

Flocculants and Coagulants: The Keys to Water and Waste Management in Aggregate Production

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INTRODUCTION

Water conservation, efficient handling of solid wastes, and lack of space for settling ponds are some of the problems currently faced by the aggregate industry. These problems have been exacerbated by the growth of cities and towns to the edge of aggregate producing operations. This trend of "outside town" operations becoming "within town" operations will continue with the growth of suburban areas and the growth of small towns and cities in most geographic areas of the country.

The expanding city phenomenon has had considerable impact on aggregate operations. Not only do operators now strive to be low cost producers, they also must be good neighbors to local populations which are quickly consuming available water and land resources. This combination of a lack of space and water has forced many operators to change production strategies. Better water and waste management plays a critical part in this strategy change.

Past practice of large ponds to settle waste solids and recover water has, due to the above mentioned problems, given way to smaller ponds that utilize flocculants and coagulants to effect faster settling rates. Water clarity can be maintained at the same level or better than that of large untreated ponds. Operations that require even stricter control of water and waste solids resort to the use of clarifiers, thickeners, and belt presses. However, all of these unit operations require the use of flocculants and coagulants for cost efficient operation.

The "art" of flocculation and coagulation has a lot more "science" than meets the eye. A variety of flocculants and coagulants is available, with different chemistries, molecular weights, charge ratios, and other attributes. It is critical that the appropriate flocculant and/or coagulant be chosen to ensure cost effective performance in a solids/liquid separation process. The

choice is dependent on process conditions, including variables such as feed particle size, water chemistry, system pH, percent feed solids, etc. This article discusses some of the salient points about flocculants and coagulants and their application in aggregate operations.

WHY USE COAGULANTS AND FLOCCULANTS?

Aggregate operations produce fine clay-laden slurries while producing a variety of sand and gravel products. This effluent stream is generally sent to a large holding pond where the solids settle out and the supernatant water is recycled back into the process. Successful water and waste management depends on the efficiency of this solids/liquid separation step. This step is even more critical when trying to reduce the size of the pond or increase the settling rate.

Most naturally occurring fine particles, such as those produced at an aggregate operation, have a negative surface charge. This charge sets up repulsion forces that reduce the tendency for the particles to agglomerate and settle. However, other factors such as particle size, particle density, and liquid density also exert considerable influence on the tendency of fine particles to settle. Stokes law, shown below, can be used to estimate the time it takes for a free falling particle in a liquid to settle.

$$V = \frac{2g r^2 (d_1 - d_2)}{9\eta}$$

- V = final velocity of particle
- r = radius of particle
- d₁ = density of particle
- d₂ = density of liquid
- η = coefficient of viscosity
- g = gravitational constant

Table 1 — Effect of particle size on settling rate

Particle Diameter (mm)	Order of Size	Total Surface Area*, cm ²	Time Required to Settle 1 foot**
10.0	Gravel	3.142	0.03 sec
1.0	Coarse Sand	3.142 x 10 ¹	0.3 sec
0.1	Fine Sand	3.142 x 10 ²	33 sec
0.01	Silt	3.142 x 10 ³	55 min
0.001	Bacteria	3.142 x 10 ⁴	92 hr
0.0001	Colloidal	3.142 x 10 ⁵	384 days
0.00001	Colloidal	3.142 x 10 ⁶	105 hr

*Area for particles of indicated size produced from a particle 10 mm in diameter

**Calculation based on a sphere with sg 2.0 at 25°C

Using Stokes Law, settling times for particles of different sizes can be estimated and are given in Table 1. These calculations are based on a spherical particle with a specific gravity of 2.0 at 25°C.

As expected, decreasing a particle's size reduces its settling rate. The main area of interest in the aggregate industry is particles in the size range of "silt." Settling times are on the order of 55 minutes per foot or 0.2 inches per minute. Since Stokes law assumes that the particle is settling freely, it is reasonable to expect that in conditions such as those typical to aggregate production, some particle-to-particle interference, or hindered settling, will occur, further slowing down the settling rate. In order to handle the same volume of effluent in a smaller pond, settling rates must be increased. The only parameter that can be influenced, according to Stokes Law, to effect increased settling rates is an increase in the particle size. By using coagulants and flocculants, particle sizes can be increased, resulting in faster settling rates.

COAGULATION

As mentioned earlier, fine aggregate particles have a negative surface charge. In order to bring these particles together, these surface charges need to be neutralized. The process of charge neutralization and bonding of particles to form microfloc particles is called coagulation. Charge neutralization is achieved by addition of a coagulant, which neutralizes the negative surface charge by its positive charge. Coagulated particles are then aggregated to larger particle sizes and settled by the addition of a flocculant. The coagulation mechanism is shown in Figure 1.

Use of natural coagulants has been documented for over 100 years. Natural coagulants such as starch, glue, guar gum, and sodium alginate were favored in most industrial applications early in this century. However, these natural coagulants eventually gave way to more cost effective, synthetic polymeric coagulants introduced in the early 1950s.

Synthetic neutral and quarternized polymeric coagulants based on ammonia and ethylene dichloride were developed by Nalco Company in the 1950s and early 1960s and these displaced many of the natural coagulants that were in use at that time. Introduction of a number of polymeric coagulants based on epichlorohydrin and dimethylamine in the late 1960s and early 1970s led to a decline in the use of ammonia- and ethylene dichloride-based coagulants. However, new coagulants, based on dimethyl ammonium chloride, were introduced by Nalco Company in the mid 1970s. The new coagulants gained rapid acceptance, and are yet some of the most widely used coagulants.

Even though coagulants based on the chemistries above are used in some potable water treatment applications, they are toxic to fish and cannot be used in applications involving open water discharge. How-

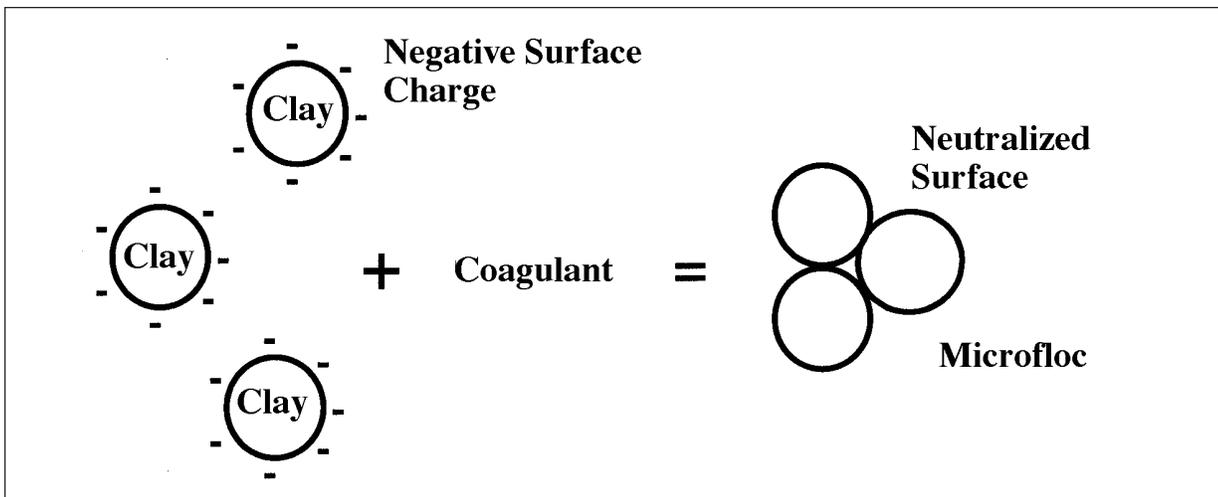


Figure 1 — Coagulation of fine clay particles in a slurry

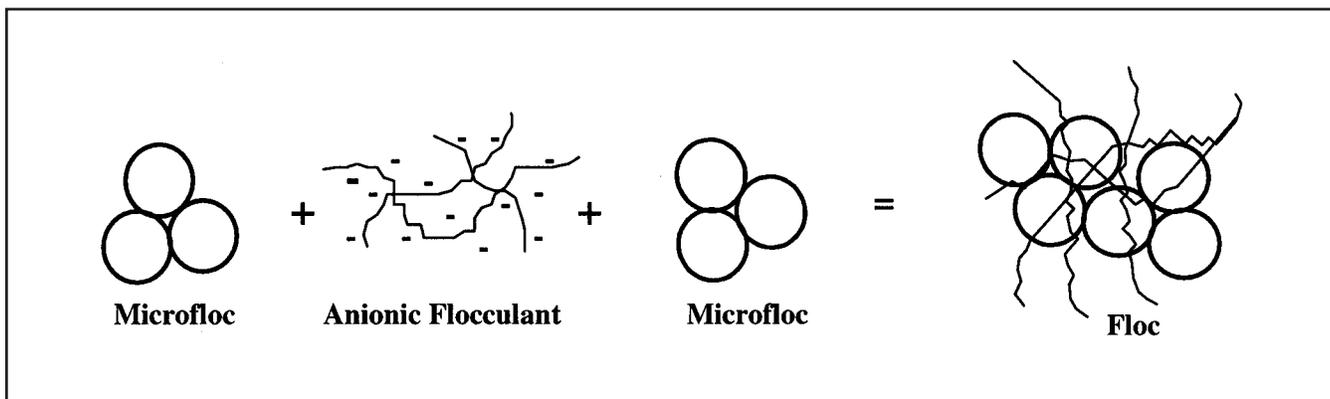


Figure 2 — Flocculation of coagulated fine clay particles

ever, there are several coagulants, such as the Nalco EN/ACT® product line, that have been developed specifically for use in such applications. These products can be safely used in applications where there is open water discharge or the potential for it. Several aggregate operations prefer the use of such products even under closed loop water use conditions.

After the surface charges of particles are neutralized and microflocs are formed, flocculants are often added to bring the microfloc particles together. Modern synthetic flocculants have gained widespread acceptance in a number of industrial applications. These products can be, and often are, tailor-made to fit a number of applications to provide a cost efficient method of improving plant productivity.

FLOCCULATION

The function of a flocculant is to bring together coagulated particles into larger aggregates and settle them. Figure 2 shows the mechanism of flocculation on fine clay particles.

A typical flocculant is a long chain hydrocarbon. These polymers consist of several (*poly*) repeating units (*mer*) and have molecular weights varying from 5 to 20 million. Molecular weights of flocculants are significantly higher than those of coagulants which range from 2,000 to 200,000.

The molecular weights of both coagulants and flocculants can be controlled and modified by changing process variables during manufacturing. Also, a variety of different functional groups can be attached to the backbone of a flocculant to give it different properties. Thus a product can be tailor-made for specific applications, resulting in synthetic polymers that are much more active than natural polymers.

Depending on its chemistry, the charge of a flocculant can be neutral, anionic, or cationic. Most aggregate operations use neutral (nonionic) or anionic flocculants. Nonionic flocculants are long chain polymers of polyacrylamides made from acrylamide monomer. Most flocculants used in aggregate applications are copolymers of acrylamide and sodium acrylate. Acrylamide-acrylate copolymers are anionic due to the presence of negatively charged carboxylate groups in the polymer. The ratio of sodium acrylate to acrylamide in the polymer determines its anionicity. A higher proportion of sodium acrylate will result in a higher charged flocculant.

FACTORS AFFECTING COAGULATION

The main factors that affect coagulation are particle size, surface charge, and water chemistry. The smaller the particle size, the greater total surface area per unit weight of solids, so it is not atypical to see an increase in the dose required to coagulate fine particles. This increase is not linear as small decreases in particle size can result in dramatic increases in coagulant requirements.

The density of the surface charge of clay particles has a direct bearing on coagulation. As the surface charge increases in density, more coagulant is required for surface charge neutralization. Care must be exercised in coagulant addition, since over-addition could result in reversal of surface charge and result in inter-particle repulsion.

A factor that is often overlooked is the chemistry of the water in which particles are suspended. Dissolved species such as Ca⁺⁺, Mg⁺⁺, Fe⁺⁺ and Fe⁺⁺⁺ help neutralize surface charge and can reduce the coagulant requirements. These ions increase the conductivity of the process water. Determining the water conduc-

tivity can assist in determining coagulant demand. Calcium and magnesium ions also determine the hardness of the water. A general rule of thumb is the higher the hardness of the water, the lower the coagulant demand.

FACTORS AFFECTING FLOCCULATION

Several factors can affect flocculation, primarily polymer type, ionic strength, water pH, slurry solids, flocculant dilution, shear, molecular weight, and process conditions. These factors, individually and collectively, have a great influence on the type of flocculant that will provide optimum performance, its optimum dose, and addition points.

POLYMER TYPE

As mentioned above, flocculants used in the aggregate industry are generally copolymers of acrylamide and sodium acrylate. This copolymer and its many variations can behave very differently in different systems. The driving force for adsorption is controlled by the mineralogical properties of the suspended solids in addition to the aqueous environment. The main molecular groups in these types of polymer are amide and carboxylate. It is known that both groups do adsorb onto the mineral surface; however, there are several studies that suggest that these functional groups have different primary roles. The primary function of the amide group in copolymers is adsorption by hydrogen bonding. The primary function of the carboxylate group is to extend the polymer chain in solution by electrostatic repulsion, enabling bridging to take place. However, this does not mean that

the carboxylate group is incapable of adsorption, but that polymer extension is its primary role in most situations.

Copolymers of acrylamide and sodium acrylate are generally more active than nonionic acrylamide polymers in spite of the fact that most particles carry a negative charge. Evidence suggests that the enhanced activity of anionic polymers is related to uncoiling or extension of the polymers.

The ideal flocculant for an application balances the need for adsorbing groups (amide group) with the desire to extend the molecule (carboxylate group). The proper ratio of these two groups is critical to their performance and will determine the degree of anionicity.

pH

The pH of the slurry plays an important role in the choice of flocculant. As the pH of the system ranges from 0 to 14, the choice of flocculant ranges from nonionic to highly anionic. Figure 3 shows typical pH ranges over which flocculants of varying anionic (acrylate type) polymers find general application.

At a pH of 4 and below, nonionic polymers show the greatest activity. At this pH range, anionic polymers are coiled up just like the nonionic polymer but they show very little activity. This is due to the fact that in anionic flocculants, the amide groups (found in the nonionic polymer) are replaced by the more inert (at low pH) carboxylate groups which reduces the number of hydrogen bonding sites available in the flocculant. Thus nonionic flocculants perform better at a lower pH range.

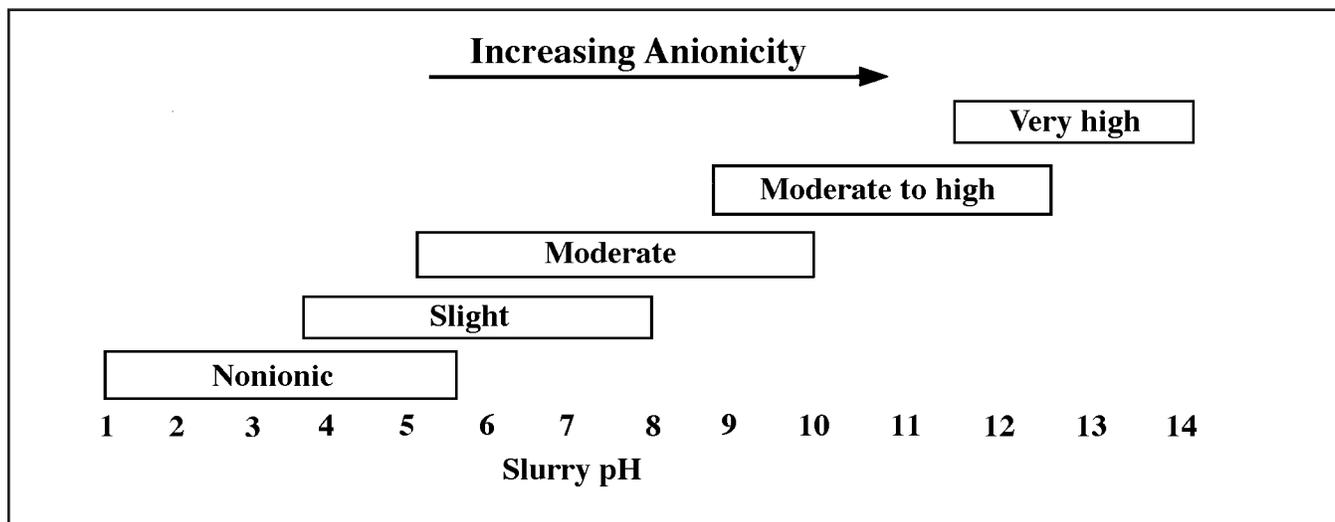


Figure 3 — Effect of pH on selection of flocculant

As the pH increases, the carboxylate groups of the anionic flocculant are ionized, and uncoiling continues until the polymer is fully uncoiled and active. In the same environment, a nonionic flocculant maintains its configuration. The activity of anionic flocculants increases with slurry pH, and at a pH range of 6 to 8, a moderately anionic flocculant will show better activity than a nonionic flocculant. The performance of a nonionic flocculant is the same at this pH as in the lower pH range.

At pH levels over 9.5, highly anionic flocculants perform the best, since a highly anionic flocculant is fully uncoiled and at the peak of activity at high pH levels. While we expect the nonionic flocculant to maintain its activity, a decrease in activity is noted. At this point, it is known that the polyacrylamide in nonionic flocculants can hydrolyze, resulting in a drop in activity. When competing reactions (chemical [hydrolysis] vs physical [adsorption]) are occurring simultaneously, a significant reduction in flocculant activity can occur. In addition to the chemistries described above, Nalco has introduced several variations by adding pendant groups to the flocculant backbone. The pendant groups are designed to provide certain performance characteristics.

SLURRY SOLIDS

When a fully activated flocculant is added to a slurry, adsorption takes place rapidly. However, it is important that the flocculant is well dispersed throughout the slurry. The concentration of solids in the slurry and the feed particle size has a strong influence on the distribution of flocculant in the slurry. The higher the concentration of solids, the more difficult it is to distribute the flocculant uniformly through the slurry. The smaller the particle size, the larger the surface area (Table 1). Therefore, when the particle size decreases and the solids concentration increases, flocculant demand increases.

FLOCCULANT DILUTION

A significant improvement in performance can be achieved by changing the dilution at which the flocculant is added to the slurry. By diluting it, the distribution of the flocculant in the slurry improves, thereby improving performance. However, the degree of dilution is usually dependent on the capacity limits of the dilution system.

SHEAR

Excessive shear or mechanical action can tear apart a floc. While distribution of the flocculant in the slurry is essential, overmixing is detrimental due to floc shear. Therefore, a balance must be found between distribution and floc shear.

MOLECULAR WEIGHT

Inter-particle bridging is an important mechanism by which the flocculant functions, and it is not surprising that the molecular weight can affect the performance. In most thickener applications, higher molecular weight results in better activity, although there are instances in which increasing molecular weight past a certain point results in loss of activity. Higher molecular weight flocculants are generally more viscous and are not easily distributed through the slurry. Since adsorption is very rapid and usually irreversible, a loss in activity results. With increasing molecular weight, the number of polymer chains per unit of weight decreases as well. There may not be enough polymer molecules to flocculate all the solids in high solids slurries.

The above factors can affect the performance of both the flocculant and the coagulant. These factors are not isolated but have significant influence on the system, with the final outcome dependent on a combination of these effects. Therefore, the art of coagulation and flocculation needs to have the attention it deserves in order to optimize aggregate production.

UNIT OPERATIONS

While a majority of aggregate operations that produce washed products use ponds as the method of effluent treatment and water recycling, scarcity of land space and a limited water supply have accelerated the trend toward the use of mechanical solids/liquid separation methods such as thickeners, clarifiers, and belt presses. All of these unit operations can assist in smooth operations, but they require coagulants and flocculants for optimum performance. As discussed earlier, proper selection and application of coagulants and flocculants is essential in making these devices run smoothly.

AUTOMATION

While it is imperative that the proper coagulant and flocculant are chosen and the points of application are optimized, manual feeding and dosing of chemicals can be inefficient. This is evident when the incoming feed to ponds, thickeners, clarifiers, or belt presses constantly fluctuates. It is impossible for even the best operators to keep up with constantly changing feed slurries. Even an operator who is constantly adjusting reagent doses tends to over- or under-correct such situations. The end result is wasted chemicals and inefficient operations.

To address feeding deficiencies and non-optimal performance, Nalco introduced the first of a series of automated process control systems in the early 1980s. These systems, called AUTOFLOC[®], used probes to measure parameters such as incoming feed solids or clarity and then used these numbers to make continuous adjustments to the coagulant and flocculant dose. Over the years, these systems have been improved. The current system, called OPTICUS[®], is a state-of-the-art self-learning intelligent process control system that can be used to control several unit operations simultaneously. It can even record historical data and keep track of product inventories.

The use of these systems has resulted in the decrease of chemical use by as much as 30%. Also, operations run smoother due to the removal of natural variability when run in the manual mode. These units are becoming increasingly popular and their use frees up valuable operator time for other essential tasks.

SUMMARY

Water, space, and environmental challenges will continue to cause problems for aggregate producers. Flocculants and coagulants, when properly chosen and applied, can go a long way toward alleviating these problems. Mastering the “art” of coagulation and flocculation is the key to improved productivity.

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