4)_{0.125}Cl_{1.25}】_n$. This is an alternative to alum, developed in Japan; the formula given above is approximate. It is available as a fairly strong acid solution containing the equivalent of 10 percent Al_2O_3 . Dilute solutions, in the range 0.4 to 3 percent, are reported to hydrolyze slowly.

Ferric Chloride ($FeCl_3 \cdot 6H_2O$). Lump or granular solid material may be either anhydrous ($FeCl_3$) or the more common hydrated form ($FeCl_3 \cdot 6H_2O$) which contains 60 percent $FeCl_3$. Solutions are corrosive, requiring storage in rubber, glass or plastic containers.

Ferrous Sulfate ($FeSO_4 \cdot 7H_2O$). Often known as copperas, this is available as powder, granules and crystals, containing 20 percent Fe . Solutions must be stored in rubber, glass or plastic containers. However, because of the ease of hydrolysis, this reagent is best used in the solid form.

Chlorinated Copperas. This is a solution of ferric iron, produced by oxidizing a solution of copperas (ferrous sulfate) by saturating it with chlorine.

Activated Silica. This is sometimes used as an adjunct to certain other pretreatment chemicals, such as aluminum sulfate, especially in water treatment. It is prepared from a dilute solution of sodium silicate (at an equivalent concentration of 1.5 percent SiO_2), by the addition of sulfuric acid, sodium bicarbonate, ammonium sulfate, chlorine or carbon dioxide. The freshly precipitated colloidal silica requires ageing for about two hours before being used.

3.2 POLYMERS

3.2.1 NATURAL POLYMERS/POLYELECTROLYTES

Starch. Starch embraces a group of complex polysaccharides obtained from vegetables. Starch was the first long-chain molecule introduced into industry, and still finds wide use. Farina starch is the most common and also generally the best, while tapioca and cereal starches find some application. Starch is available in several forms, depending upon whether it is prepared by heating with water or with caustic soda, in the latter case treated with calcium chloride, which renders it soluble in water. An advantage of starch is that it is nontoxic and, hence, compatible with the needs of e.g. the food industry.

Glue and Gelatines. These comprise various proteinaceous materials derived from animal tissues. The polymers contain both

anionic and cationic groups, the ionization of which is sensitive to changes in pH and ionic salt concentration, resulting in a very versatile and varied range of flocculants.

Guar Gums. Guar gum is an important non-ionic natural product, being a polysaccharide of which the major commercial source is the seed of a small legume, *Cyamopsis tetragonoloba*, which is indigenous to the Mediterranean regions. The gum consists of the ground endosperm of the seeds and is dispersed in water for use as a flocculant. The main constituent is a galactomann derivative with a molecular weight of about 220,000, present at a level of about 80 percent in typical commercial forms such as the Jaguar reagents available from Stein Hall & Co. and Guartec and Galactasol available from General Mills Inc. It is reported that, in uranium processing, the beneficial effects of guar are rapidly lost if the pulp is allowed to stand, probably resulting from acid hydrolysis. An increase in temperature is harmful for acid-leach slurries, causing a reduction in flocculating effect, until at 122° F (50° C) the performance of guar is similar to that of glue. While enzymic breakdown of guar solution readily occurs in the presence of ferric ions, this may be avoided by stabilizing the solution with iron-chelating agents such as citric, oxalic, or tartaric acids, or by use of an insolubilizing agent such as orthophosphoric acid.

Tannins. These complex polysaccharides have been widely used in the treatment of raw water and sewage. They are subject to degradation on storage. They are generally most effective under acidic conditions.

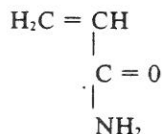
Sodium Alginate. This is a polysaccharide derived from seaweed, of particular use in potable water treatment and in food-stuffs. It is precipitated by the soluble calcium salts present in some hard waters, to offset which the commercial product contains a small amount of Na_2CO_3 , making it suitable for waters containing up to 500 mg/litre of equivalent $CaCO_3$.

Sundry Natural Polymers. Various other natural materials also find use as flocculating agents, examples being locust bean gum (carob), cactus extract, carrageen moss, linseed, and albumin.

3.2.2 SYNTHETIC POLYMERS/POLYELECTROLYTES

Polyelectrolytes constitute a large and growing body of synthetic organic polymers which first became available in the early 1950s. Most are derived from acrylamide, the inclusion of appropriate groups in the polymer structure making it possible to produce neutral, anionic or cationic materials with molecular weights ranging up to about 10^7 .

The basic 'building brick' of this family of polyacrylamides is, thus, the acrylamide monomer molecule:

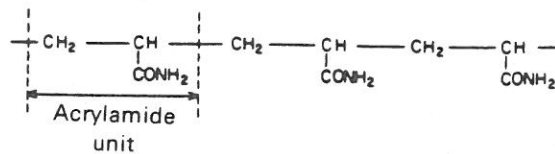


As summarized diagrammatically in Figure 6, by a combination of polymerization, hydrolysis and substitution, the three basic types of polyelectrolyte may be made from this monomer. In Figure 6(c), for the cationic polymer, the R in the quaternary ammonium group (inside the circle) is usually a derivative of methane (CH_4) or ethane (C_2H_6). The proportion of acrylate groups (i.e., the hydrolysed unit) in the anionic polymers of Figure 6(b) is known as the 'percent hydrolysis'; as this increases, so does the overall ionic charge.

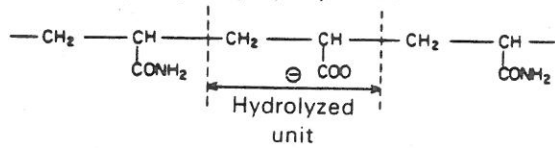
All three types of polyacrylamides are generally marketed as powders, although solutions and emulsions are also sometimes available. A common characteristic is their high viscosity and

FIGURE 6 EXAMPLES OF THE THREE BASIC TYPES OF POLYELECTROLYTES BASED ON ACRYLAMIDE: (a) NONIONIC OR NEUTRAL, (b) ANIONIC, (c) CATIONIC

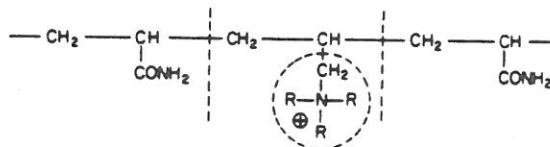
Non-ionic polyacrylamide



Anionic partly hydrolyzed polyacrylamide

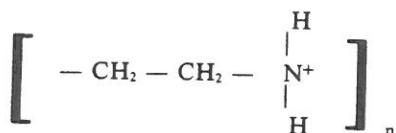


Cationic polyacrylamide partly substituted with quaternary ammonium group

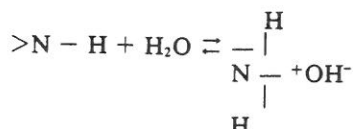


the general difficulty of making them into solutions; as a consequence, it is normal practice to produce a 'concentrated' stock solution of only 1 percent and to dilute this to about 0.01 to 0.1 percent for use.

Cationic polyelectrolytes are also often derived from polyethyl-imine:



Having lower molecular weights than polyacrylamides, these polyelectrolytes are available as moderately concentrated solutions. In water, the amino nitrogens react to form positively charged sites:



The above reaction shows that alkaline solutions are formed. Since each molecule of polymer contains many nitrogen atoms, it will also contain a large number of positively-charged sites. As acid is added, the overall charge density will increase, whereas it will decrease under increasingly alkaline conditions.

3.23 ADVANTAGES OF POLYMER FLOCCULANTS

The four chief advantages in using polymer flocculants are:

- less sludge is produced, therefore the costs of removing it are less;
- if the sludge is to be incinerated, polymers are safe to burn and are low-residue, in other words, they contribute less inert solids;
- handling and storage is simpler;
- polymers are less corrosive to equipment than inorganic conditioners.

3.24 MIXING AND STORING POLYMERS

Polymer flocculants are all cold-water soluble but those supplied in powder form require careful dissolution and hydration if they are to be used effectively and economically.

Synthetic polyelectrolyte powders swell and then dissolve very slowly to form highly viscous solutions even at concentrations below 1 percent. It is, therefore, customary to prepare a stock solution at a concentration of 0.5 to 1.0 percent, and then to dilute this down to about 0.1 to 0.01 percent shortly before use. Natural polymers can be prepared as more concentrated solutions, up to 5 percent, the viscosity of their solutions being lower.

There are various devices to disperse the polymer powder into a turbulent stream of water, avoiding the formation of undissolved clumps of powder which turn into gel or "fish eyes."

Powdered material is fed into a venturi or other type of disperser which gives high differential velocities between the powder and water systems. This velocity sweeps powder particles away from the powder-water impact point and prevents lump formation.

The mixture of polymer and water is then discharged into the first of one or more agitated tanks, which allow ageing for about one hour, during which the powder dissolves completely. The intensity of agitation is of considerable importance since, if too high, it will cause the polymer to degrade due to rupturing of the long chain molecules. Low-speed paddle stirrers are, therefore, advisable, rather than high-speed propeller mixers. High-intensity mixing without shear is the objective. In-line static mixers can be used to mix Mannich polymers or coagulants but polymer emulsions and dry polymers require more mixing.

The solution can be stored in a tank and the concentration may be adjusted by water addition. The water used for make up should be bacteria free and, if possible, free of excessive ionic concentrations. Mains water is ideal, but flocculants can be made up in sea water or even in solvent extraction plant raffinate under some conditions.

Before use (except with centrifuging), the stock solution must be diluted further, so as to facilitate the rapid and thorough dispersion of the reagent in the slurry to be treated. In general, the greater the dilution the better, the actual level being dictated by practical considerations. Typically, the diluted concentration should be below 0.1 percent. Dilution may be done either batch-wise or continuously.

Fully automated units are available for the preparation of polyelectrolyte solutions. This includes a variable-speed powder screw feeder, a disperser fed with a metered flow of water, and a series of three ageing chambers equipped with low-speed paddle stirrers (200 rpm in the first chamber, 92 rpm in the second and third chambers). The system is actuated by high and low level probes in a fourth chamber, which holds the stock solution ready for it to be fed by the dosing pump to the in-line dilution point and thence to the point of application. With the ageing chambers having a total capacity of 1000 litres, at a typical ageing time of 1 hour, this compact unit provides a hourly output of 264 gal (1000 l) of stock solution.

MacKenzie says that normal practice is to have two reagent storage tanks, one of which is mixing and hydrating and the other is delivering and metering.

Polymers also can be supplied in liquid form. This form would be the choice in a humid environment where stored dry polymer could turn into a brick from absorbing moisture. However, in dry areas where there are great distances between population centers, dry polymer is preferred to save on transportation/delivery costs. Dry polymer has more active molecules per pound than liquid and is, therefore, more concentrated.

Some operators have had problems in storing liquid polymer, saying that it agglomerates in the storage tanks. Polymer manufacturers say it is a question of improper handling. New plants are designed for using either liquid or dry polymer.

4. CHOOSING THE RIGHT COAGULANT OR FLOCCULANT

The selection of the optimum reagent at the optimum concentration is still considered an art by many in the field. Full attention must be paid to variables such as degree of agitation, convenience, cost, availability, toxicity and health hazards, and general compatibility with the overall process. While certain of these factors can be adequately appraised from general published data, ultimately it has been almost always necessary to resort to trial-and-error tests, with the final decision generally only made on the basis of full-scale operating experience under normal plant conditions. However, increasingly sophisticated laboratory-scale test procedures are being developed that can often be of great assistance.

One polymer manufacturer claims that their new selection procedure for belt filter presses is 90 to 95 percent accurate and takes most of the trial and error out of polymer selection. First, they identify the general type of polymer that would work on the slurry in question. If the plant in question is already in operation, their people go there to observe the polymer currently being used and document the performance. A new plant presents a much more difficult situation. In that case, experience with a slurry of similar type, pH, and percent solids is the biggest help. Their people then take a 5-gallon sample and simulate the successive shear forces of the belt filter press being used. After the

decision on a specific polymer has been made, they check their selection by running the sample through one of two small belt filter presses at their own plant, using the selected polymer. Their accuracy has run 90 to 95 percent in scale-up.

The procedure itself was tested on 5-gallon samples from 50 to 60 sites before it was used with customers.

Another factor in improving the selection process is the number of polymer types now offered. This same company offers twenty-five types, aiming for what they call "runability," a polymer that will work over a broader range of conditions. (The Mannich polymers that are widely used can operate only in a narrow pH range: 6.5 to 7.1 or 7.2.) Their research has produced a stabilized polymer that is not adversely affected by a higher pH.

5. COST

A frequent negative cited regarding polymer conditioners is their cost. Polymer manufacturers are aware of this criticism but counter by saying it is the overall cost that must be figured. When polymers are compared with other conditioners such as ferric chloride and lime, their cost is offset by lower sludge trucking cost, lower maintenance costs, and higher throughput.

Safety is another factor to consider in cost trade-offs. Mannich polymers are widely used because of their low cost on a per-pound basis, but some of these polymers have free formaldehyde or free di-methylamines. Now that these chemicals are known to be health risks, some plants will not permit their use.

Cost can be attacked in other ways. One way is to improve cake dryness prior to hauling or incineration. It should be borne in mind that, although a highly flocculated solid may filter much faster than the dispersed particles, it may also have a higher residual moisture content which will increase the cost of a subsequent operation such as drying. Furthermore, a highly flocculated cake is compressible and is likely to collapse if subjected to too high a pressure, so that design and operation of associated filtration equipment require particular care.

Static rather than dynamic mixing units have been found in one case to reduce the amount of coagulant required by 45 percent. They replaced fixed-speed stirrers that were over-mixing in some zones and under-mixing in others. Energy costs also were lowered because of the fixed-speed stirrers' being eliminated.

6. TRANSFER AND MIXING WITH SLURRY

6.1 TRANSFER

Flocculant solutions are expensive and should be metered into the slurry with care and accuracy. Orthodox metering and pumping equipment may be used to control the flow of polyelectrolyte solution from the stock tank to the point of usage, provided due attention is given to the tendency of these solutions to be degraded by high shear forces. Centrifugal or gear pumps should, therefore, not be used. Diaphragm pumps or progressive cavity pumps are satisfactory.

Velocity should be low in the pipes and orifices used to transfer the flocculant solution to the slurry and to transfer the treated slurry to the filter. High-velocity shear gradients can rip the flocs apart. A well flocculated slurry easily can be greatly harmed as it is pumped to a filter. Even solutions of reagents may be affected by pumping that ruptures the long-chain molecules.

6.2 MIXING

As with the mixing of the polymer with water, the mixer of that solution with the slurry should be simple and reliable, with a minimum of moving parts. Static mixers can be used as the polymer solution is fed to the filter with additional water.

Some slurries require more mixing, some less, depending on their characteristics.

7. APPLICATIONS

Polymers can be used to condition any slurry and, if properly used, will enhance performance, but they're most commonly used with dilute slurries or sludges dewatered on belt filter presses. Polymers are also used with vacuum filters, centrifuges, filter presses, and drying beds. However, here are some high solids concentration sludges that do not need polymers.

Polymers are used to condition municipal sewage for filtration and they also are used in industrial and mineral filtration. Industrial applications include paper mills, cyanide removal, and electroplating waste water to remove metals. In the latter, there is one process that allows recovery of certain metals.

In hydrometallurgical operations where filtration is used as a solid-liquid separation process, there is a small loss of dissolved values associated with the moisture content of the discarded filter cake. The use of flocculants can reduce this dissolved loss by a number of mechanisms:

- reduction in the moisture content of the cake;
- increased filter duty resulting from flocculant addition can sometimes free primary or first-stage filters for use as second-stage filters;
- increased permeability of the cake resulting from flocculant addition can increase the rate of passage of wash water and so permit the use of a larger volume of wash water;
- flocculants can improve cake discharge and so reduce the "blow-back" of filtrate during discharge;
- flocculants can bind fines into the cake and reduce cloth blinding. (Cloth blinding reduces cloth permeability and increases dissolved loss.)

Figure 7 gives some typical examples of the application of a variety of flocculants. The original units and (1966) U.S. prices have been retained since their primary value is comparative rather than absolute.

8. TRENDS

While coagulation and flocculation have a long history as pre-treatment options prior to solid/liquid separation, new products for these systems come on the market with a rapidity that makes it difficult to keep current.

The old stand-bys continue to have their place, with the new developments occurring in the synthetic polymer field. The impetus for this activity comes from at least two sources. One is the discovery that hitherto "safe" chemicals are, in fact, health hazards in the plants. The other is the need for wastewater filtration in applications where wastewater no longer can be discharged without treatment. Polymer manufacturers are directing their efforts toward developing products to help solve these problems.

There are also new ways of mining, for example, coal mining, that generate fines and fine refuse requiring conditioning before dewatering.

The requirements for polymers, therefore, seem to be growing. Cost usually is not a deterrent, especially when it can be shown that overall cost will be lower.

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FIGURE 7 TYPICAL FLOCCULANTS AND SOME OF THEIR APPLICATIONS

Trade Name	Composition	Type or Mechanism	Typical Application	Normal Range of pH Effectiveness	Normal Effective-Concentration	Approx. Price per lb*	Manufacturer
Alum	Al ₂ (SO ₄) ₃ · XH ₂ O	Electrolytic coagulation	Water treatment	5 to 10	15 ppm	2¢	Inorganic chemical manufacturers
Ferric sulfate	Fe ₃ (SO ₄)XH ₂ O	Electrolytic coagulation	Water treatment and chemical processing	Any	5 to 10 ppm	2¢	Inorganic chemical manufacturers
Sodium CMC	Sodium carboxymethylcellulose	Coagulation and bridging	Mineral processing	3 to 9	0.03 to 0.5 lb/ton	50¢	Hercules, DuPont
Kelgin W	Algins	Coagulation and bridging	Water treatment	4 to 11	Up to 5 ppm	\$1.50	Kelco Co.
Separan	Acrylamide polymer	Bridging	Chemical processing	2 to 10	0.2 to 10 ppm	\$1.00 to \$2.00	Dow Chemical Co.
Fibrefloc	Animal glue	Electrolytic	Waste treatment	1 to 9	5 to 30 ppm	18¢	Armour & Co.
Corn starch	Corn starch	Bridging	Mineral processing	2 to 10	10 lb/ton	7¢	—
Polynox	Polyethylene oxide	Bridging	Chemical processing	2 to 10	1 to 50 ppm	\$2.00	Union Carbide
Silica sol	Activated silica sol	Electrolytic coagulation	Waste treatment	4 to 6	1 to 20 ppm	1.5¢ as sodium silicate	Inorganic chemical manufacturers
Sodium aluminate	Sodium aluminate	Coagulation	Water treatment	3 to 12	2 to 10 ppm	10¢	National Aluminate
Guar gum	Guar gum	Bridging	Mineral processing	2 to 12	0.02 to 0.3 lb/ton	35¢	General Mills
Sulfuric acid	H ₂ SO ₄	Electrolytic	Waste treatment	1 to 5	Highly variable	1¢	Inorganic chemical manufacturers
Optimer	Acrylamide polymer	Bridging	Wastewater treatment	5.5 to 11	Variable	\$1.00 to \$2.00	Nalco

* 1966 prices, for comparison only.