PART 2

UNIT OPERATIONS OF WATER TREATMENT
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COAGULATION AND FLOCCULATION

The processes of coagulation and flocculation are employed to separate suspended solids from water whenever their natural subsidence rates are too slow to provide effective clarification. Water clarification, lime softening, sludge thickening, and dewatering depend on correct application of the theories of coagulation and flocculation for their success.

Taking surface water clarification as an example, turbid raw water contains suspended matter—both settleable solids, particles large enough to settle quiescently, and dispersed solids, particles which will not readily settle. A significant portion of these nonsettleable solids may be colloidal. Each particle is stabilized by negative electric charges on its surface, causing it to repel neighboring particles, just as magnetic poles repel each other. Since this prevents these charged particles from colliding to form larger masses, called flocs, they do not settle. Coagulation is the destabilization of these colloids by neutralizing the forces that keep them apart. This is generally accomplished by adding chemical coagulants and applying mixing energy. Aluminum salts, iron salts, or polyelectrolytes are the chemicals usually used.

Figure 8.1 illustrates how these chemicals reduce the electric charges on colloidal surfaces, allowing the colloidal particles to agglomerate into flocs. These initially small flocs join, creating larger, settleable agglomerates. The destabilization step is coagulation (charge neutralization); the floc-building stage is flocculation.

The terms coagulation and flocculation are often used interchangeably; however, when seen as two different mechanisms they can provide a better understanding of clarification and dewatering.

COAGULATION

Colloidal species encountered in raw water and wastewater include clay, silica, iron and other heavy metals, color, and organic solids such as the debris of dead organisms. Colloids may also be produced in precipitation processes such as lime softening. Oil in wastewater is frequently colloidal.

Among the wide variety of colloidal materials in water, there is a broad distribution of particle sizes. Table 8.1 shows how particle size affects the tendency of particles to settle in quiet water. Colloids always require coagulation to achieve
FIG. 8.1 (a) *Coagulation:* The addition of a coagulant neutralizes charges, collapsing the "cloud" surrounding the colloids so they can agglomerate. (b) *Flocculation:* The bridging of the floculent chemical between agglomerated colloidal particles forms large settleable flocs.

An effective size and settling rate; but even larger particles, which are not truly colloidal and would settle if given enough time, may require coagulation to form larger, faster settling floc.

When insufficient settling time is available in a treatment plant to remove suspended solids, coagulation and flocculation may cause them to grow in size and settle rapidly enough to overcome the physical limitation of the plant design.

Colloids are categorized as hydrophobic (water hating) or hydrophilic (water loving). Hydrophobic colloids do not react with water; most natural clays are hydrophobic. Hydrophilic colloids react with water; the organics causing color are hydrophilic. Of importance in water treatment, the hydrophilic colloids may

<table>
<thead>
<tr>
<th>Typical</th>
<th>mm</th>
<th>μm</th>
<th>Surface area (total)</th>
<th>Settling time, 1 m fall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel</td>
<td>10</td>
<td>10,000</td>
<td>3.14 cm²</td>
<td>1 s</td>
</tr>
<tr>
<td>Coarse sand</td>
<td>1</td>
<td>1,000</td>
<td>31.4 cm²</td>
<td>10 s</td>
</tr>
<tr>
<td>Fine sand</td>
<td>0.1</td>
<td>100</td>
<td>314 cm²</td>
<td>125 s</td>
</tr>
<tr>
<td>Silt</td>
<td>0.01</td>
<td>10</td>
<td>0.314 m²</td>
<td>108 min</td>
</tr>
<tr>
<td>Bacteria</td>
<td>0.001</td>
<td>1</td>
<td>3.14 m²</td>
<td>180 hr</td>
</tr>
<tr>
<td>Colloidal matter</td>
<td>0.0001</td>
<td>0.1</td>
<td>31.4 m²</td>
<td>755 days</td>
</tr>
</tbody>
</table>

**NOTE:** Particles larger than 100 μm are visible to the naked eye and are considered to be settleable solids. In the range of 10–100 μm, they are considered to be turbid. Below 10 μm they are considered colloidal. Particles larger than 0.1 μm are visible by light microscope; below 0.1 μm, the electron microscope is used for detection.
chemically react with the coagulant used in the treatment process. So hydrophilic colloids require more coagulant than hydrophobic, which do not chemically react with the coagulant. For example, removal of color from a water having an APHA color of 50 requires higher coagulant dosages than removal of 50 JTU turbidity.

Several theories have been advanced to describe the colloidal particle and the forces surrounding it. For practical purposes the determination of the nature and strength of the particle charge is all that is needed to define the colloidal system. The particle charge strength, illustrated as the layer surrounding the colloid in Figure 8.1, affects how closely colloids can approach.

**ZETA POTENTIAL**

Zeta potential is a measurement of this force. For colloids in natural water sources in a pH range of 5 to 8, the zeta potential is generally $-14$ to $-30$ mV; the more negative the number, the stronger the particle charge. As the zeta potential diminishes, the particles can approach one another more closely, increasing the likelihood of collision. In a conventional clarification system at a pH of 6 to 8, coagulants provide the positive charges to reduce the negative zeta potential. Coagulation usually occurs at a zeta potential which is still slightly negative, so complete charge neutralization is not usually required. If too much coagulant is added, the particle surface will become positively charged (a positive zeta potential), and the particle will be redispersed.

Coagulants may be required in high pH water treatment systems, such as in lime softening. Calcium carbonate particles also carry a negative charge, and cationic coagulants may be useful in reducing residual colloidal hardness. Magnesium hydroxide, on the other hand, carries a positive charge until the pH exceeds 11; so in lime or lime-soda softening processes where both CaCO$_3$ and Mg(OH)$_2$ precipitate, the oppositely charged particles coprecipitate. This coprecipitation in past geologic periods produced the mineral dolomite, CaCO$_3$·MgCO$_3$. The coagulation and flocculation of materials other than silt and color, which are the common targets of a water clarification program, are discussed in the chapter on precipitation processes.

Zeta potential is determined indirectly from data obtained in observing particle motion under a microscope. Figure 8.2 $a$ and $b$ shows typical instruments employed for this determination. Zeta potential measurements have been used successfully to monitor plant coagulant dosages. However, for selecting the best coagulant, zeta potential readings alone are not reliable. Observation of results in a jar test remain the best method of coagulant selection.

Somehow related to zeta potential in a qualitative way is streaming current, an electric current produced when colloidal particles are trapped in a capillary tube or a confined space with water flowing past them at high velocity. The adsorbed charges, or counter-ions, are stripped from the surface of the colloid and pass along with the water until the velocity is dissipated. The flow of ions constitutes an electric current that is measurable by an instrument called the streaming current detector (SCD). As is true with zeta potential, if coagulants have neutralized the charge on the colloids, the current is reduced to zero. Streaming current detectors require frequent maintenance to control plugging of the close clearances in the water passage spaces. In many cases, the head of the detector (a piston or plunger reciprocating in a closed cup) can be kept clear by an ultrasonic cleaning device. The SCD can produce an output signal to control the coagulation process.
One of the variables that needs study in each system is the time factor; the speed or rate of charge neutralization varies with the type of colloid present and with temperature. Therefore, a sample taken immediately after coagulant addition is usually inadequate. Typically, an equilibration time of 5 to 10 min is needed before putting the sample through the SCD.
Mixing is required to supplement coagulant addition to destroy stability in the colloidal system. For particles to agglomerate they must collide, and mixing promotes collision. Brownian movement, the random motion imparted to small particles by bombardment by individual water molecules, is always present as a natural mixing force. However, additional mixing energy is almost always required. High intensity mixing, which distributes the coagulant and promotes rapid collisions, is most effective. The frequency and number of particle collisions are also important in coagulation. In a low turbidity water, the addition of solids such as clay or the recycle of previously settled solids may be required to increase the number of particle collisions.

**FLOCCULATION**

The floc formed by the agglomeration of several colloids may not be large enough to settle or dewater at the desired rate. A flocculant gathers together floc particles in a net, bridging from one surface to another and binding the individual particles into large agglomerates as shown in Figure 8.3. Alum, iron salts, and high molecular weight polymers are common flocculants. Flocculation is promoted by slow mixing, which brings the flocs gently together; too high a mixing velocity tears them apart, and they seldom re-form to their optimum size and strength. Flocculation not only increases the size of floc particles, but it also affects the physical nature of the floc. Sludges and slurries, when flocculated, dewater at faster rates on sand beds and in mechanical dewatering equipment because of the less gelatinous structure of the floc.

**FIG. 8.3** Photomicrographs illustrating the coagulation process. (Left) Turbid river water, showing fine dispersion of tiny solid particles. (Right) Same water treated with coagulant. Particles are "collected" in the floc. (130×)
It is apparent that the processes of (a) charge neturalization, or coagulation, and (b) floe building, or flocculation, are so different that each system containing the chemically treated solids being processed has its own physical constraints. These are outlined in Table 8.2.

In an attempt to develop a mathematical procedure to express some of these variables, hydraulic engineers have examined this problem of fluid mechanics and have developed the concepts of velocity gradient and shear rate, or "G factor."

\[ G \text{- FACTOR (shear rate)} = \frac{0.25 \text{ ft/s}}{0.01 \text{ ft}} = 25 \text{ s}^{-1} \]

**FIG. 8.4** Illustration of velocity gradient and shear rate.

Figure 8.4 illustrates the basis of these concepts. In this illustration, the differential velocity between two particles 0.01 ft apart is 0.25 ft/s, so the shear rate \( G \) is 25 s\(^{-1}\). Obviously, it is impractical to measure the G factor in this way, but fortunately further development of the mathematical model shows that shear rate is also related to rate of energy input (power) per unit volume (equivalent to detention time in the process) and water viscosity. The latter has a direct bearing on the frequency of particle collisions and explains, in part, the strong influence of water temperature on both coagulation and flocculation. The formula is:

\[ G \text{ factor} = \sqrt{\frac{P}{V \mu}} \text{ in s}^{-1} \]

where \( P \) is power input, in ft lb/s (hp \( \times 550 \)) (watts)

\( V \) is volume in the process, \( \text{ft}^3 \) (m\(^3\))

\( \mu \) is viscosity, in (lb)(s)/ft\(^2\) (viscosity in centipoises \( \times 2.1 \times 10^{-5} = \text{lb(s)/ft}^2 \))

The G factor usually recommended for most coagulation units is about 900 s\(^{-1}\) for a 30-s mixing time, varying inversely with time. The required mixing time is
usually established by bench tests, as described later. The recommended G factor for flocculation is lower, varying from about 50 for a cold, colored water carrying a very fragile floc, to about 200 for a solids contact lime softener on warm river water. Again, the G factor for flocculation must be determined by bench testing, and this should lead to a design of flocculator which can be varied in speed and power input as river conditions change and lead to fluctuations in solids concentration and sensitivity of floc to shear.

**COAGULATION AND FLOCCULATION CHEMICALS**

Historically, metal coagulants (alum and iron salts) have been most widely used in water clarification. These products function both as coagulants and flocculants. When added to water, they form positively charged species in the typical pH range for clarification, about 6–7. This hydrolysis reaction produces insoluble gelatinous aluminum or ferric hydroxide.

\[
\begin{align*}
\text{Al}_2(SO_4)_3 + 6H_2O & \rightarrow 2\text{Al}(OH)_3\downarrow + 3H_2SO_4 \\
\text{FeCl}_3 + 3H_2O & \rightarrow \text{Fe(OH)}_3\downarrow + 3\text{HCl}
\end{align*}
\]

(1)

(2)

Note that the by-products are hydroxide precipitates and mineral acids; the latter react with alkalinity in the water, reducing pH and producing a second by-product, CO\textsubscript{2}. Sometimes the gaseous CO\textsubscript{2} by-product interferes with the coagulation process by coming out of solution, adsorbing on the hydrous precipitate, and causing floc flotation rather than settling.

**FIG. 8.5** The effect of coagulant dosage on pH range limitations. The optimum pH remains almost constant, but the pH range becomes less restrictive as coagulant dosage increases.
Polyaluminum chloride, a product in wide use in Japan, avoids the problem of alkalinity reduction. When the material hydrolyzes, the floe formed incorporates the chloride ion into the floe structure so it is not available to produce acid, reduce alkalinity, and form by-product CO$_2$. Even if there are no suspended solids in the water initially, the metal coagulants form floes which enmesh the destabilized colloids. However, the voluminous sludges produced by the addition of metal coagulants create disposal problems because they are usually difficult to dewater. This is why alum and iron salts are not often used to improve efficiency of centrifuges, filter presses, and other dewatering devices.

Metal coagulants are particularly sensitive to pH and alkalinity. If pH is not in the proper range, clarification is poor, and iron or aluminum may be solubilized and cause problems to the water user. The lower the coagulant dosage, the more sensitive the floe is to pH changes (Figure 8.5). Table 8.3 lists some important properties of common coagulants.

The introduction of activated silica in the 1940s significantly improved the performance of alum and iron salts as coagulants and flocculants in water clarification. The subsequent development of a variety of organic polymers called polyelectrolytes in the next decade was an even more spectacular contribution to water treatment technology.

Polyelectrolytes are large water-soluble organic molecules made up of small building blocks called monomers, repeated in a long chain. They usually incorporate in their structures ion exchange sites which give the molecule an ionic charge. Those having a positive charge are cationic, and those with a negative charge are anionic. These molecules react with colloidal material in the water by neutralizing charge or by bridging (tying together) individual particles to form a visible, insoluble precipitate or floc.

### TABLE 8.3 Properties of Common Coagulants

<table>
<thead>
<tr>
<th>Common name</th>
<th>Formula</th>
<th>Equiv. weight</th>
<th>pH at 1%</th>
<th>Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum</td>
<td>Al$_2$(SO$_4$)$_3$·14H$_2$O</td>
<td>100</td>
<td>3.4</td>
<td>Lump—17% Al$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Liquid—8.5% Al$_2$O$_3$</td>
</tr>
<tr>
<td>Lime</td>
<td>Ca(OH)$_2$</td>
<td>40</td>
<td>12</td>
<td>Lump—as CaO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Powder—93-95%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Slurry—15-20%</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>FeCl$_3$·6H$_2$O</td>
<td>91</td>
<td>3-4</td>
<td>Lump—20% Fe</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Liquid—20% Fe</td>
</tr>
<tr>
<td>Ferric sulfate</td>
<td>Fe$_2$(SO$_4$)$_3$·3H$_2$O</td>
<td>51.5</td>
<td>3-4</td>
<td>Granular—18.5% Fe</td>
</tr>
<tr>
<td>Copperas</td>
<td>FeSO$_4$·7H$_2$O</td>
<td>139</td>
<td>3-4</td>
<td>Granular—20% Fe</td>
</tr>
<tr>
<td>Sodium aluminate</td>
<td>Na$_2$Al$_2$O$_4$</td>
<td>100</td>
<td>11-12</td>
<td>Flake—46% Al$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Liquid—26% Al$_2$O$_3$</td>
</tr>
</tbody>
</table>

Polyaluminum chloride, a product in wide use in Japan, avoids the problem of alkalinity reduction. When the material hydrolyzes, the floe formed incorporates the chloride ion into the floe structure so it is not available to produce acid, reduce alkalinity, and form by-product CO$_2$. Even if there are no suspended solids in the water initially, the metal coagulants form floes which enmesh the destabilized colloids. However, the voluminous sludges produced by the addition of metal coagulants create disposal problems because they are usually difficult to dewater. This is why alum and iron salts are not often used to improve efficiency of centrifuges, filter presses, and other dewatering devices.

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Polyelectrolytes are large water-soluble organic molecules made up of small building blocks called monomers, repeated in a long chain. They usually incorporate in their structures ion exchange sites which give the molecule an ionic charge. Those having a positive charge are cationic, and those with a negative charge are anionic. These molecules react with colloidal material in the water by neutralizing charge or by bridging (tying together) individual particles to form a visible, insoluble precipitate or floc.

**TAILORING POLYELECTROLYTES**

The performance of these materials can be modified to suit the nature of the colloidal matter to be removed from the water. These modifications include varia-
tions in molecular weight and ion exchange capacity. These materials can also be produced without an ionic charge; these are called nonionic polymers. Although they are not, strictly speaking, polyelectrolytes, nonionic polymers exhibit many of the same flocculating properties in solution, and are generally considered as part of the general polyelectrolyte family of compounds.

Although most polyelectrolytes are synthetic organic materials, nature also produces an endless variety of such materials. Some of these are chemically processed to improve performance and are commercially available.

The cationic polyelectrolytes are either polyamines or quaternary amines. In water, a polyamine hydrolyzes as follows:

\[
\text{R-NH}_2 + \text{H}_2\text{O} \rightarrow \text{R-NH}^+\cdot\text{H}^+ + \text{OH}^-
\]

Because of the hydrolysis to yield \(\text{OH}^-\), at high pH, the reaction is forced to the left, and the polymer becomes nonionic. This is illustrated by Figure 8.6, which shows loss in exchange capacity for a specific polyamine as pH increases.

In contrast, the quaternary polymers are but slightly affected by pH, remaining positively charged over a broad pH range (Figure 8.6).

The anionic polymers incorporate a carboxyl group (\(-\text{COOH}\)) in their structure. These ionize in the following manner:

\[
\text{R-COOH} \rightarrow \text{R-COO}^- + \text{H}^+
\]

The hydrogen ion forces the reaction to the left, so anionics become nonionic at low pH.

The ionic nature of polyelectrolytes is only one factor determining the performance of these materials as coagulants and flocculants. Other factors, such as the polar nature of nonionic bonds in the molecule, molecular size, and molecular geometry, also play a large part and may in some cases overshadow the effects of charge and charge density. Hence, high molecular weight nonionic polymers are

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**FIG. 8.6** Generalized plot showing loss of cationic strength for tertiary polyamines as pH increases, and relative pH independence of quaternary amine coagulants.
effective flocculants in many systems because of their ability to attract and hold colloidal particles at polar sites on the molecule. Furthermore, because of their molecular size, they can bridge together many small particles. Less sludge is generated by organic polymers than by inorganic salts, since they do not add weight or chemically combine with other ions in the water to form a precipitate. Organic polymers do not affect the pH of the water and generally do not require pH adjustment for effective use.

So, as a general rule, cationics are designed to work at lower pH values, anionics at higher. Nonionics and quaternaries are only slightly influenced by pH. The general rule should not be interpreted to mean that anionic polymers do not work at low pH value; it simply means they are no longer ionic. They may produce good results in flocculating solids at low pH simply because of their nonionic bonds. The same applies to cationics; even though they are not charged at high pH, they may act as effective coagulants because of their polar groups.

Organic polymers overcome many of the problems inherent in the use of alum or iron salts. These polymers are long chain organic molecules made up of small building blocks, called monomers, repeated along the chain. Depending on the selection of monomers and processing methods, a wide variety of polymers can be made of various configurations and molecular weights. Molecular weight is proportional to polymer chain length; the wide selection of structures and molecular weights makes it possible to design a polymer specifically for a given coagulation or flocculation problem, but this is seldom practical for economic reasons.

Organic polymers used in water treatment are of two major types, coagulants and flocculants. Coagulants are positively charged molecules of relatively low molecular weight. Although they exhibit some tendency for bridging, they are not particularly effective flocculants. Flocculant polymers have much higher molecular weights, providing long bridges between small flocs to enhance particle growth. Flocculants are either cationic, anionic, or nonionic. The flocculant that

### Table 8.4 Some Characteristics of Organic Polymers

<table>
<thead>
<tr>
<th>Class</th>
<th>Mol. wt. ranges</th>
<th>Form and availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cationic coagulants</td>
<td>Below 100,000</td>
<td>All are available as aqueous solutions</td>
</tr>
<tr>
<td>Polyamines</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyquaternaries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PolyDADMAC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epi-DMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Cationic flocculants</td>
<td>Over 1,000,000</td>
<td>Powders or emulsions</td>
</tr>
<tr>
<td>Copolymers of:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylamide and DMAEM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylamide and DADMAC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mannich amines</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Nonionic flocculants</td>
<td>Over 1,000,000</td>
<td>Powders or emulsions</td>
</tr>
<tr>
<td>Polyacrylamides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Anionic flocculants</td>
<td>Over 1,000,000</td>
<td>Powders or emulsions</td>
</tr>
<tr>
<td>Polycrylates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copolymers of acrylamide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>and acrylate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Note:** DADMAC: diallyl-dimethyl ammonium chloride; Epi: epichlorhydrin; DMA: dimethylamine; DMAEM: dimethyl-aminoethyl-methacrylate.
works best in any system can be determined only through laboratory screening and in-plant testing. Polymer flocculants, unlike coagulants, are not selected for neutralization. Table 8.4 lists some characteristics of commonly used organic coagulants and flocculants used in water treatment.

Unlike inorganic salts, polymers do not produce voluminous, gelatinous floc. In applications where additional solids improve results, inorganic coagulants or clay may be required to supplement the use of polymers. Polymers do not affect pH, nor is their performance as sensitive to the pH of the treated water as metal coagulants.

**ACTIVATED SILICA**

Some inorganic compounds can be polymerized in water to form inorganic polymer flocculants. Activated silica (sometimes identified as $\text{SiO}_2$) is an example. When sodium silicate, which contains alkali, is diluted to 1.5 to 2.0% and then partially neutralized (usually with chlorine or sodium bicarbonate), the silica becomes colloidal and then begins to slowly polymerize. After aging for 15 to 30 min, the solution is diluted to about 0.5 to 1.0% SiO$_2$ arresting further polymerization, producing activated silica. Although this preparation procedure is complicated, this is a very effective flocculant for such applications as assisting alum treatment for color removal and improving the softening of organic-containing waters, such as some of the colored well waters in Florida.

**APPLICATIONS OF COAGULATION AND FLOCCULATION**

A sample of turbid water in a graduated cone separates into two layers, the settleable and the colloidal solids (Figure 8.7.) In raw water clarification a coagulant is almost always used since the colloidal haze must be removed to produce the low turbidity demanded by most water-using processes. In wastewater clarification, a coagulant is required only where the suspended solids create a problem in meeting effluent guidelines; here a flocculant may be required to speed the settling rate.

Two types of laboratory tests are used to select the best chemical and approximate dosage level required for clarification: (1) the jar test, and (2) the cylinder test. The jar test is used when the stream to be clarified has less than approximately 5000 mg/L suspended solids. Raw water clarification, settling of biological solids, and most primary waste streams are in this category. The cylinder test is used for heavy slurry streams where suspended solids exceed approximately 5000 mg/L. Coal and mineral processing wastes and the sludge resulting from a primary clarification are examples of heavy slurries.

The jar test simulates the types of mixing and settling conditions found in a clarification plant. The laboratory unit for running these tests (Figure 8.8) allows up to six individual tests to be run simultaneously. The jar tester has a variable speed motor that allows control of the mixing energy in the jars.

Clarification results are sensitive to chemical dosage, mixing energy, and length of mixing. Figure 8.9 shows a typical sequence in jar testing where a colloidal haze is removed. The coagulant is added with high energy to disperse it in the water and promote increased frequency of collisions. The duration may be
FIG. 8.7  The solid particles in the left cone are a conglomeration of materials of various particle sizes, identified as suspended solids. After settling for 30 min, two fractions are obtained (right cone): settleable solids, expressed as milliliters per liter, and turbidity, expressed in nephelometric units.

FIG. 8.8  This type of gang-stirrer is widely used for jar testing both as a research tool and a plant control device.
FIG. 8.9  (a) The coagulant is measured into a sample of turbid water with a high degree of mixing. (b) After coagulant addition, particle growth occurs because of charge neutralization. Additional coagulant or a high molecular flocculant may then be added. (c) After flocculation, at a very low stirring speed—10 to 15 r/min, for example—the sample is examined after an established time period. Note the fine, pinpoint floc which has escaped entrapment by the larger floc. (d) The supernatant is examined and tested after 5 to 10 min settling time, and the nature and volume of the floc may be recorded. In some cases, the floc is reclaimed for use in the next series of jar tests.
short, less than 1 min. The actual mixing time is refined as the test regimen proceeds—in essence, defining the optimum G factor. A polymer flocculant, if required, is added during the last few seconds of the rapid mix. In the slow mix period which follows, floc building proceeds until the floc becomes so big that shear forces finally overcome the bridging forces, breaking the floc apart. This limits the size of the floc. After slow mixing for an optimum period of time, found only by repeated tests (usually 5 to 20 min), the jars are allowed to settle for 5 to 10 minutes.

Jars with different chemicals or the same chemical at different dosages are run side by side and the results compared. Floc settling rate, final clarity or suspended solids, and volume of sludge produced (if measurable) are contrasted between jars. Although clarity can be judged by the eye, the more accurate standard mea-

FIG. 8.10 Turbidimeter used for continuously monitoring a raw water stream to assist in the control of coagulant dosage. (Courtesy of Hach Company.)
FIG. 8.11 Cylinder tests on a coal slurry. After chemical treatment, the 500-mL cylinder is inverted several times to mix and induce flocculation, and the drop in solids interface is measured at fixed time intervals, as shown above.

Measurement is made with a turbidimeter (Figure 8.10). Other quality tests such as pH, BOD, color, COD, and soluble metals, are run on the settled water to establish performance standards.

The cylinder test, designed to indicate how fast the suspended solids will settle, employs a 500-mL stoppered graduated cylinder, stopwatch, and labware for dosing the chemical being evaluated. The slurry sample is placed in the cylinder, chemical is added, and the cylinder gently inverted several times. Mixing is much less severe than in the jar test because solids are present at much higher levels, so that frequent collisions can occur at the lower mixing energy. After mixing, the cylinder is set upright, and the interface between the water and the settling solids observed. Time and solids level are recorded, and the data are plotted on a graph. As in the jar test, a number of analytical tests can be run on the clear water; however, rapid settling rate is usually the goal. By running coagulants and flocculants at different dosages and comparing settling rates, the most effective products are selected. Figure 8.11 illustrates the results of cylinder tests conducted on a coal slurry.
COLOR REMOVAL

The selection of an effective chemical program for the removal of color from water is accomplished by jar testing as in the case of suspended solids removal, but there are pronounced differences in results: The floc produced from coagulated organic matter is fragile, so it is very important that the jar test device be operated in a manner that duplicates mixing energy and flocculation shear corresponding to what would prevail in full-scale equipment.

For the most part, color in water is a mixture of colloidal organic compounds that represent breakdown products of high molecular weight substances produced by living cells. (See Chapters 4 and 6.) These materials are analogous to the polyelectrolytes used in water treatment—as a matter of fact, natural organics like starch have been used both as dispersants and flocculants since the earliest days of water treatment science. They are variously identified as humic acid (a polymer containing phenolic groups), polysaccharides (polymers similar to sugar and cellulose), polypeptides (protein polymers), and lignins and tannins (other relatives of cellulose). For the most part, these substances are anionic or nonionic polymers. It is not surprising, then, that they are coagulated by cationic materials, and the amount of coagulant needed is directly proportional to the color.

Alum is commonly selected as the first coagulant to be evaluated in the jar test. After the alum demand has been satisfied, excess alum produces a floc that ties the coagulated particles together. The pH range is extremely narrow, usually about 4.8 to 5.5, and variation in pH usually disperses the floc and creates a haze. Most natural colored waters are low in alkalinity, so the alum used for coagulation often destroys the natural alkalinity, and the addition of an alkali may be needed for pH adjustment. After coagulation and formation of the alum floc, an anionic polymer is usually used to strengthen the floc and to hasten sedimentation. A complicating factor is temperature; many colored waters are found in Canada and the northern United States, and the selected program must be effective at 32°F, where viscosity greatly increases shear forces and hinders sedimentation; this complicatesthe jar test procedure. Another potential complication is the usual need for pH correction of the finished water to render it less corrosive than water at pH 5.5. The color matter in water behaves much like an acid-base indicator, and an increase in pH usually results in a color increase—which may not be a serious problem in most cases.

Certain of the cationic polyelectrolytes are useful for the partial replacement of alum in the color removal process, permitting treatment at a higher pH and reducing the destruction of alkalinity by the high alum dosage otherwise required.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Conventional alum program</th>
<th>Alum-polyamine program</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum dosage, mg/L</td>
<td>55</td>
<td>35</td>
</tr>
<tr>
<td>Aluminate dosage, mg/L</td>
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<td>30</td>
</tr>
<tr>
<td>Nonionic polymer, mg/L</td>
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<tr>
<td>Polyamine, mg/L</td>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>pH</td>
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<td>6.5</td>
</tr>
<tr>
<td>Color</td>
<td>5–10</td>
<td>5–10</td>
</tr>
</tbody>
</table>

TABLE 8.5 Chemical Treatment of Colored Water
(Florida swamp drainage at 400 APHA color)
Table 8.5 compares the results of a conventional alum program to alum-polyamine treatment.

Wastewaters containing color, such as pulp/paper mill discharges, are sometimes even more difficult to treat than natural water sources. Experience and ingenuity are needed to screen potential coagulants; this is an area of water treatment that is still more an art than a science. An example of this was a study of a textile wastewater where the color could not be removed by alum treatment followed by pH correction with alkali—yet it could be treated by aluminate, followed by pH correction by acid. A theory was developed to explain this—but only after the investigator had worked out the solution by trial and error.

**PLANT DESIGN**

The flowsheet of a surface water clarification plant shows how the principles of coagulation and flocculation apply to actual plant design. Generally, the lower the suspended solids in the process stream, or the higher the required effluent clarity, the more critical is mixing to the final results. Surface water is relatively low in suspended solids and removal to a low concentration of residual solids is usually required. For this reason many water plants are designed with flash mixing and flocculation mixing. The jar test protocol of rapid and slow mixing, which works best for raw water clarification, is duplicated on the plant scale. Flash mixing is accomplished in several ways: in-line hydraulic mixing (Figure 8.12), and high-speed mixing in a small mixing basin (Figure 8.13). The coagulant is added at or

![FIG. 8.12 High energy in-line mixer used for optimizing the effectiveness of polymer coagulants in water treatment systems. (Courtesy of Mixing Equipment Company.)](image-url)
FIG. 8.13  Flash mixers are designed to disperse chemicals throughout the water instantaneously, prior to flocculation.  (Courtesy of FMC Corporation, Material Handling Division.)

FIG. 8.14  Reel-type paddle flocculator in a municipal water treatment plant.  (Courtesy of Envi- rex, a Rexnord Company.)
before the flash mix. Mixing can also be accomplished by (1) hydraulic jumps in open channels, (2) venturi flumes, and (3) pipelines with tortuous baffles. However, these do not maintain the necessary G factor at low flows, so are somewhat limited in application.

Flocculation mixing occurs in gently stirred compartments. Two common flocculator designs are the horizontal reel (Figure 8.14) and the turbine mixer (Figure 8.15). Variable speed motors may be provided to allow variation in mixing energy. Some plants employ hydraulic flocculation mixing, but this has limited use because its effectiveness falls off at reduced flows.

Silt or color removal in raw water is done using two basic treatment schemes: conventional clarification or direct filtration. The most common plant operation is conventional: rapid mix, slow mix, sedimentation, and filtration (Figure 8.16). Historically, alum has been most widely used, because the optimum pH is often below 6.0. It is fed at the head of the plant, sometimes in conjunction with alkali for pH control. Iron salts are seldom used. Because alum floe is light, a polymer flocculant is usually required to reduce the carryover of floe from the settling basin to the filters.

Polymer coagulants often are used to either replace or reduce inorganic salts. The polymer coagulant is added at the flash mix. In some water, alum can be replaced only if clay is fed to add enough to the raw water to ensure high collision frequency and to add weight to the floc. An alternate method is to return sludge from the bottom of the settling basin to the rapid mix.

When the color or turbidity is very low in the raw water, direct filtration is often practiced in water clarification plants. In a direct filtration plant, water passes through flash mixing, sometimes a flocculator, and then directly to the filters (Figure 8.17). There are so few solids in the water that the filters do not plug excessively. A polymer is used as the primary coagulant in this process, since inorganic salts add solids which could clog the filter.
Wastewater streams usually have higher solids than raw water and the required suspended solids removal may not be as stringent. Generally, for wastewater clarification, hydraulic mixing has been widely used in the past; but newer plants are being designed with mechanical mixing similar to raw water clarification plants to improve removal of suspended solids.
SUGGESTED READING