Everything you want to know about
Coagulation & Flocculation....
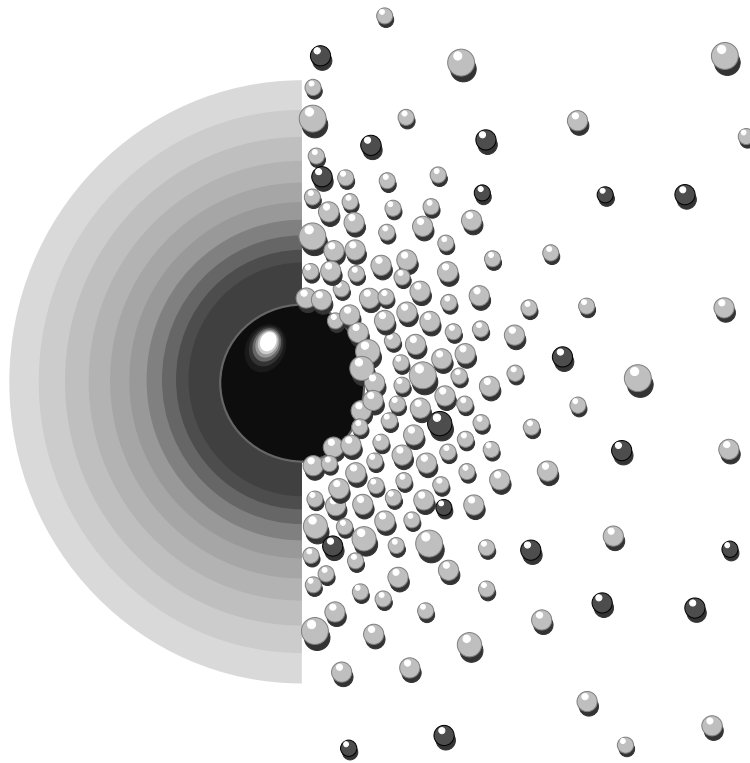
Zeta-Meter

Fourth Edition
April 1993

Your Comments
We hope this guide will be helpful. If you have any
suggestions on how to make it better, or if you have
additional information you think would help other
readers, then please drop us a note or give us a call.
Future editions will incorporate your comments.

Contents

Introduction
A Word About This Guide

The removal of suspended matter from water is one of the major goals of water treatment. Only disinfection is used more often or considered more important. In fact, effective clarification is really necessary for completely reliable disinfection because microorganisms are shielded by particles in the water.

Clarification usually involves:
• coagulation
• flocculation
• settling
• filtration

This guide focuses on coagulation and flocculation: the two key steps which often determine finished water quality.

Coagulation control techniques have advanced slowly. Many plant operators remember when dosage control was based upon a visual evaluation of the flocculation basin and the clarifier. If the operator's *eyeball* evaluation found a deterioration in quality, then his common sense response was to increase the coagulant dose. This remedy was based upon the assumption that if a little did some good, then more ought to do better, but it often did worse.

The competency of a plant operator depended on his years of experience with that specific water supply. By trial, error and oral tradition, he would eventually encounter every type of problem and learn to deal with it.

Reliable instruments now help us understand and control the clarification process. Our ability to measure turbidity, particle count, zeta potential and streaming current makes coagulation and flocculation more of a science, although art and experience still have their place.

We make zeta meters and happen to be a little biased in favor of zeta potential. In this guide, however, we have attempted to give you a fair picture of all of the tools at your disposal, and how you can put them to work.

Chapter 1
The Electrokinetic Connection

Particle Charge Prevents Coagulation

The key to effective coagulation and floccu-lation is an understanding of how individ-ual colloids interact with each other. Tur-bidity particles range from about .01 to 100 microns in size. The larger fraction is relatively easy to settle or filter. The smaller, colloidal fraction, (from .01 to 5 microns), presents the real challenge. Their settling times are intolerably slow and they easily escape filtration.

The behavior of colloids in water is strongly influenced by their electrokinetic charge. Each colloidal particle carries a like charge, which in nature is usually negative. This *like* charge causes adjacent particles to repel each other and prevents effective agglomeration and flocculation. As a result, charged colloids tend to remain discrete, dispersed, and in suspension.

On the other hand, if the charge is signifi-cantly reduced or eliminated, then the colloids will gather together. First forming small groups, then larger aggregates and finally into visible floc particles which settle rapidly and filter easily.
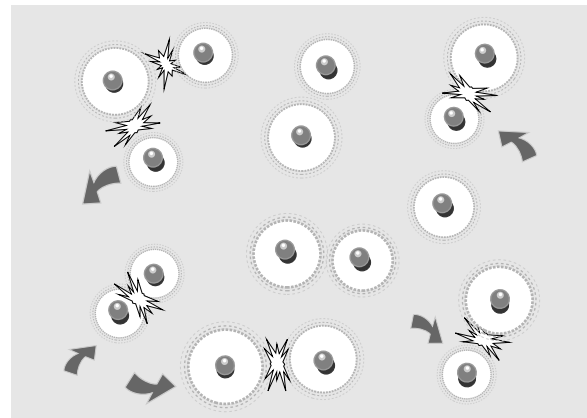
Charged Particles repel each other
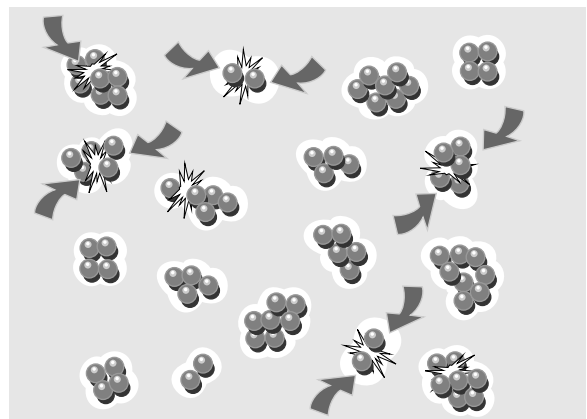
Uncharged Particles are free to collide and aggre-gate.

Microscopic Electrical Forces

The Double Layer

The double layer model is used to visualize the ionic environment in the vicinity of a charged colloid and explains how electrical repulsive forces occur. It is easier to understand this model as a sequence of steps that would take place around a single negative colloid if the ions surrounding it were suddenly stripped away.

We first look at the effect of the colloid on the positive ions, which are often called *counter-ions.* Initially, attraction from the negative colloid causes some of the positive ions to form a firmly attached layer around the surface of the colloid. This layer of counter-ions is known as the *Stern layer.*

Additional positive ions are still attracted by the negative colloid but now they are repelled by the positive Stern layer as well as by other nearby positive ions that are also

trying to approach the colloid. A dynamic equilibrium results, forming a diffuse layer of counter-ions. The diffuse positive ion layer has a high concentration near the colloid which gradually decreases with distance until it reaches equilibrium with the normal counter-ion concentration in solution.

In a similar but opposite fashion, there is a lack of negative ions in the neighborhood of the surface, because they are repelled by the negative colloid. Negative ions are called *co-ions* because they have the same charge as the colloid. Their concentration will gradually increase as the repulsive forces of the colloid are screened out by the positive ions, until equilibrium is again reached with the co-ion concentration in solution.

Positive Counter-Ion

Negative Co-Ion

Highly Negative Colloid

Stern Layer

Diffuse Layer

Ions In Equilibrium With Solution
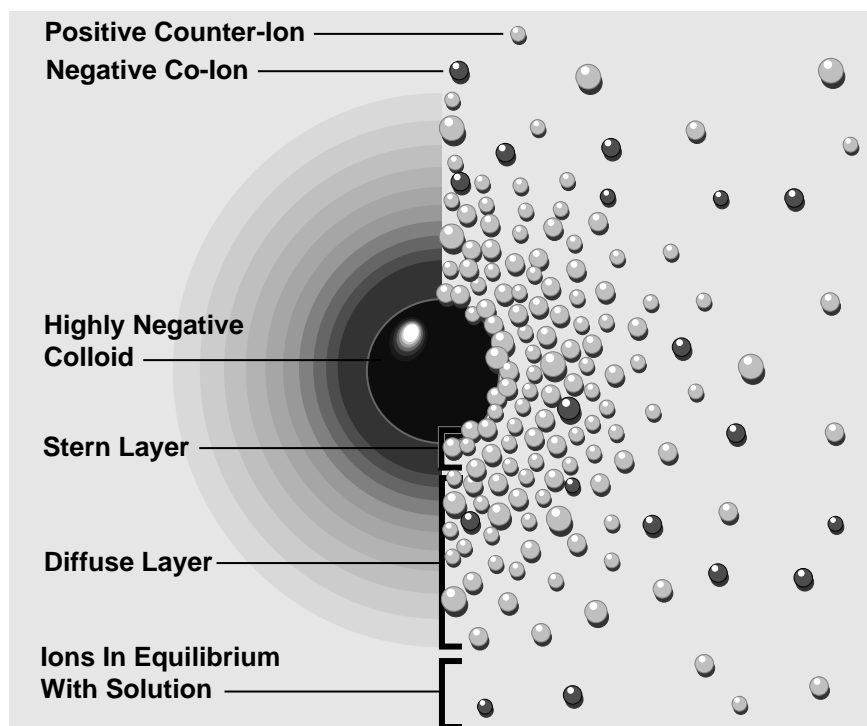
Two Ways to Visualize the Double Layer
The left view shows the change in charge density around the colloid. The right shows the distribution of positive and negative ions around the charged colloid.
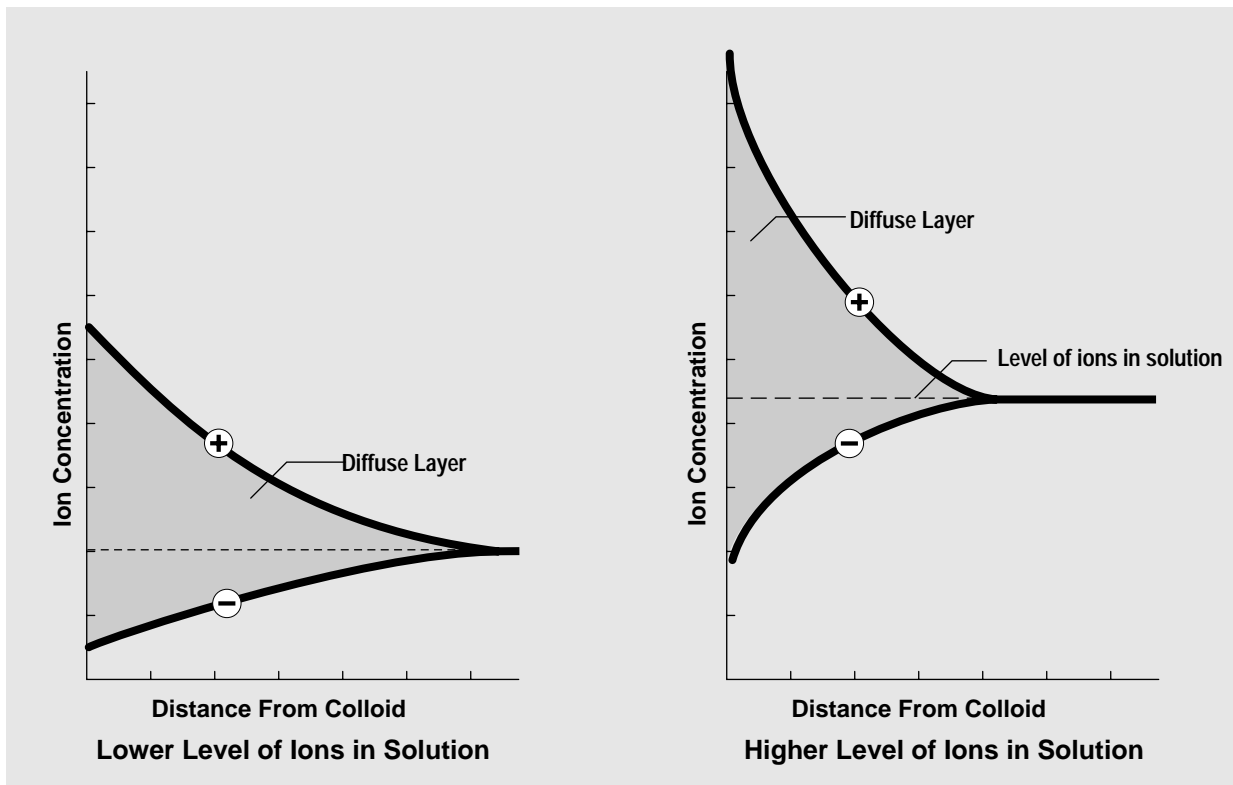
Double Layer Thickness
The diffuse layer can be visualized as a charged atmosphere surrounding the colloid. At any distance from the surface, its charge density is equal to the difference in concentration of positive and negative ions at that point. Charge density is greatest near the colloid and rapidly diminishes towards zero as the concentration of positive and negative ions merge together. The attached counter-ions in the Stern layer and the charged atmosphere in the diffuse layer are what we refer to as the *double layer.*

The thickness of the double layer depends upon the concentration of ions in solution. A higher level of ions means more positive ions are available to neutralize the colloid.

The result is a thinner double layer. Decreasing the ionic concentration (by dilution, for example) reduces the number of positive ions and a thicker double layer results.

The type of counter-ion will also influence double layer thickness. *Type* refers to the valence of the positive counter-ion. For instance, an equal concentration of aluminum (Al^{+3}) ions will be much more effective than sodium (Na^+) ions in neutralizing the colloidal charge and will result in a thinner double layer.

Increasing the concentration of ions or their valence are both referred to as *double layer compression.*

Variation of Ion Density in the Diffuse Layer
Increasing the level of ions in solution reduces the thickness of the diffuse layer. The shaded area represents the net charge density.
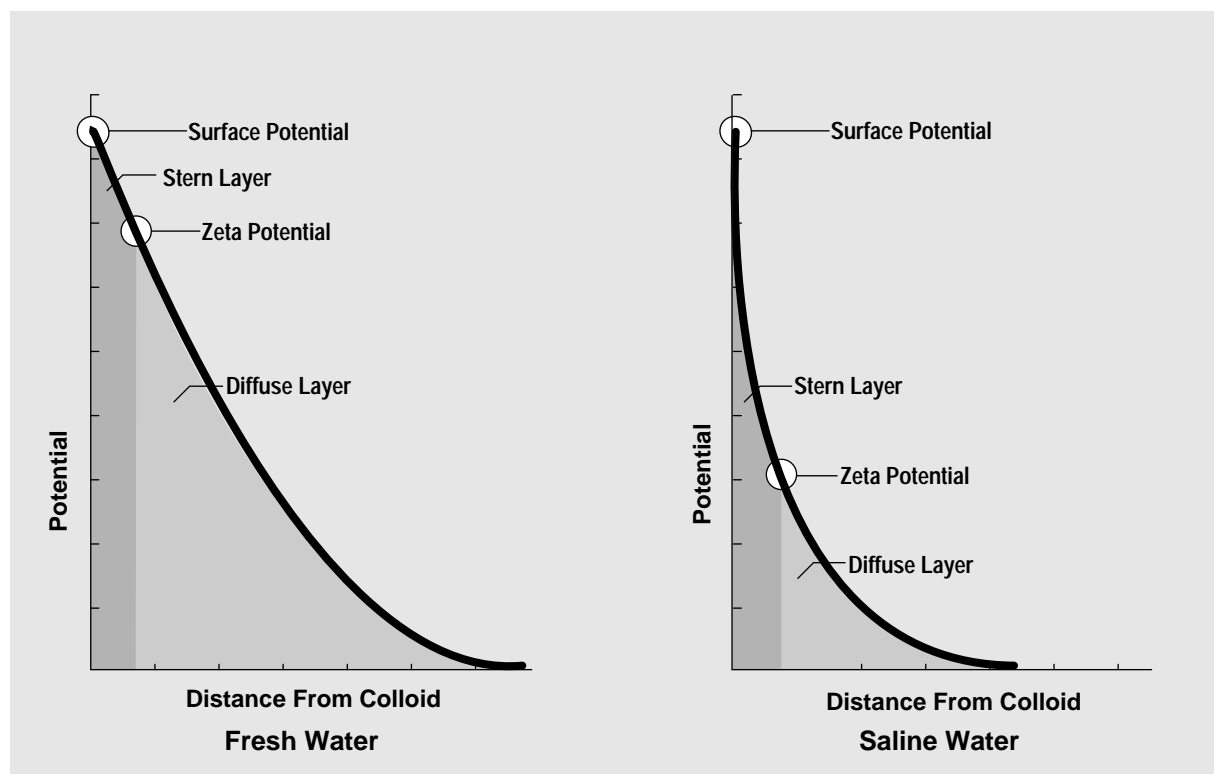
Zeta Potential

The negative colloid and its positively charged atmosphere produce an electrical potential across the diffuse layer. This is highest at the surface and drops off progressively with distance, approaching zero at the outside of the diffuse layer. The potential curve is useful because it indicates the strength of the repulsive force between colloids and the distance at which these forces come into play.

A particular point of interest on the curve is the potential at the junction of the Stern layer and the diffuse layer. This is known as the *zeta potential.* It is an important feature because zeta potential can be measured in a fairly simple manner, while the surface potential cannot. Zeta potential is an effective tool for coagulation control because changes in zeta potential indicate changes in the repulsive force between colloids.

The ratio between zeta potential and surface potential depends on double layer thickness. The low dissolved solids level usually found in water treatment results in a relatively large double layer. In this case, zeta potential is a good approximation of surface potential. The situation changes with brackish or saline waters; the high level of ions compresses the double layer and the potential curve. Now the zeta potential is only a fraction of the surface potential.

Zeta Potential vs Surface Potential

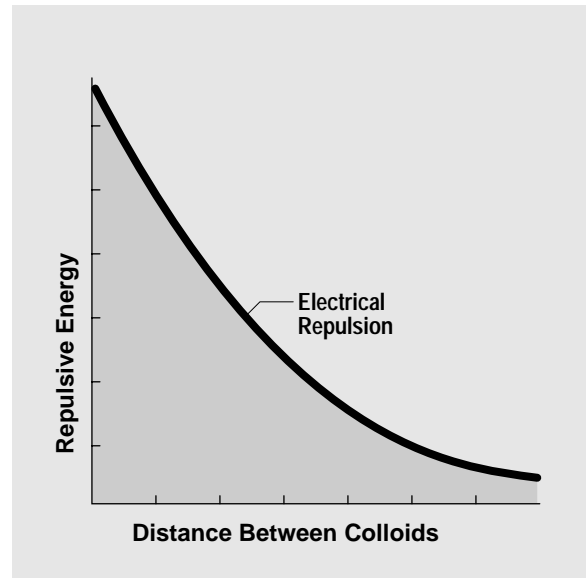The relationship between Zeta Potential and Surface Potential depends on the level of ions in solution. In fresh water, the large double layer makes the zeta potential a good approximation of the surface potential. This does not hold true for saline waters due to double layer compression.

Balancing Opposing Forces

The DLVO Theory (named after Derjaguin, Landau, Verwery and Overbeek) is the classic explanation of how particles interact. It looks at the balance between two opposing forces - electrostatic repulsion and van der Waals attraction - to explain why some colloids agglomerate and flocculate while others will not.

Repulsion

Electrostatic repulsion becomes significant when two particles approach each other and their electrical double layers begin to overlap. Energy is required to overcome this repulsion and force the particles together. The level of energy required increases dramatically as the particles are driven closer and closer together. An electrostatic repulsion curve is used to indicate the energy that must be overcome if the particles are to be forced together. The maximum height of the curve is related to the surface potential.

Attraction

Van der Waals attraction between two colloids is actually the result of forces between individual molecules in each colloid. The effect is additive; that is, one molecule of the first colloid has a van der Waals attraction to each molecule in the second colloid. This is repeated for each molecule in the first colloid and the total force is the sum of all of these. An attractive energy curve is used to indicate the variation in attractive force with distance between particles.

Electrostatic repulsion is always shown as a positive curve.
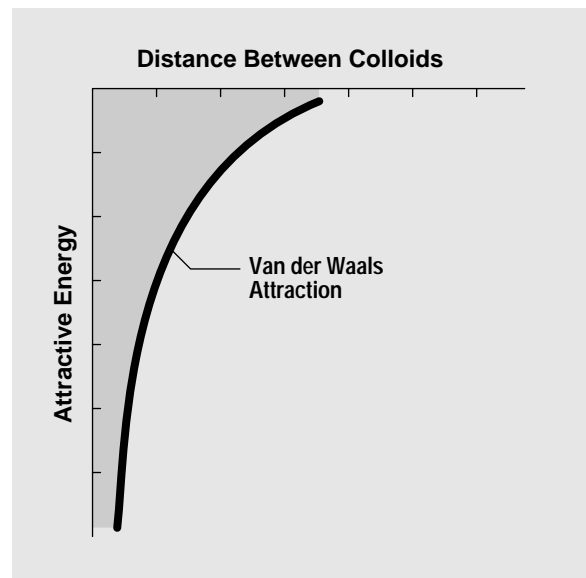
Van der Waals attraction is shown as a negative curve.

The Energy Barrier

The DLVO theory combines the van der Waals attraction curve and the electrostatic repulsion curve to explain the tendency of colloids to either remain discrete or to flocculate. The combined curve is called the *net interaction energy*. At each distance, the smaller energy is subtracted from the larger to get the net interaction energy. The net value is then plotted - above if repulsive, below if attractive - and the curve is formed.

The net interaction curve can shift from attraction to repulsion and back to attraction with increasing distance between particles. If there is a repulsive section, then this region is called the *energy barrier* and its maximum height indicates how resistant the system is to effective coagulation.

In order to agglomerate, two particles on a collision course must have sufficient kinetic energy (due to their speed and mass) to *jump over* this barrier. Once the energy barrier is cleared, the net interaction energy is all attractive. No further repulsive areas are encountered and as a result the particles agglomerate. This attractive region is often referred to as an *energy trap* since the colloids can be considered to be trapped together by the van der Waals forces.
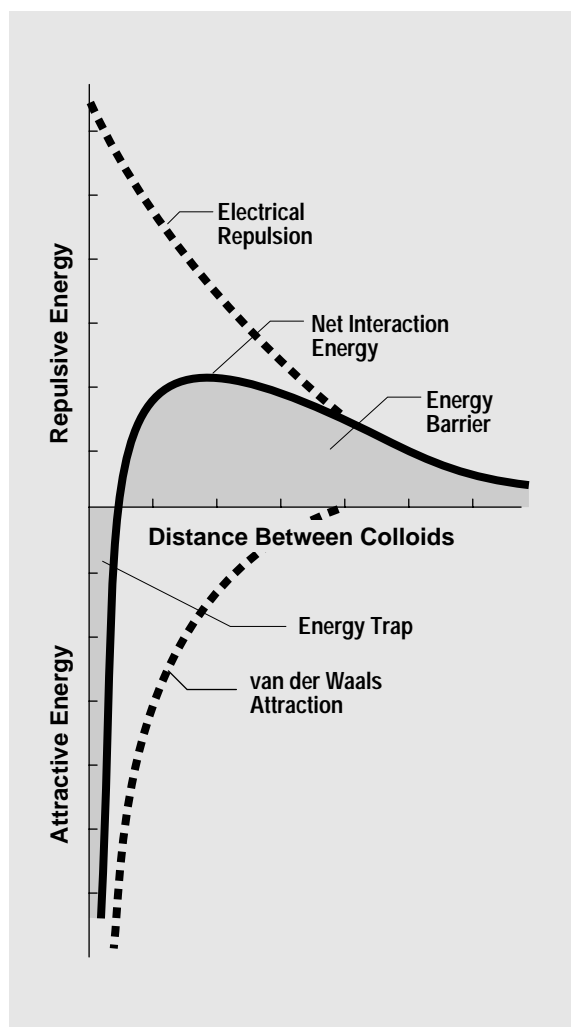
Interaction
The net interaction curve is formed by subtracting the attraction curve from the repulsion curve.

Lowering the Energy Barrier

For really effective coagulation, the energy barrier should be lowered or completely removed so that the net interaction is always attractive. This can be accomplished by either compressing the double layer or reducing the surface charge.

Compress the Double Layer

Double layer compression involves adding salts to the system. As the ionic concentration increases, the double layer and the repulsion energy curves are compressed until there is no longer an energy barrier. Particle agglomeration occurs rapidly under these conditions because the colloids can just about fall into the van der Waals "trap" without having to surmount an energy barrier.

Flocculation by double layer compression is also called *salting out* the colloid. Adding massive amounts of salt is an impractical technique for water treatment, but the underlying concept should be understood, and has application toward wastewater flocculation in brackish waters.
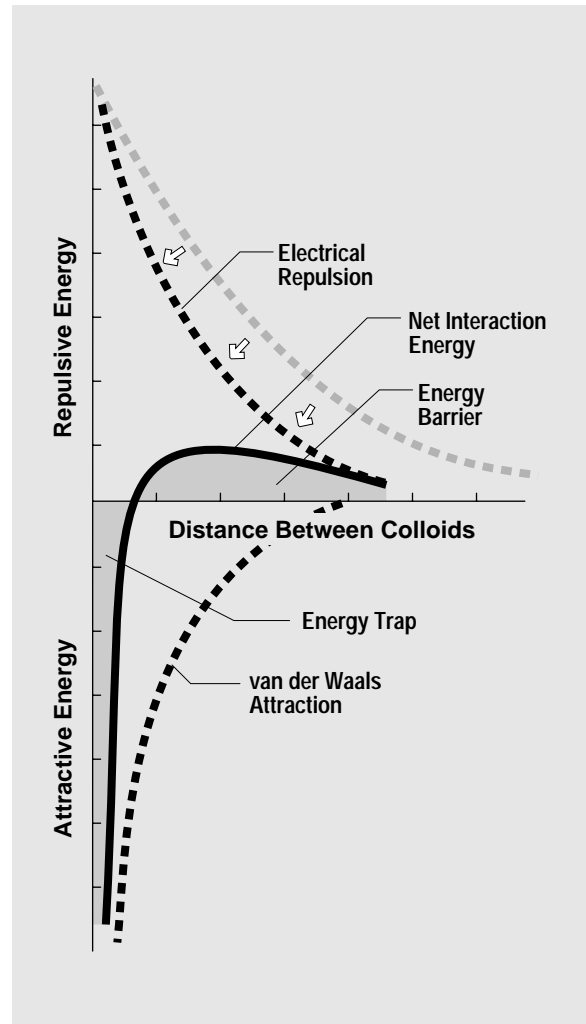
Compression
Double layer compression squeezes the repulsive energy curve reducing its influence. Further compression would completely eliminate the energy barrier.

Lower the Surface Charge

In water treatment, we lower the energy barrier by adding coagulants to reduce the surface charge and, consequently, the zeta potential. Two points are important here.

First, for all practical purposes, *zeta potential is a direct measure of the surface charge* and we can use zeta potential measurements to control charge neutralization.

Second, *it is not necessary to reduce the charge to zero.* Our goal is to lower the energy barrier to the point where the particle velocity from mixing allows the colloids to overwhelm it.

The energy barrier concept helps explain why larger particles will sometimes flocculate while smaller ones in the same suspension escape. At identical velocities the larger particles have a greater mass and therefore more energy to get them over the barrier.
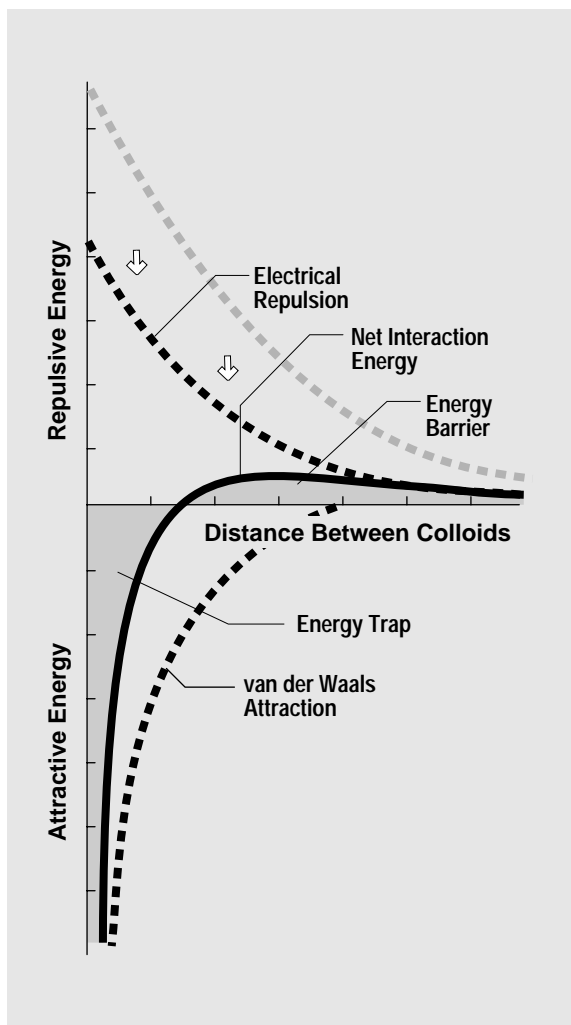
Charge Reduction
Coagulant addition lowers the surface charge and drops the repulsive energy curve. More coagulant can be added to completely eliminate the energy barrier.

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Chapter 2
Four Ways to Flocculate

Coagulate, Then Flocculate

In water clarification, the terms *coagulation* and *flocculation* are sometimes used interchangeably and ambiguously, but it is better to separate the two in terms of function.

Coagulation takes place when the DLVO energy barrier is effectively eliminated; this lowering of the energy barrier is also referred to as *destabilization*.

Flocculation refers to the successful collisions that occur when the destabilized particles are driven toward each other by the hydraulic shear forces in the rapid mix and flocculation basins. Agglomerates of a few colloids then quickly bridge together to form microflocs which in turn gather into visible floc masses.

Reality is somewhere in between. The line between coagulation and flocculation is often a somewhat blurry one. Most coagulants can perform both functions at once. Their primary job is charge neutralization but they often adsorb onto more than one colloid, forming a bridge between them and helping them to flocculate.

Coagulation and flocculation can be caused by any of the following:
- double layer compression
- charge neutralization
- bridging
- colloid entrapment

In the pages that follow, each of these four tools is discussed separately, but the solution to any specific coagulation-flocculation problem will almost always involve the simultaneous use of more than one of these. Use these as a check list when planning a testing program to select an efficient and economical coagulant system.

Double Layer Compression

Double layer compression involves the addition of large quantities of an indifferent electrolyte (e.g., sodium chloride). The *indifference* refers to the fact that the ion retains its identity and does not adsorb to the colloid. This change in ionic concentration compresses the double layer around the colloid and is often called *salting out.*

The DLVO theory indicates that this results in a lowering or elimination of the repulsive energy barrier. It is important to realize that salting out just compresses the colloid's sphere of influence and does not necessarily reduce its charge.

In general, double layer compression is not a practical coagulation technique for water treatment but it can have application in industrial wastewater treatment if waste streams with divalent or trivalent counterions happen to be available.

Highly Negative Colloid

Stern Layer

Diffuse Layer

Ions In Equilibrium With Solution
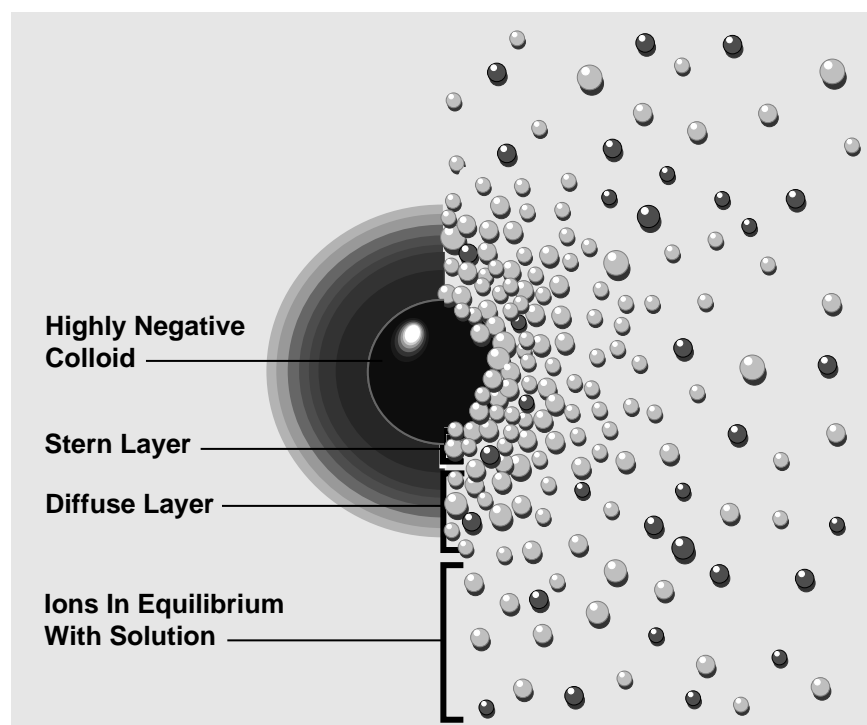
Compression
Flocculation by double layer compression is unusual, but has some application in industrial wastewaters. Compare this figure to the one on page 2.

Charge Neutralization

Inorganic coagulants (such as alum) and cationic polymers often work through *charge neutralization.* It is a practical way to lower the DLVO energy barrier and form stable flocs. Charge neutralization involves adsorption of a positively charged coagulant on the surface of the colloid. This charged surface coating neutralizes the negative charge of the colloid, resulting in a near zero net charge. Neutralization is the key to optimizing treatment before sedimentation, granular media filtration or air flotation.

Charge neutralization alone will not necessarily produce dramatic *macroflocs* (flocs that can be seen with the naked eye). This is demonstrated by charge neutralizing with cationic polyelectrolytes in the 50,000-200,000 molecular weight range. *Microflocs* (which are too small to be seen) may form but will not aggregate quickly into visible flocs.

Charge neutralization is easily monitored and controlled using zeta potential. This is important because overdosing can reverse the charge on the colloid, and redisperse it as a positive colloid. The result is a poorly flocculated system. The detrimental effect of overdoing is especially noticeable with very low molecular weight cationic polymers that are ineffective at bridging.

Slightly Negative Colloid

Stern Layer

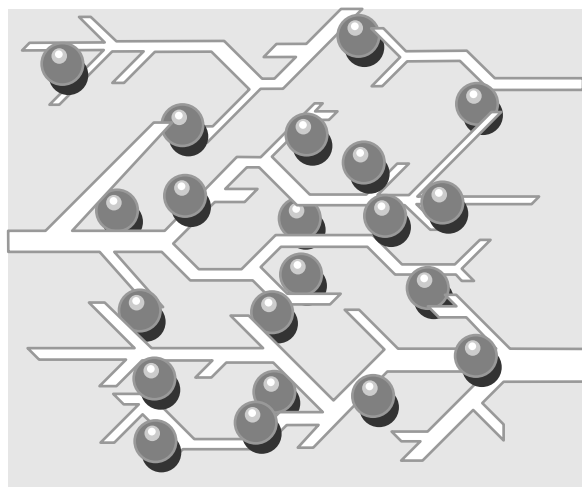**Diffuse Layer**

Ions In Equilibrium With Solution
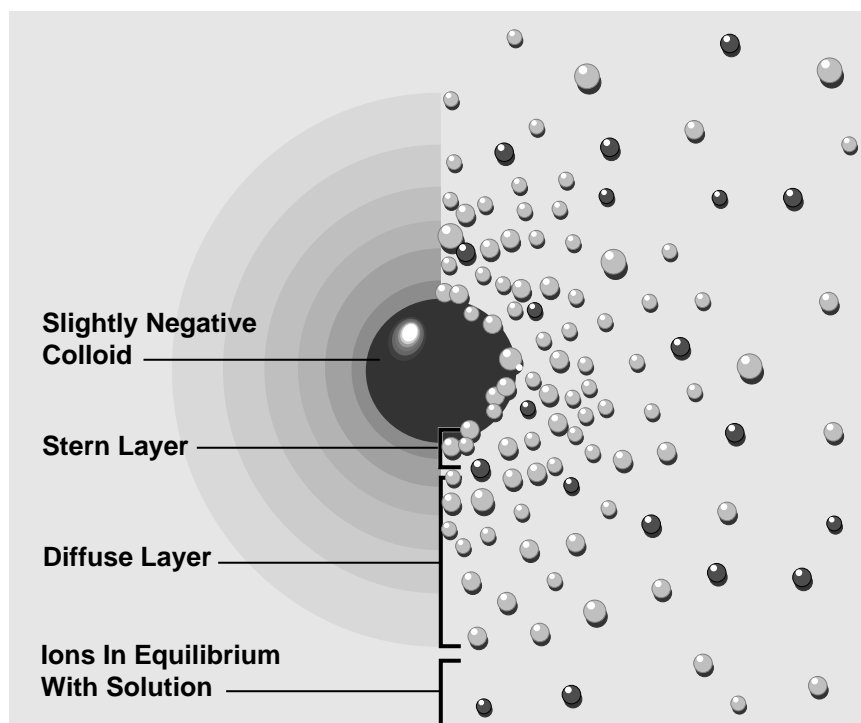
Charge Reduction
Lowering the surface charge drops the repulsive energy curve and allows van der Waals forces to reduce the energy barrier. Compare this figure with that on the opposite page and the one on page 2.

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Bridging

Bridging occurs when a coagulant forms threads or fibers which attach to several colloids, capturing and binding them together. Inorganic primary coagulants and organic polyelectrolytes both have the capability of bridging. Higher molecular weights mean longer molecules and more effective bridging.

Bridging is often used in conjunction with charge neutralization to grow fast settling and/or shear resistant flocs. For instance, alum or a low molecular weight cationic polymer is first added under rapid mixing conditions to lower the charge and allow microflocs to form. Then a slight amount of high molecular weight polymer, often an anionic, can be added to bridge between the microflocs. The fact that the bridging polymer is negatively charged is not significant because the small colloids have already been captured as microflocs.

Colloid Entrapment

Colloid entrapment involves adding relatively large doses of coagulants, usually aluminum or iron salts which precipitate as hydrous metal oxides. The amount of coagulant used is far in excess of the amount needed to neutralize the charge on the colloid. Some charge neutralization may occur but most of the colloids are literally swept from the bulk of the water by becoming enmeshed in the settling hydrous oxide floc. This mechanism is often called *sweep floc.*
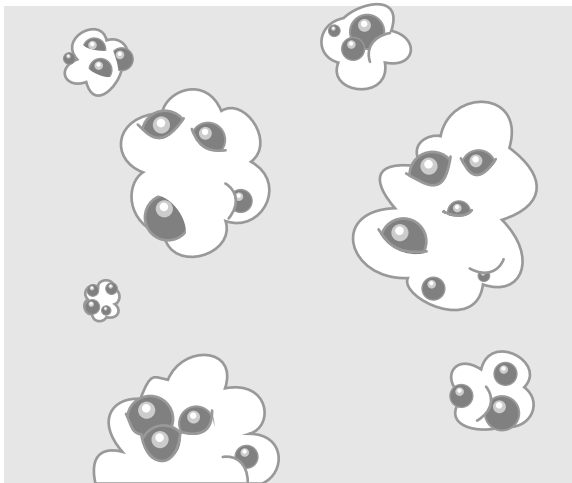
Sweep Floc
Colloids become enmeshed in the growing precipitate.

Bridging
Each polymer chain attaches to many colloids.

Chapter 3
Selecting Polyelectrolytes

An Aid or Substitute for Traditional Coagulants

The class of coagulants and flocculants known as polyelectrolytes (or polymers) is becoming more and more popular. A proper dosage of the right polyelectrolyte can improve finished water quality while significantly reducing sludge volume and overall operating costs.

On a price-per-pound basis they are much more expensive than inorganic coagulants, such as alum, but overall operating costs can be lower because of a reduced need for pH adjusting chemicals and because of lower sludge volumes and disposal costs. In some cases they are used to supplement traditional coagulants while in others they completely replace them.

Polyelectrolytes are organic macromolecules. A polyelectrolyte is a polymer; that is, it is composed of many *(poly)* monomers *(mer)* joined together. Polyelectrolytes may be fabricated of one or more basic monomers (usually two). The degree of polymerization is the number of monomers (building blocks) linked together to form one molecule, and can range up to hundreds of thousands.

Picking the Best One

Because of the number available and their proprietary nature, it can be a real challenge to select the best polyelectrolyte for a specific task. The following characteristics are usually used to classify them; manufacturers will often publish some of these, but not always with the desired degree of detail:
• type (anionic, non-ionic, or cationic)
• molecular weight
• basic molecular structure
• charge density
• suitability for potable water treatment

Preliminary bench testing of polyelectrolytes is an important part of the selection process, even when the polymer is used as a flocculant aid for an inorganic coagulant. Adding an untested polyelectrolyte without knowing the optimum dosage, feed concentration or mixing requirements can result in serious problems, including filter clogging.

It is important to note that, within the same family or type of polymer, there can be a large difference in molecular weight and charge density. For a specific application, one member of a family can have just the right combination of properties and greatly outperform the others.

Characterizing Polymers

Molecular Weight

The overall size of a polymer determines its relative usefulness for bridging. Size is usually measured as molecular weight. Manufacturers do not use a uniform method to report molecular weight. For this reason, two similar polymers with the same published molecular weight may actually be quite different.

In addition, molecular weight is only a measure of average polymer length. Each molecule in a drum of polymer is not the same size. A wide range can and will be found in the same batch. This distribution of molecular weights is an important property and can vary greatly.

Molecular Weight Range	General Description
10,000,000 or more	Very High
1,000,000 to 10,000,000	High
200,000 to 1,000,000	Medium
100,000 to 200,000	Low
50,000 to 100,000	Very Low
Less than 50,000	Very, Very Low

Structure

Two similar polyelectrolytes with the same composition of monomers, molecular weight, and charge characteristics can perform differently because of the way the monomers are linked together. For example, a product with two monomers A and B could have a regular alternation from A to B or could have groups of A's followed by groups of B's.

Charge Density

Relative charge density is controlled by the ratio of charged and uncharged monomers used. The higher the residual charge, the higher the density. In general, the relative charge density and molecular weight cannot both be increased. As a result, the ideal polyelectrolyte often involves a tradeoff between charge density and molecular weight.

Type of Polymer

Polyelectrolytes are classified as non-ionic, anionic or cationic depending upon the residual charge on the polymer in solution.

Non-ionic polyelectrolytes are polymers with a very low charge density. A typical non-ionic is a polyacrylamide. Non-ionics are used to flocculate solids through bridging.

Anionic polyelectrolytes are negatively charged polymers and can be manufactured with a variety of charge densities, from practically non-ionic to very strongly anionic. Intermediate charge densities are usually the most useful. Anionics are normally used for bridging, to flocculate solids. The acrylamide-based anionics with very high molecular weights are very effective for this.

Negative colloids can sometimes be successfully flocculated with bridging-type long chain anionic polyelectrolytes. One possible explanation is that a colloid with a net negative charge may actually have a mosaic of positive and negative regions. Areas of positive charge could serve as points of attachment for the negative polymer.

Anionic polyelectrolytes may be capable of flocculating large particles, but a residual haze of smaller colloids will almost always remain. These must first have their charge neutralized in order to flocculate.

Cationic polyelectrolytes are positively charged polymers and come in a wide range of families, charge densities and molecular weights. The variety available offers great flexibility in solving specific coagulation and flocculation problems, but makes selecting the right polymer more complicated.

High molecular weight cationic polyelectrolytes can be thought of as *double acting* because they act in two ways: charge neutralization and bridging.

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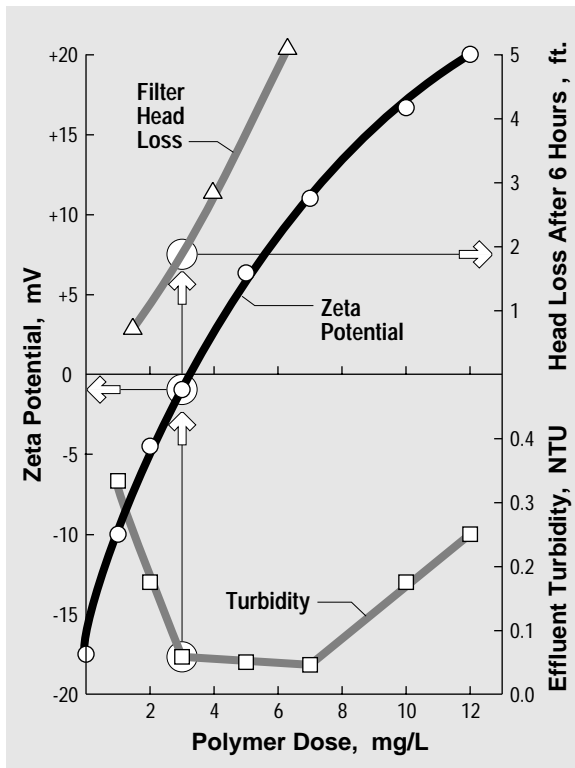
Direct Filtration with Cationic Polymers

It is often possible to eliminate or bypass conventional flocculation and sedimentation when raw water supplies are low in turbidity on a year-round basis. For new plants, this can mean a significant savings in capital cost. Coagulant treated water is then fed directly to the filters in what is known as the direct filtration process. Cationic polymers are usually very effective in this type of service.

In this example, polymer dosage, filter effluent turbidity and filter head loss after 6 hours of operation were plotted together. The minimum turbidity level is produced by a dose of 7 mg/L at a corresponding zeta potential of +10 mV. A polymer dose of 3 mg/L was selected as a more practical optimum because it produces almost the same turbidity at a substantial savings in polymer and with a much lower head loss through the filter. The result is a target zeta potential of -1mV.
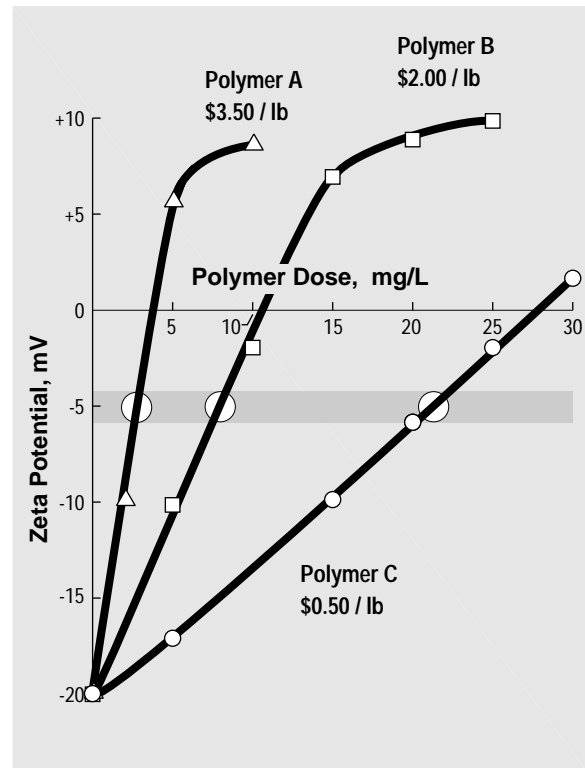
Cationic Polymer Screening

The true cost of a polymer is not its price per pound but the cost per million gallons of water treated. Plots of zeta potential versus polymer dosage can be used to determine the relative dose levels of similar polyelectrolytes.

In this example the target zeta potential was set at -5 mV. The corresponding doses are: 3 mg/L for Polymer A, 8 mg/L for Polymer B and 21 mg/L for Polymer C. The cost per million gallons *($/MG)* is estimated by converting the dosage to pounds per million gallons and then multiplying by the price per pound.

The result is $88/MG for Polymer A, $133/MG for Polymer B and $88/MG for Polymer C. If all other considerations are equal, then Polymers A & C are both economical choices.

Enhancing Polymer Effectiveness

Dual Polymer Systems

Two polymers can help if no single polymer can get the job done. Each has a specific function. For example, a highly charged cationic polymer can be added first to neutralize the charge on the fine colloids, and form small microflocs. Then a high molecular weight anionic polymer can be used to mechanically bridge the microflocs into large, rapidly settling flocs.

In water treatment, dual polymer systems have the disadvantage that more careful control is required to balance the counter-acting forces. Dual polymers are more common in sludge dewatering, where overdosing and the appearance of excess polymer in the centrate or filtrate is not as important.

Preconditioning

Inorganic coagulants may be helpful as a coagulant aid when a polyelectrolyte alone is not successful in destabilizing all the particles. Pretreatment with inorganics can also reduce the cationic polymer dose and make it more stable, requiring less critical control.
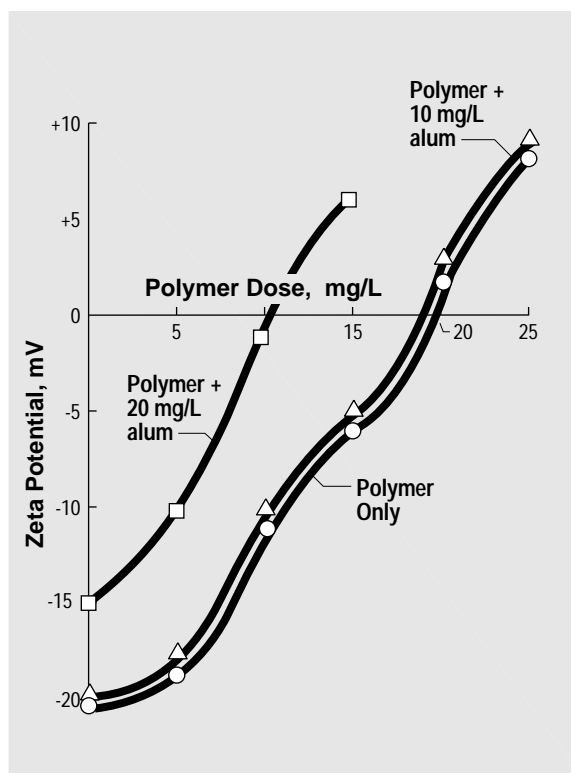
Preconditioning Polymers with Alum
The effect of preconditioning can be evaluated by making plots of zeta potential versus polymer dosage at various levels of preconditioning chemical. In this example, the required dosage of cationic polymer was substantially reduced with 20 mg/L of alum while 10 mg/l of alum was not effective.

Polymer Packaging and Feeding

Polyelectrolytes can be purchased in powder, solution and emulsion form. Each type has advantages and disadvantages. If possible, feed facilities should allow any type to be used.

Dry powder polymers are whitish granular powders, flakes or beads. Their tendency to absorb moisture from the air and to stick to feed screws, containers and drums is a major nuisance. Dry polymers are also difficult to wet and dissolve rather slowly. Fifteen minutes to 1 hour may be required.

Solution polymers are often preferred to dry powders because they are more convenient. A little mixing is usually sufficient to dilute liquid polymers to feed strength. Active ingredients can vary from a few percent to 50 percent.

Emulsion polymers are a more recent development. They allow very high molecular weight polymers to be purchased in convenient liquid form. Dilution with water under agitation frees the gel particles in the emulsion allowing them to dissolve in the water. Sometimes activators are required for preparation. Emulsions are usually packaged as 20-30% active ingredients.

Prepared batches of polymer are normally used within 24-48 hours to prevent loss of activity.

In addition, polymers are almost always more effective when fed as dilute solutions because they are easier to disperse and uniformly distribute. Using a higher feed strength may mean that a higher polymer dose will be required.

Typically, maximum feed strength is between 0.01 to 0.05%, but check with the polymer manufacturer for specific recommendations.

Stock polymer solutions are usually made up to 0.1 to 0.5% as a good compromise between storage volume, batch life, and viscosity. Diluting the stock solution by about 10:1 with water will usually drop the concentration to the recommended feed level. The polymer and dilution water should be blended in-line with a static mixer or an eductor.
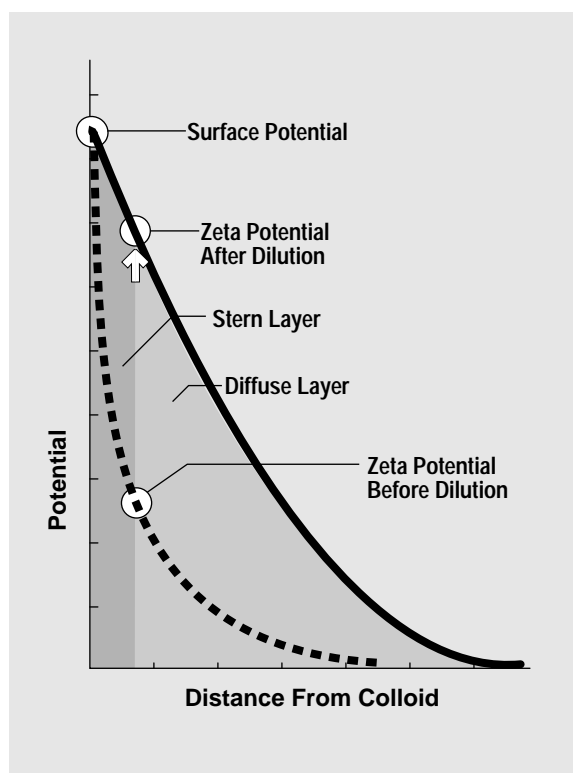
Using Cationic Polymers in Brackish Waters
In brackish waters, the correct cationic polymer dose is often concealed by the effect of double layer compression, which drops the zeta potential but not the surface potential.

Diluting the treated sample with distilled water will give an indication of whether enough polymer has been added. If the surface potential is still high, then dilution will cause the zeta potential to increase and more cationic is required.

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Interferences

Cationic polymers can react with negative ions in solution, forming chemical bonds which impair their performance. Greater doses are then required to achieve the same degree of charge neutralization or bridging. This is more noticeable in wastewater treatment.

Examples of interfering substances include sulfides, hydrosulfides and phenolics, but even chlorides can reduce polymer effectiveness.

Even pH should be considered, since particular polymer families may perform well in some pH ranges and not others.

pH Effects
Zeta potential curves can be used to evaluate the sensitivity of a cationic polymer to changes in pH. For this particular polymer the effect is quite large. It can be much less for other products.

Phenol Interference
The effect of phenols on this cationic polymer was evaluated by plotting zeta potential curves.

Chapter 4
Using Alum and Ferric Coagulants

Time Tested Coagulants

Aluminum and ferric compounds are the traditional coagulants for water and waste-water treatment. Both are from a family called metal coagulants, and both are still widely used today. In fact, many plants use one of these exclusively, and have no provision for polyelectrolyte addition.

Metal coagulants offer the advantage of low cost per pound. In addition, selection of the optimum coagulant is simple, since only a few choices are available. A distinct disadvantage is the large sludge volume produced, since sludge dewatering and disposal can be difficult and expensive.

Aluminum and ferric coagulants are soluble salts. They are added in solution form and react with alkalinity in the water to form insoluble hydrous oxides that coagulate by sweep floc and charge neutralization.

Metal coagulants always require attention to pH conditions and consideration of the alkalinity level in the raw and treated water. Reasonable dosage levels will frequently result in near optimum pH conditions. At other times, chemicals such as lime, soda ash or sodium bicarbonate must be added to supplement natural alkalinity.

Aluminum Sulfate (Alum)

Alum is one of the most widely used coagulants and will be used as an example of the reactions that occur with a metal coagulant. Ferric coagulants react in a generally similar manner, but their optimum pH ranges are different.

When aluminum sulfate is added to water, hydrous oxides of aluminum are formed. The simplest of these is aluminum hydroxide ($Al(OH)_3$) which is an insoluble precipitate. But several, more complex, positively charged soluble ions are also formed, including:
- $Al_6(OH)_{15}^{+3}$
- $Al_7(OH)_{17}^{+4}$
- $Al_8(OH)_{20}^{+4}$

The proportion of each will vary, depending upon both the alum dose and the pH after alum addition. To further complicate matters, under certain conditions the sulfate ion (SO_4^{-2}) may also become part of the hydrous aluminum complex by substituting for some of the hydroxide (OH^{-1}) ions. This will tend to lower the charge of the hydroxide complex.
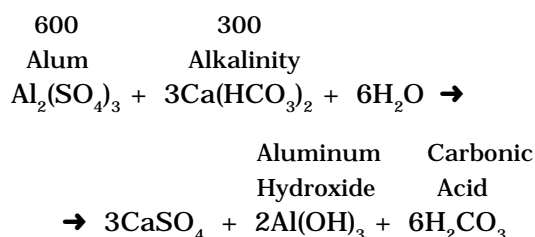
How Alum Works

The mechanism of coagulation by alum includes both charge neutralization and sweep floc. One or the other may predominate, but each is always acting to some degree. It is probable that charge neutralization takes place immediately after addition of alum to water. The complex, positively charged hydroxides of aluminum that rapidly form will adsorb to the surface of the negative turbidity particles, neutralizing their charge (and zeta potential) and effectively lowering or removing the DLVO energy barrier.

Simultaneously, aluminum hydroxide precipitates will form. These additional particles enhance the rate of flocculation by increasing the chances of a collision occurring. The precipitate also grows independently of the colloid population, enmeshing colloids in the sweep floc mode.

The type of coagulation which predominates is dependent on both the alum dose and the pH after alum addition. In general, sweep coagulation is thought to predominate at alum doses above 30 mg/L; below that, the dominant form depends upon both dose and pH.

Alkalinity is required for the alum reaction to successfully proceed. Otherwise, the pH will be lowered to the point where soluble aluminum ion (Al^{+3}) is formed instead of aluminum hydroxide. Dissolved aluminum ion is an ineffective coagulant and can cause "dirty water" problems in the distribution system. The reaction between alum and alkalinity is shown by the following:

$$\underset{\text{Alum}}{\underset{600}{Al_2(SO_4)_3}} + \underset{\text{Alkalinity}}{\underset{300}{3Ca(HCO_3)_2}} + 6H_2O \rightarrow$$

$$\rightarrow 3CaSO_4 + \underset{\text{Hydroxide}}{\underset{\text{Aluminum}}{2Al(OH)_3}} + \underset{\text{Acid}}{\underset{\text{Carbonic}}{6H_2CO_3}}$$

Estimating Alkalinity Requirements

This equation helps us develop several simple rules of thumb about the relation between alum and alkalinity.

Commercial alum is a crystalline material, with 14.2 water molecules (on average) bound to each aluminum sulfate molecule. The molecular weight of $Al_2(SO_4)_3 \bullet 14.2H_2O$ is 600.

Alkalinity is a measure of the amount of bicarbonate (HCO_3^{-1}), carbonate (CO_3^{-2}) and hydroxide (OH^{-1}) ion. The reaction shows alkalinity in its bicarbonate (HCO_3^-) form which is typical at pH's below 8, but alkalinity is always expressed in terms of the equivalent weight of calcium carbonate ($CaCO_3$), which has a molecular weight of 100. The three $Ca(HCO_3)_2$ molecules then have an equivalent molecular weight of 3 x 100 or 300 as $CaCO_3$.

The rules of thumb are based on the ratio of 600 (alum) to 300 (alkalinity):
- 1.0 mg/L of commercial alum will consume about 0.5 mg/L of alkalinity.
- There should be at least 5-10 mg/L of alkalinity remaining after the reaction occurs to keep the pH near optimum.
- Raw water alkalinity should be equal to half the expected alum dose plus 5 to 10 mg/L.

1.0 mg/L of alkalinity expressed as $CaCO_3$ is equivalent to:
- 0.66 mg/L 85% quicklime (CaO)
- 0.78 mg/L 95% hydrated lime ($Ca(OH)_3$)
- 0.80 mg/L caustic soda (NaOH)
- 1.08 mg/L soda ash (Na_2CO_3)
- 1.52 mg/L sodium bicarbonate ($NaHCO_3$)

When to Add Alkalinity

If natural alkalinity is insufficient then add artificial alkalinity to maintain the desired level. Hydrated lime, caustic soda, soda ash or sodium bicarbonate may be used to raise the alkalinity level.

Alkalinity should always be added up-stream, before alum addition, and the chemical should be completely dissolved by the time the alum reaction takes place. Alum reacts instantaneously and will proceed to other end products if sufficient alkalinity is not immediately available. This requirement is often ignored in an effort to minimize tanks and mixers, but poor performance is the price that is paid.

When alum reacts with natural alkalinity, the pH is decreased by two different means: the bicarbonate alkalinity of the system is lowered and the carbonic acid content is increased. This is often an advantage, since optimum pH conditions for alum coagulation are generally in the range of about 5.0 to 7.0, while the pH range of most natural waters is from about 6.0 to 7.8.

At times, some of the alum dose is actually being used solely to lower the pH to its optimum value. In other words, a lower alum dose would coagulate as effectively if the pH were lowered some other way. At larger plants it may be more economical to add sulfuric acid instead.

It is important to note that not all sources of artificial alkalinity have the same effect on pH. Some produce carbonic acid when they react and lower the pH. Others do not. Optimum pH conditions should be taken into account when selecting an alkalinity source.
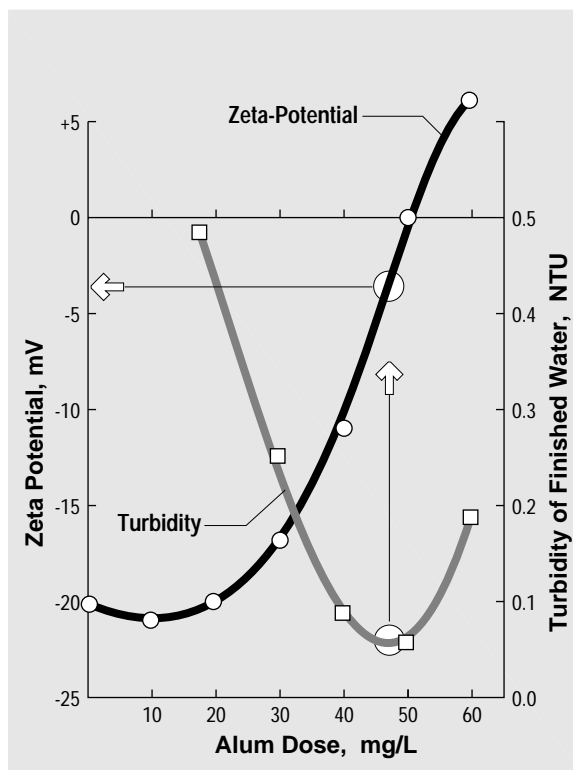
Zeta Potential Control of Alum Dose

There is no single zeta potential that will guarantee good coagulation for every treatment plant. It will usually be between 0 and -10 mV but the target value is best set by test, using pilot plant or actual operating experience.

Once the target ZP is established, then these correlations are no longer necessary, except for infrequent checks on a weekly, monthly, or seasonal basis. Control merely involves taking a sample from the rapid mix basin and measuring the zeta potential. If the measured value is more negative than the target ZP, then increase the coagulant dose. If it is more positive, then decrease it.

In this example a zeta potential of -3 mV corresponds to the lowest filtered water turbidity and would be used as the target ZP.

pH Effects

Charge

There is a strong relation between pH and performance, but there is no single optimum pH for a specific water. Rather, there is an interrelation between pH and the type of aluminum hydroxide formed. This in turn determines the charge on the hydrous oxide complex. Other ions come into play as well. The effect of pH on charge can be evaluated using a zeta potential curve and direct measurement of zeta potential is a better method of process control than pH.

Solubility of Aluminum

A second important aspect of pH is its effect on solubility of the aluminum (Al^{+3}) ion. Insufficient alkalinity allows the pH to drop to a point where the aluminum ion becomes highly soluble. Dissolved aluminum can then pass right through the filters. After filtration, pH is usually adjusted upward for corrosion control. The higher pH converts dissolved aluminum ion to insoluble aluminum hydroxide which then flocculates in the distribution system and almost guarantees "dirty water" complaints.
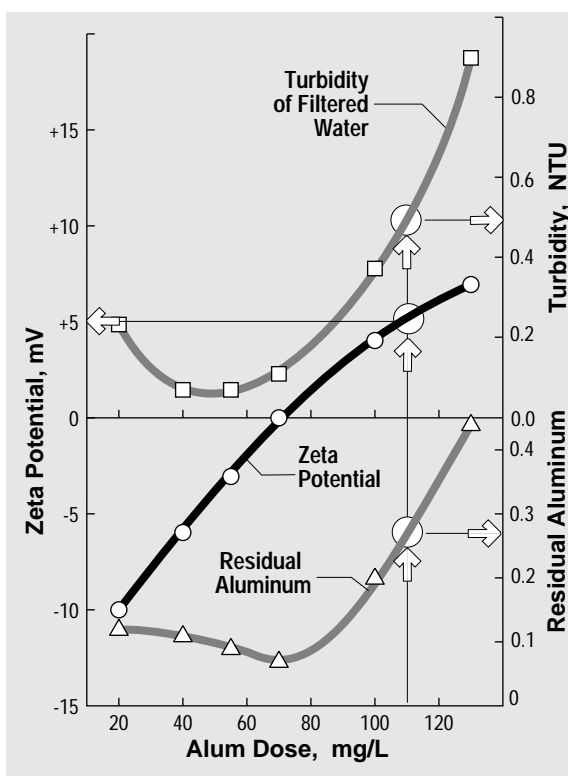

Effect of pH on Alum Floc

The charge on alum floc is strongly effected by pH. This example shows the effect of pH on zeta potential and residual color for a highly colored water. The alum dose was held constant at 60 mg/L.

Overdosing

Changes in zeta potential are good indicators of overdosing. This plant should operate at a zeta potential of about -5 mV. Overdosing produced a zeta potential of +5 mV and is accompanied by a marked increase in residual aluminum in the finished water. Monitoring of turbidity is not effective for control because the lag time between coagulant addition and filtration is several hours.

Coagulant Aids

**Tailoring Floc Characteristics**

Polyelectrolytes which enhance the floccu-
lating action of metal coagulants (such as
alum), are called *coagulant aids* or *floccu-
lant aids*.

They provide a means of tailoring floc size,
settling characteristics and shear strength.
Coagulant aids are excellent tools for
dealing with seasonal problem periods
when alum alone is ineffective. They can
also be used to increase plant capacity
without increasing physical plant size.

Activated silica was used for this purpose
before organic polymers became popular.
Activated silica produces large, dense, fast
settling alum flocs and simultaneously
toughens it to allow higher rates of filtration
or longer filter runs. A disadvantage is the
fairly precise control that is needed during
preparation of the activated silica. Silica is
prepared *(activated)* on-site by partially
neutralizing a sodium silicate solution, then
aging and diluting it.

Polyelectrolyte coagulant aids have the
advantages of activated silica and are
simpler to prepare.

Cationic polymers are charge neutralizing
coagulant aids. They can reduce the alum
or ferric dose while simultaneously increas-
ing floc size and toughening it. They also
reduce the effect of substances that inter-
fere with metal coagulants. Long chain,
high molecular weight cationics operate via
mechanical bridging in addition to charge
neutralization. Charge neutralizing can be
monitored using zeta potential, while the
bridging effect should be evaluated using
jar testing.
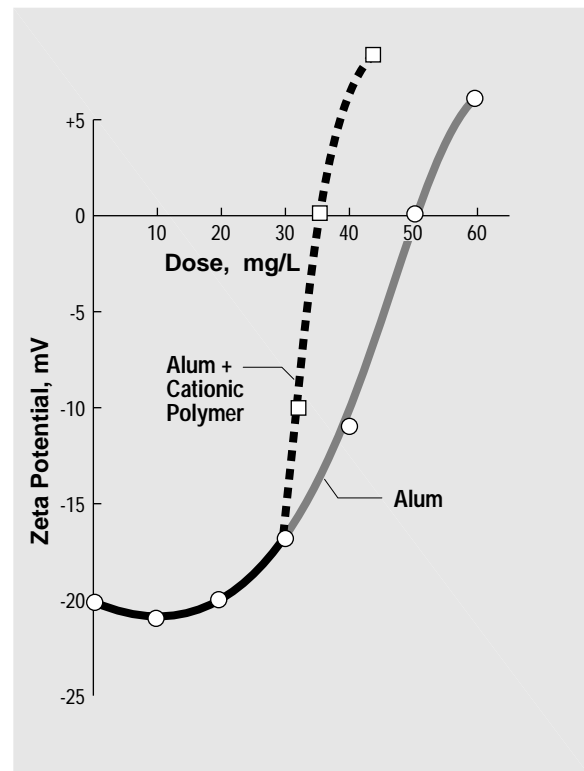
Cationic Coagulant Aid
Zeta potential curves can be used to evaluate the
charge neutralizing properties of cationic polymers.

Anionic and non-ionic polymers are
popular because a small amount can
increase floc size several times. Anionic
and non-ionic polyelectrolytes work best
because their very high molecular weight
promotes growth through mechanical
bridging. It is important to allow microflocs
to form before adding these polymers. In
addition, excess amounts can actually
inhibit flocculation. Jar testing is the best
way to establish the optimum dosage.
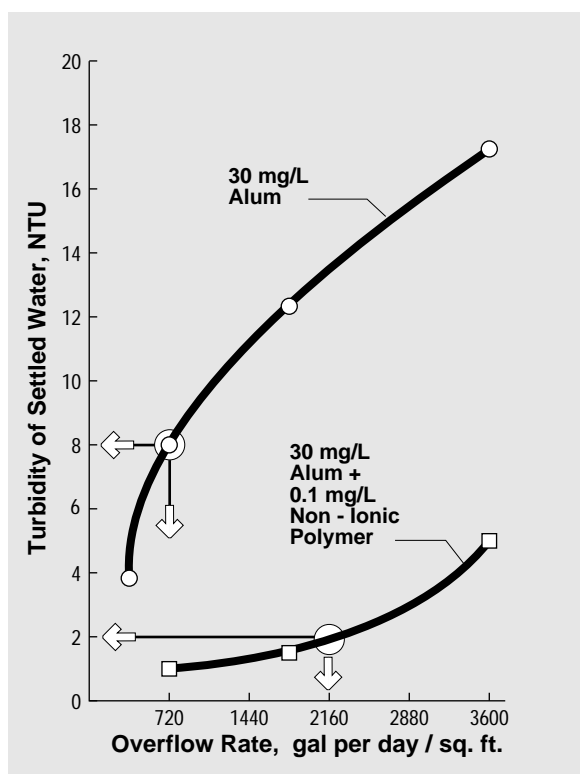
Non-Ionic Polymer Increases Settling Capacity
Jar tests were used to evaluate the effect of a very
small amount of non-ionic polymer on settling rates.
Sedimentation velocities were converted to equivalent
settling basin overflow rates to illustrate the dramatic
effect of the polymer. With no polymer the turbidity
was 8 NTU at an overflow rate of 720 gallons per day
per square foot. After the polymer was added, the
flow rate could be tripled with the settled water
turbidity actually improving at the same time.
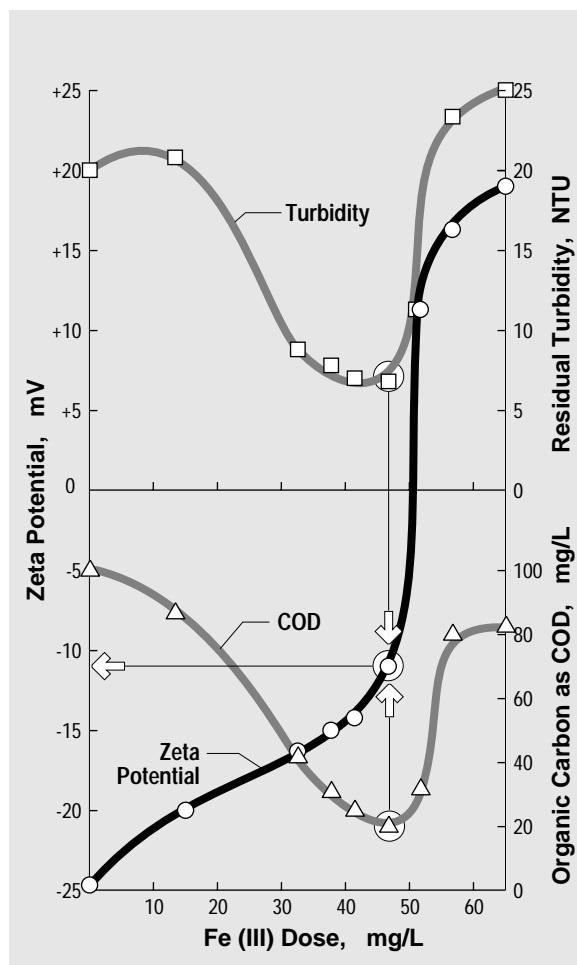
Wastewater Coagulation with Ferric Chloride
These curves are for coagulation of a municipal
trickling filter effluent. In this case, the optimum zeta
potential is -11mv. Overdosing by only 5 mg/L
causes a significant deterioration in performance, and
is accompanied by a large change in zeta potential.
Overdosing by 10 mg/L results in almost complete
deterioration.

Chapter 5
Tools for Dosage Control

Jar Test

An Undervalued Tool
We usually associate the jar test with a tedious dosage control tool that seems to take an agonizingly long time to set up, run and then clean up after. As a result the true versatility of the humble jar test is often overlooked.

The following applications for jar testing may be more important than its use in routine dosage control. It is studies such as these where the jar test has its major value, since the results are worth the time and effort to do the test properly:
- selection of primary coagulant
- comparison of coagulant aids
- optimizing feed point for pH adjusting chemicals
- mixing energy and mixing time studies (rapid mix and flocculation)
- optimizing feed point for coagulant aids
- evaluating dilution requirements for coagulants
- estimating settling velocities for sedimentation basin sizing
- studying effect of rapid changes in mixing energy
- evaluating effect of sludge recycling
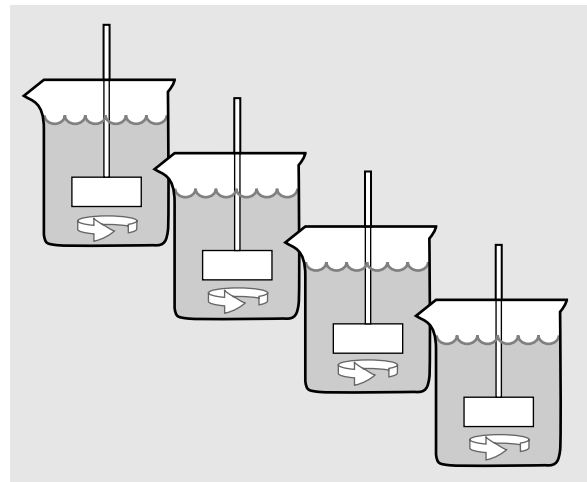
Jar Testing
A tedious but valuable tool which allows side by side comparison of many operating variables.

Jar Test Apparatus

Many commercial laboratory jar test units are in use today. The Phipps & Bird six place gang stirrer is very traditional. It has 1" x 3" flat blade paddles and is usually used with 1.5 liter glass beakers. A disadvantage is the large vortex that forms at high stirring speeds.

Some provision is usually made for drawing off a settled sample from below the water surface. Siphon type draw-offs are frequently used for glass beakers.

Camp improved the Phipps & Bird design by using 2-liter glass beakers outfitted with vortex breaking stators. These were especially suitable for mixing studies because Camp developed curves for mixing intensity (G) versus stirrer speed using this design.

Gator or Wagner jars are a relatively recent improvement and are square plexiglas jars with a liquid volume of 2 liters. These are now commercially available, and have several advantages over traditional glass beakers. First, they are less fragile and allow for easy insertion of a sample tap, thus avoiding the need for a siphon type draw-off. Their square shape helps dampen rotational velocity without the need for stators while their plexiglas walls offer much greater thermal insulation than glass, thus minimizing temperature change during testing.
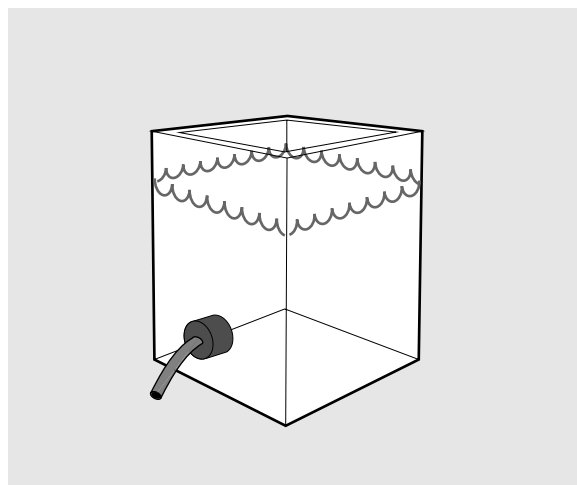
The Gator Jar

The original design was constructed of 1/4 inch thick plexiglas. It measures 11.5 cm square (inside) by an overall depth of 21 cm. The sample tap is located 10 cm below the water surface. Liquid volume is 2000mL. The tap consists of a piece of soft tubing and a squeeze clamp, or a small plastic spigot.

Settling Studies

The data from a well thought out jar test can be used to realistically size settling basins and to evaluate the ability of coagulant aids to increase the hydraulic capacity of existing basins. Surface overflow rate *(gallons per day per square foot)* is more important than retention time in determining the hydraulic capacity of a settling basin, and is calculated from the velocity of the slowest settling floc that we want to remove. In practical terms, a settling rate of 1 cm/minute is equal to an overflow rate of 360 gallons per day per square foot.

Jar test settling data is obtained by drawing off samples at a fixed distance below the water surface, at various time intervals after the end of rapid mixing and flocculation. Settling velocity and overflow rate are calculated for each time interval and the sample reflects the quality that we can expect at that overfow rate.

The Gator jar has a convenient sample draw-off located 10 cm below the water surface. Samples are usually withdrawn at intervals of 1, 2, 5, and 10 minutes after the mixers are stopped. These correspond to settling velocities of 10, 5, 2 and 1 cm/minute which are equivalent to settling basin overflow rates of 3600, 1800, 720 and 360 gallons per day per square foot.

The results of the overflow rate studies can be plotted on regular (arithmetic) graph paper, or on semi-logarithmic paper (with turbidity on the log scale) or on logarithmic graph paper. Actual plant operating results can also be plotted on the same graphs for comparison.

See page 24, *Non-Ionic Polymer Increases Settling Capacity,* for an example of a settling study.

Predicting Filtered Water Quality

For water treatment, it is important to remember that our ultimate goal is to produce the best filtered water. We often assume that the best settled water will always correspond to the best filtered water, but that is not necessarily so. In fact, substantial savings may be realized by optimizing filtered water quality instead.

Bench scale testing can be used in conjunction with jar tests to predict filtered water quality. Whatman #40 filter paper (or equivalent) provides a good simulation. Use fresh filter paper for each jar and discard the first portion filtered.
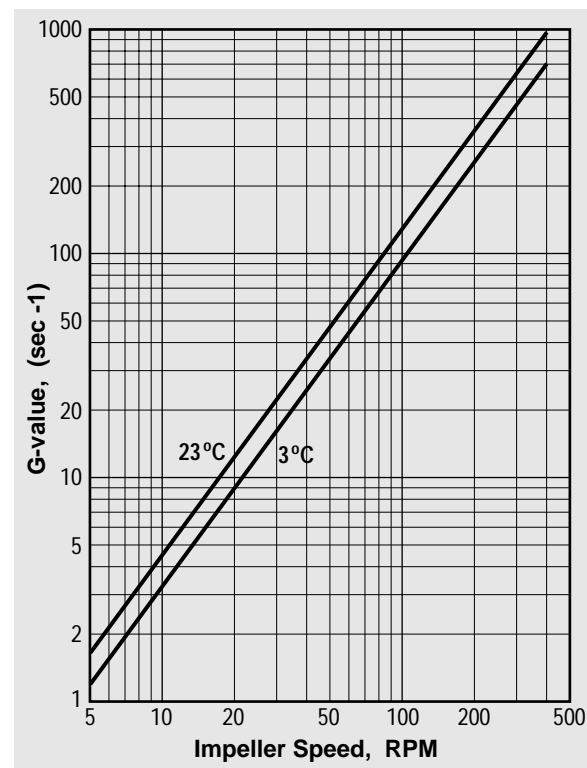
G Curves for the Gator Jar
These are for the Gator Jar, with a 1x3 inch Phipps and Bird stirrer paddle. See *Chapter 6, Tips on Mixing* for a discussion of the G value and its importance as a rational measure of mixing intensly.

Jar Test Checklist

Routine jar test procedures should be tailored to closely match actual conditions at the plant. This may take some experimentation since full scale mixing conditions are only approximated in the jar test and treatment is on a batch instead of a flow-through basis.

Conditions to match up include:
• sequence of chemical addition
• rapid mixing intensity and time
• flocculation intensity and time

Visually evaluated variables include:
• time for first floc formation
• floc size
• floc quality
• settling rate

Immediately after rapid mixing the following can be determined:
• zeta potential
• pH

Later, after slow mixing and settling, samples can be carefully drawn off and analyzed for:
• turbidity
• color
• filterability number
• particle count
• residual coagulant
• filtered water turbidity
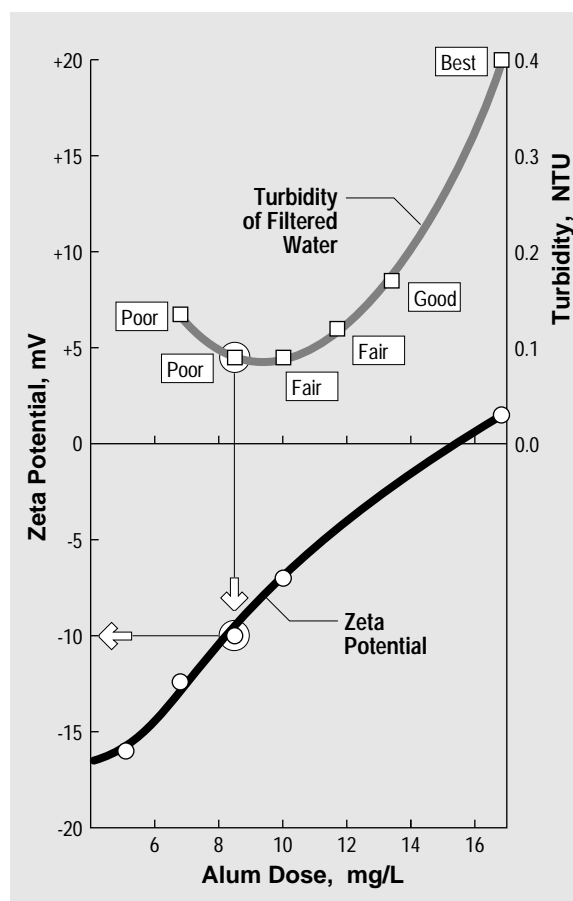
Limitations of Visual Evaluation

Routine jar testing is time consuming, and plant operators often fall back on visual evaluation as a basis of comparison. Unfortunately, visual judgments can be surprisingly misleading. In the example above, the visual evaluation *(Poor, Fair, etc.)* was of absolutely no help in selecting an economical alum dose.

28

Zeta Potential

Easily Understood

Zeta potential is an excellent tool for coagulant dosage control, and we are proud to have pioneered the use of our instrument in water treatment over 25 years ago. Operation of a Zeta-Meter is relatively simple and only a short time is required for each test. The results are objective and repeatable and, most importantly, the techniques can be easily learned.

The principle of operation is easy to understand. A high quality stereoscopic microscope is used to comfortably observe turbidity particles inside a chamber called an electrophoresis cell. Electrodes placed in each end of the cell create an electric field across it. If the turbidity particles have a charge, then they move in the field with a speed and direction which is easily related to their zeta potential.

Our Zeta-Meter 3.0 - Simple & Reliable

The Zeta-Meter 3.0 is a microprocessor-based version of our popular instrument. The sample is poured into the cell, then the electrodes are inserted and connected to the Zeta-Meter 3.0 unit. First, the instrument determines specific conductance and helps select the appropriate voltage to apply. Then, when the electrodes are energized the particles begin to move and are tracked using a grid in the microscope eyepiece.

Tracking simply involves pressing a button and holding it down while a colloid traverses the grid. When the track button is released the instrument instantly calculates and displays the zeta potential. A single tracking takes a few seconds, and a complete run takes only minutes.
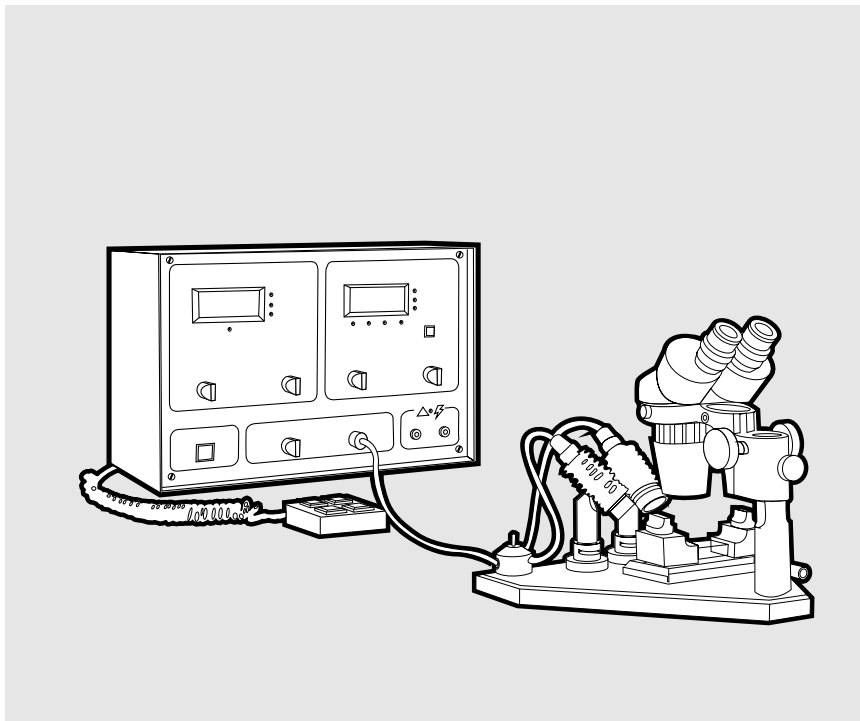
Zeta-Meter System 3.0
A standard parallel printer can be directly connected for a "hard copy" of your test run.

A Practical Design

The Zeta-Meter 3.0 is designed to be mistake-proof. It recognizes impractical results and tracking times that are too short. A "clear" button allows these or other inconsistent results to be deleted without losing the rest of your data.

Statistics are also maintained by the Zeta-Meter 3.0, and can be reviewed at any time. Pressing a "status" button causes the unit to display the total number of colloids tracked, their average zeta potential and standard deviation, a statistical measure of the spread of the individual data values.

A printer can be connected to the Zeta-Meter 3.0 unit to record the entire run. The output shows the value obtained for each colloid as well as a statistical summary of the entire test.

Simplified Coagulant Dose Control

The zeta potential that corresponds to optimum coagulation will vary from plant to plant. The optimal value is often called the target zeta potential and is best established first by correlation with jar tests or pilot units, and then with actual plant performance.

Once a target value is set, routine control is relatively simple and merely involves measuring the zeta potential of a sample from the flash mix. If the measured value is more negative than the target value, just increase the primary coagulant dose. If it is more positive, then lower the dose.

Other Applications of Zeta Potential

You can also use zeta potential analysis for the following useful applications:

- screening of primary coagulants
- cost comparison of cationic polyelectrolytes
- optimum pH determinations
- checking quality of delivered cationic polyelectrolyte
- optimizing feed point for pH adjusting chemicals
- evaluating dilution/mixing requirements for cationic polyelectrolytes

Streaming Current

On-Line Zeta-Potential . . . . Almost

A limitation on the zeta potential technique is that it is not a continuous on-line measuring instrument. The streaming current detector was developed in response to this need. Its main advantage is rapid detection of plant upsets.

Streaming current is really nothing more than another way to measure zeta potential, but it is actually related to the zeta potential of a solid surface, such as the walls of a cylindrical tube, and not the zeta potential of the turbidity or floc particles.

Forcing a flow of water through a tube induces an electric current (called the *streaming current*) and voltage difference (called the *streaming potential*) between the ends of the tube. Some of the particles in the liquid will loosely adhere to the walls of the cylinder and will affect the zeta potential of the wall. As a result the streaming current or streaming potential of the wall will reflect to some degree the zeta potential of the particles in suspension.

Commercial Instruments

Most commercial streaming current devices use an oscillating flow to eliminate background electrical signals. A piston in a cylinder (called a *boot*) is very common. The piston oscillates up and down at a relatively low frequency (about 4 cycles per second) causing the sample to flow in an alternating fashion through the space between the piston and cylinder. The flow of water creates an AC streaming current, due to the zeta potential of the cylinder and piston surface. It is this current which is measured and amplified by the detector.

A Useful Monitor

Streaming current is useful as an on-line monitor of zeta potential. However, it is only an indication because the value is not scaled. That is, a change in 10 streaming current units does not correspond directly to a zeta potential change of 10 mV. In addition, the zero position is often shifted significantly from true zero and is not stable.

Streaming current and streaming potential are both excellent ways to keep track of on-line conditions, but should be calibrated with a zeta meter. A change in the streaming current tells you that it is time to take a sample and measure the zeta potential.
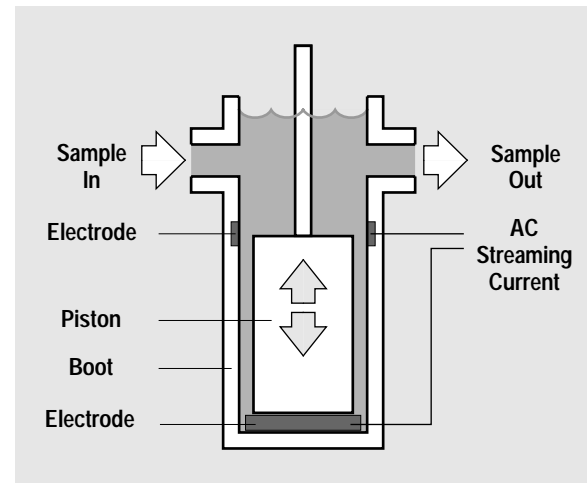
Oscillating Piston Streaming Current Detector
The AC signal is electrically amplified and conditioned to produce a signal that is proportional to the zeta potential.
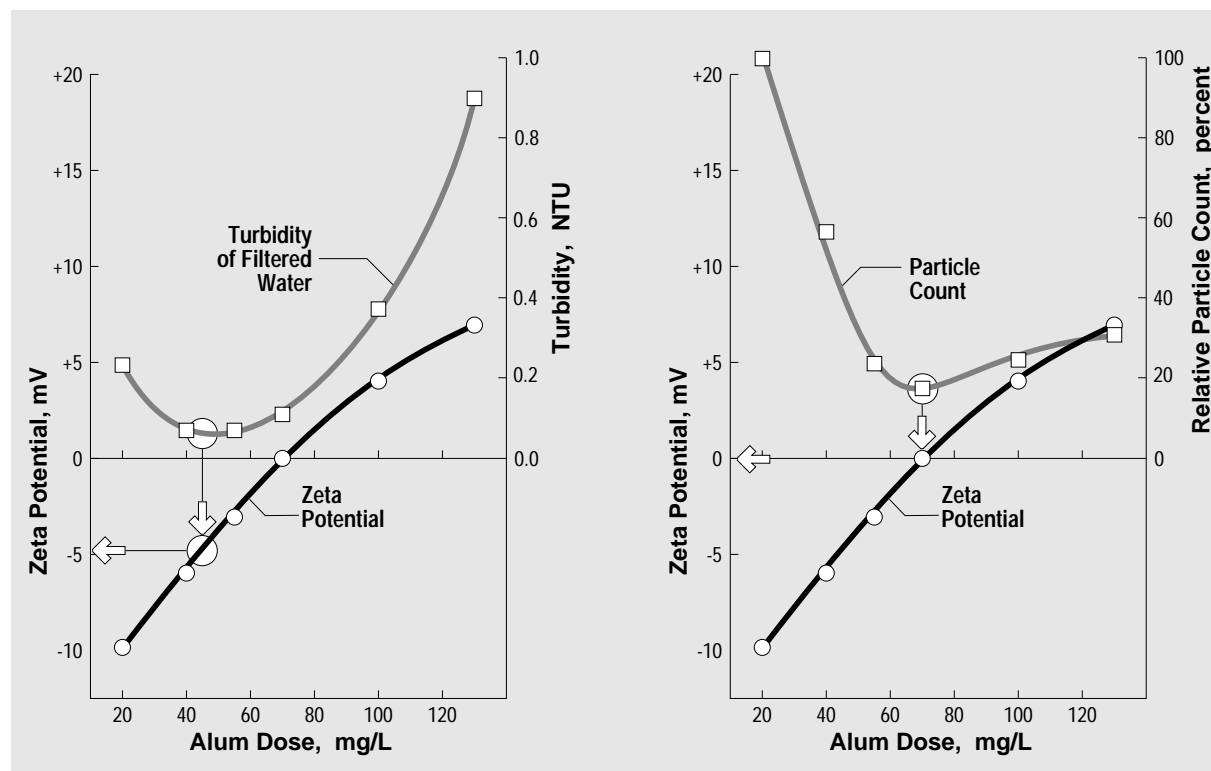
Turbidity and Particle Count

Finished water turbidity is often used to gauge the effectiveness of a water treatment plant, but it is important to remember that there is no direct relation between the amount of suspended matter, or number of particles, and the turbidity of a sample.

Most turbidity measurements are based upon nephelometry. A light beam is passed through the water sample and the particles in the water scatter the light. The turbidimeter measures the intensity of scattered light, usually at an angle of 90° to the light beam and the intensity is expressed in standard turbidity units.

The angle of peak scatter and the amount of light scattered are both influenced by the size of the particles. Other factors, such as the nature and concentration of the particles will also effect the turbidity measurement.

Particle size analyzers quantify the actual particle count and the distribution with size. Particle counters are much more expensive than turbidimeters and are not commonly found in water treatment plants.

Particle Count vs. Turbidity

Simultaneous plots of zeta potential and turbidity are often used to determine the target zeta potential and alum dose. The curve can shift if particle counts are used to judge performance instead. In this example, the target zeta potential was -5 millivolts using turbidity as a criteria. This results in an alum dose of 45 mg/L. When particle count was used, the target zeta potential is 0 millivolts, and the corresponding alum dose is 70 mg/L. Surprisingly, the particle count is almost triple at the lower dose determined by the turbidity standard.

Chapter 6
Tips on Mixing

Basics

Mixing patterns are often complex and are difficult to describe, so we usually classify mixers based upon how closely they approximate one of two idealized flow patterns: complete mixing or plug flow.

Ideal plug flow means that each volume of water remains in the reactor for exactly the same amount of time. If a slug of dye were injected into the flow as a tracer, then all the dye would appear at the outlet at the same time. Ideal plug flow is very difficult to achieve. In general, the reaction basin must be very long in comparison to its width or diameter before the mixing pattern begins to approximate plug flow.

Complete mixing basins are always instantaneously blended throughout their entire volume. As a result, an incoming volume of water immediately loses its identity and is intermixed with the water that entered previously. A complete-mix reactor is also called a back-mix reactor because its contents are always blended backwards with the incoming flow. If a slug of dye tracer was injected into the basin, then some of it would immediately appear in the outgoing flow. The concentration of dye would drop steadily as the dye in the basin backmixed with the clear incoming water and was diluted by it.
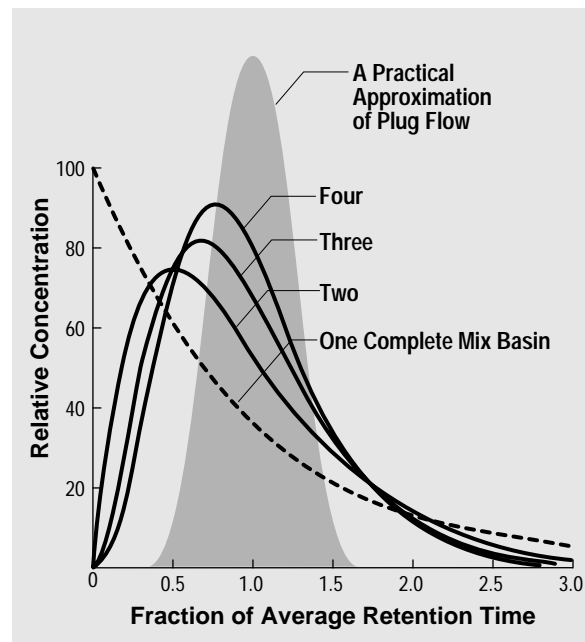
Retention Time Curves
When several complete mix reactors are placed in a series then the chance of the same particle quickly exiting each basin is very small. The overall retention time pattern then changes and becomes more regularly distributed around the average.

Rapid Mixing

Plug Flow versus Complete Mix

Recommendations for the best type of rapid mixing are confusing at best. The extremely fast times for the reaction of alum with alkalinity (less than 1 second) and for the rapid formation of the aluminum hydroxide microfloc (less than 10 seconds) have produced advocates of in-line instantaneous blenders (plug flow) as well as tubular plug flow reactors, all with reaction times of a few seconds. A plug flow reactor insures that an equal amount of coagulant is available to each particle for an equal amount of time. This is important if the reaction time is truly only a few seconds long.

Others have found that the traditional complete-mix-type basin with turbine- or propeller-type impellers is entirely adequate and have even recommended extending the reaction time to several minutes (instead of the standard 30-60 seconds suggested in some state standards) in order to enhance the initial stages of flocculation.

This apparent conflict can be explained by considering the two possible types of coagulation: charge neutralization and sweep floc. For sweep coagulation, extremely short mix times are not required since most of the colloids are captured by becoming enmeshed in the growing precipitate. For alum, dosages above about 30 mg/L will produce sweep coagulation. Lower dosages result in a combination of sweep and charge neutralization or just charge neutralization, depending on the pH and the alum dose. Clearly, the choice of mixing regimes is not easy.

Mixing Intensity

The type and intensity of agitation is also important. Turbulent mixing, characterized by high velocity gradients, is desirable in order to provide sufficient energy for interparticle collisions. Propeller mixers are not as well suited as turbine mixers. Propellers put more energy into circulating the basin contents, while turbine mixers shear the water, inducing the higher velocity gradients and the small high multidirectional velocity currents that promote particle collisions.

High intensity throughout the rapid mix basin may not be as important as the scale and intensity of turbulence at the point of coagulant addition. In a turbine-type complete-mix basin, the mixing intensity will not be uniform throughout the basin. The impeller discharge zone occupies about 10 per cent of the total volume and has a shear intensity approximately 2.5 times the average.

There is an upper limit to mixing intensity because high shear conditions can break up microflocs and delay or prevent visible floc formation. Coagulants which act through charge neutralization can sometimes recover from this during flocculation (examples include alum and low molecular weight cationic polyelectrolytes). Bridging-type flocculants are not as resilient and may not recover. This may be because the long polymer chains are cut, breaking their particle-to-particle bridges. The charge on the polymer fragments may even interfere with attempts to re-coagulate the system, although a polymer of opposite charge may help.

G-Value

The G-value concept is a rough approximation of mixing intensity. It is based upon input power, basin volume and viscosity. For water, at 10°C, the G value can be expressed in terms of horsepower per 1000 gallons of basin volume:

$$G = 387 \text{ x (HP per 1000 gal)}^{1/2}$$
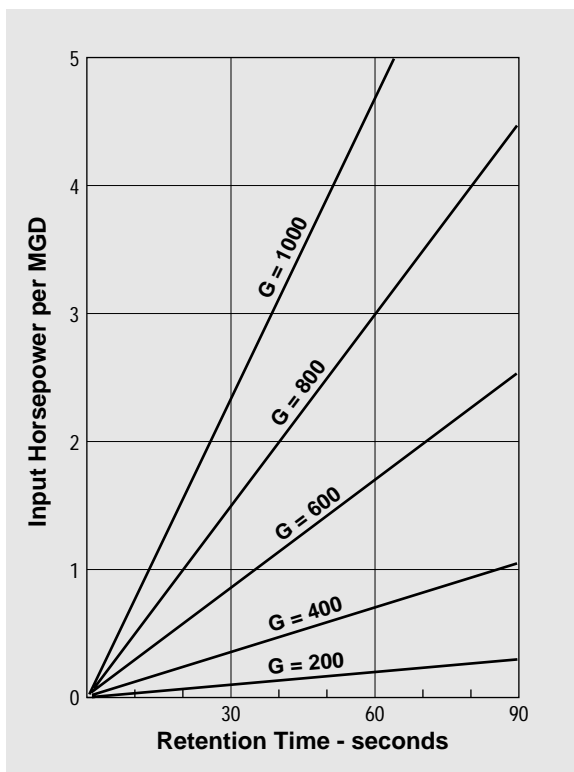
Practical G-Value Relationships
The relation between retention time and input horsepower per million gallons per day (MGD) of flow is linear for any selected G-value. This figure can be used to estimate the G-value or the power requirement to produce a specific G-value. It is calculated at 10° C. The input horsepower will be a percentage of the mixer motor power, in the range of 70 - 85%.

Rules of Thumb for Rapid Mixing

The purpose of rapid mixing is two-fold. First, it should efficiently disperse the coagulating chemicals. Second, and just as important, it should provide conditions that favor the formation of microfloc particles. The characteristics of this microfloc will determine the success of the flocculation step.

It is difficult to offer hard and fast rules for rapid mixers. In fact, many rapid mix alternatives provide satisfactory results.

Back-mix reactors generally work best if they follow these guidelines:
- Stators and square tanks funnel more energy into mixing than into circulation.
- Flat blade turbines provide more shear intensity than propeller types.
- Chemicals should be introduced at the agitator blade level.
- For sweep coagulation using alum or ferric compounds, G-values of between 300 and 1200 sec^{-1} in combination with retention times of 20 seconds to several minutes have produced satisfactory results.
- When cationic polyelectrolytes are used as a primary coagulant, then a G-value range of 400-700 is more appropriate. Overly long retention times (longer than 1-2 minutes), rapid changes in G value, and G values above 1000 can all be detrimental.
- Consider tapered velocity gradients to provide a transition from rapid mixing to flocculation. This may be important if the primary coagulant is a polymer.

Plug flow reactors may be more appropriate if charge neutralization predominates over sweep floc. G-values of 3000-5000 with retention times of about 1/2 second are usually recommended.

Flocculation

Rate of Flocculation

In general the rate of flocculation is controlled by two factors:

- concentration of particles (both free colloids and floc)
- velocity gradient

A greater number of particles provides more opportunity for collisions to occur between colloids or between floc particles and colloids. This increases the rate of capture. Higher velocity gradients also provide more opportunities for collisions, but the shear forces from too high a velocity gradient can break up larger flocs and will limit the maximum floc size.

Creating Collisions

The velocity gradients in a full scale flocculation basin can be created by a variety of mechanisms, including baffled chambers, rotating paddles, reciprocating blades and turbine-type mixers. Baffled chambers are limited because the velocity gradient is controlled only by the flow rate, while mechanical systems offer the ability to independently control shear intensity.

The efficiency of a mechanical system should be judged by its ability to produce a uniform distribution of eddy currents throughout the basin. Some of the energy in a mechanical flocculator will unavoidably go into rotating the water rather than creating velocity gradients. This is particularly true in horizontally rotating units with large paddles. Stators can be used to dampen this tendency. A wire-mesh-type paddle provides more shear with less rotation of the basin contents than a solid paddle. Turbine-type mixers suffer from a large variation in velocity gradients which are high near the mixer and low near the basin walls.

Tapered Flocculation

You can reduce the time required for complete flocculation by using a number of flocculation basins in series. If possible each basin should approximate plug flow conditions. The advantage of several basins is two-fold. First, the overall flow pattern begins to approximate plug flow, even if each basin is well mixed. In other words, it is unlikely that a specific particle will spend a short time period in each basin. With plug flow, the average retention time and overall basin volume can be reduced by more than half as compared to a single well-mixed basin.

Second, the velocity gradient can be varied from basin to basin. This is sometimes called "tapered flocculation". The purpose of the first one or two basins is to capture stray colloids. High shear intensities favor this, since the high velocities maximize the number of collisions. High shear conditions will also limit floc size, thereby creating more particles and again increasing the probability of collision. To achieve this, the flocculator speed in the first one or two basins should be adjusted to limit floc size, with the first basin at a higher speed than the second.

The third and fourth basins are the floc growing stages. They should produce a large fast setting floc. Velocity gradients are progressively lowered to avoid floc breakup. A long chain anionic polyelectrolyte can be added here if necessary to mechanically bridge and toughen the growing flocs.

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Zeta-Meter
1621 Industry Court Ste 101
Harrisonburg, VA 22802

Telephone 540-908-3410
Toll Free (USA) 800-474-0105

E-mail .... info@zeta-meter.com

http://www.zeta-meter.com