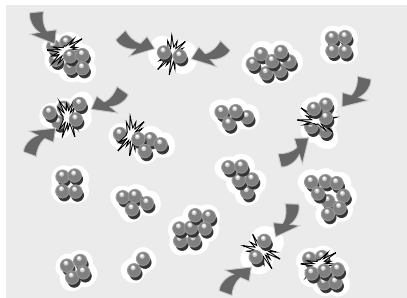

Zeta Potential: A Complete Course in 5 Minutes

The Interaction of Colloids

Electrokinetics and Colloid Behavior

Zeta potential can help you understand and control colloidal suspensions. Examples include complex biological systems such as blood and functional ones like paint. Colloidal suspensions can be as thick as paste (like cement) or as dilute as the turbidity particles in a lake. Water, milk, wine, clay, dyes, inks, paper and pharmaceuticals are good examples of useful colloidal systems. Water is a common suspending liquid, although non-aqueous liquids are used as well. In many cases, the performance of a suspension can be improved by understanding the effect of colloidal behavior on such properties as viscosity, settling and effective particle size.

We can often tailor the characteristics of a suspension by understanding how individual colloids interact with one another. At times we may want to maximize the



Uncharged Particles are free to collide and aggregate.

repulsive forces between them in order to keep each particle discrete and prevent them from gathering into larger, faster settling agglomerates. Examples include pharmaceuticals and pastes. Sometimes we have the opposite goal and want to separate the colloid from the liquid. Removing the repulsive forces allows them to form large flocs that settle fast and filter easily. Viscosity is another property that can be modified by varying the balance between repulsion and attraction.

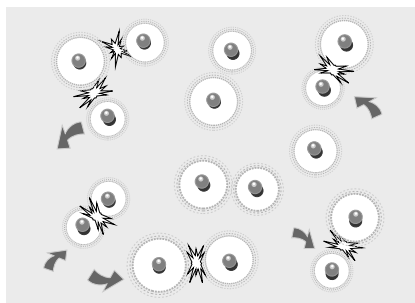
In some cases, an in-between state of weak aggregation can be the best solution. Paints are a good example. Here, the weak aggregation causes viscosity to be a function of shear rate. Stirring will produce enough shear to reduce the viscosity and promote blending.

Reversible aggregation is also useful in controlling the settling

behavior of concentrated suspensions. On standing, a weak matrix of flocculant particles is formed. This prevents the closely packed sediment that would form and cause “caking” problems if the particles were highly stabilized and remained completely discrete.

Surface forces at the interface of the particle and the liquid are very important because of the microscopic size of the colloids. One of the major surface effects is electrokinetic. Each colloid carries a “like” electrical charge which produces a force of mutual electrostatic repulsion between adjacent particles. If the charge is high enough, the colloids will remain discrete, disperse and in suspension. Reducing or eliminating the charge has the opposite effect — the colloids will steadily agglomerate and settle out of suspension or form an interconnected matrix. This agglomeration causes the characteristics of the suspension to change.

Particle charge can be controlled by modifying the suspending liquid. Modifications include changing the liquid’s pH or changing the ionic species in solution. Another, more direct technique is to use surface active agents which directly adsorb to the surface of the colloid and change its characteristics.



Charged Particles repel each other.

The diffuse layer can be visualized as a charged atmosphere surrounding the colloid.

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 its neutralizing ions were suddenly stripped away.

We first look at the effect of the colloid on the positive ions (often called *counter-ions*) in solution. 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*.

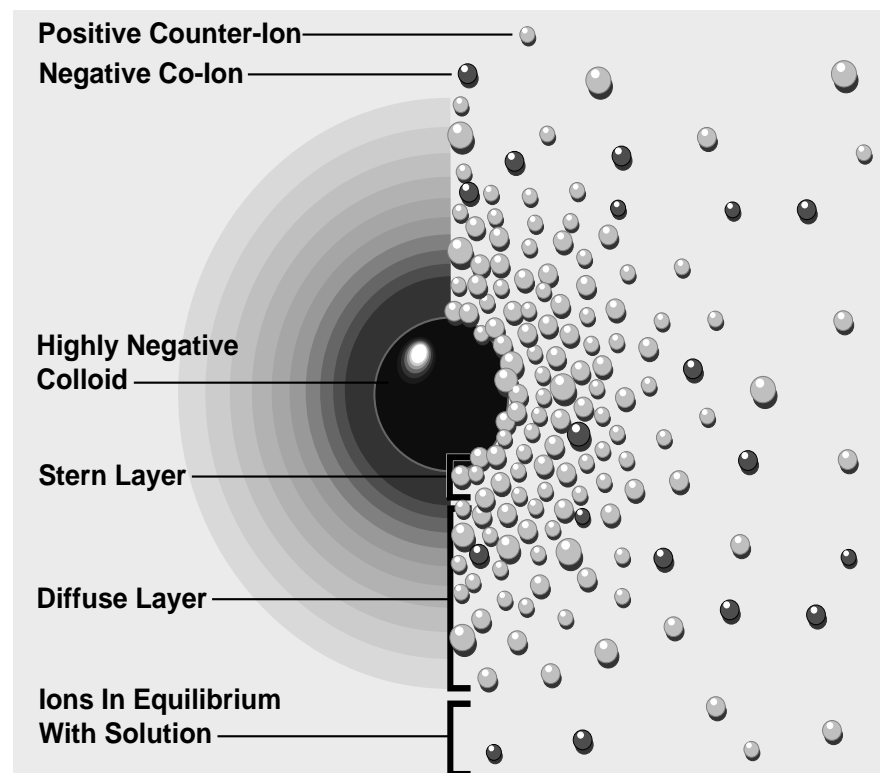
Additional positive ions are still attracted by the negative colloid, but now they are repelled by the Stern layer as well as by other positive ions that are also trying to approach the colloid. This dynamic equilibrium results in the formation of a *diffuse layer* of counter-ions. They have a high concentration near the surface which gradually decreases with distance, until it reaches equilibrium with the counter-ion concentration in the 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 with distance, as the repulsive forces of the colloid are screened out by the positive ions, until equilibrium is again reached.

The diffuse layer can be visualized as a charged atmosphere surrounding the colloid. The charge density at any distance from the surface is equal to the difference in concentration of positive and negative ions at that point. Charge density is greatest near the colloid and gradually diminishes toward zero as the concentration of positive and negative ions merge together.

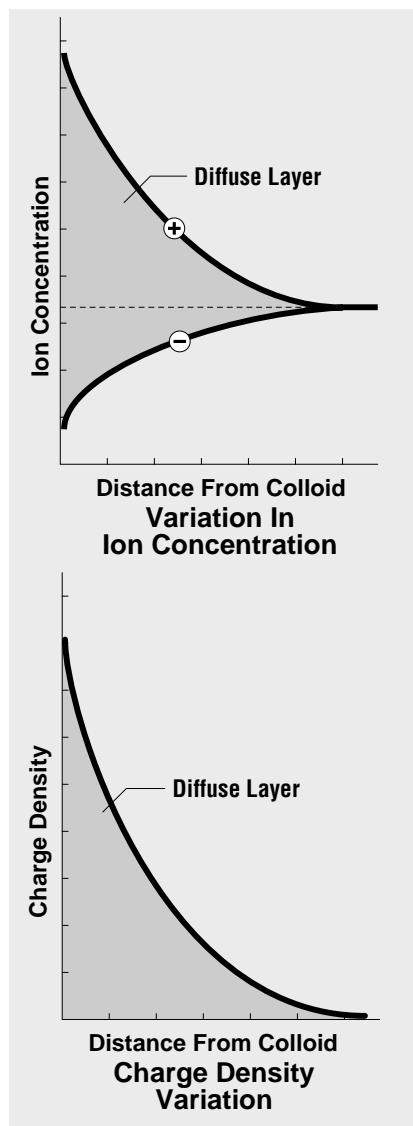
The attached counter-ions in the Stern layer and the charged atmosphere in the diffuse layer are what we refer to as the *double layer*. The thickness of this layer depends upon the type and concentration of ions in solution.



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.

The electrokinetic potential between the surface of the colloid and any point in the mass of the suspending liquid is referred to as the surface potential.



Variation of Ion Density in the Diffuse Layer

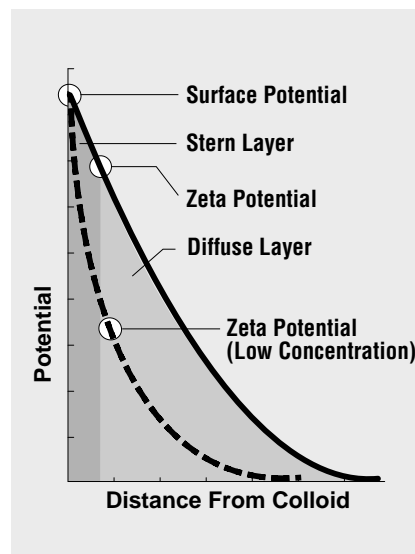
The figures above are two representations of the change in charge density through the diffuse layer. One shows the variation in positive and negative ion concentration with distance from a negative colloid. The second shows the net effect — the difference in positive and negative charge density.

Zeta Potential

The double layer is formed in order to neutralize the charged colloid and, in turn, causes an electrokinetic potential between the surface of the colloid and any point in the mass of the suspending liquid. This voltage difference is on the order of millivolts and is referred to as the surface potential.

The magnitude of the surface potential is related to the surface charge and the thickness of the double layer. As we leave the surface, the potential drops off roughly linearly in the Stern layer and then exponentially through the diffuse layer, approaching zero at the imaginary boundary of the double layer. The potential curve is useful because it indicates the strength of the electrical force between particles and the distance at which this force comes into play.

A charged particle will move with a fixed velocity in a voltage field. This phenomenon is called electrophoresis. The particle's mobility is related to the dielectric constant and viscosity of the suspending liquid and to the electrical potential at the boundary between the moving particle and the liquid. This boundary is called the slip plane and is usually defined as the point where the Stern layer and the diffuse layer meet. The Stern layer is



Zeta Potential vs. Surface Potential

The relationship between zeta potential and surface potential depends on the level of ions in the solution.

considered to be rigidly attached to the colloid, while the diffuse layer is not. As a result, the electrical potential at this junction is related to the mobility of the particle and is called the *zeta potential*.

Although zeta potential is an intermediate value, it is sometimes considered to be more significant than surface potential as far as electrostatic repulsion is concerned.

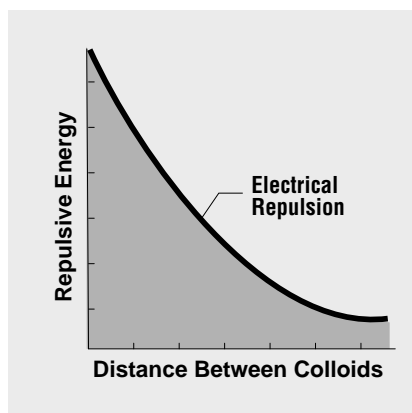
Zeta potential can be quantified by tracking the colloidal particles through a microscope as they migrate in a voltage field.

The DLVO theory explains the tendency of colloids to agglomerate or remain discrete.

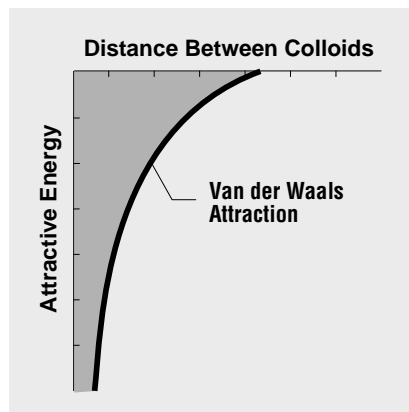
The Balance of Repulsion & Attraction

The DLVO Theory (named after Derjaguin, Landau, Verwey and Overbeek) is the classical explanation of the stability of colloids in suspension. It looks at the balance between two opposing forces — electrostatic repulsion and van der Waals attraction — to explain why some colloidal systems agglomerate while others do not.

Electrostatic repulsion becomes significant when two colloids approach each other and their double layers begin to interfere. Energy is required to overcome this repulsion. An electrostatic repulsion curve is used to indicate the energy that must be overcome if the particles are to be forced together. It has a maximum value when they are almost touching and decreases to zero outside the double layer. The maximum energy is related to the surface potential and the zeta potential.



Electrostatic Repulsion is always shown as a positive curve.



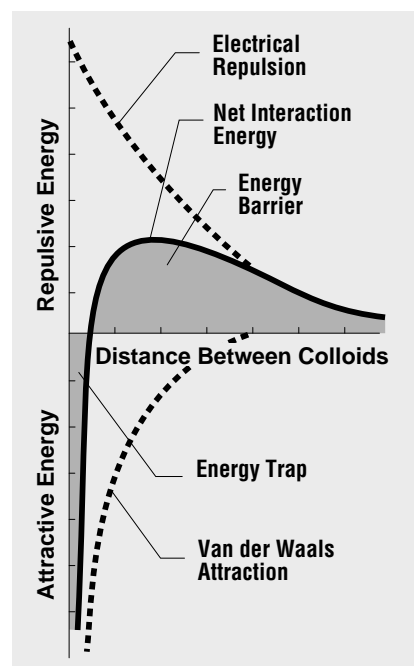
Van der Waals Attraction is shown as a negative curve.

Van der Waals attraction 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 van der Waals force with distance between the particles.

The DLVO theory explains the tendency of colloids to agglomerate or remain discrete by combining the van der Waals attraction curve with the electrostatic repulsion curve to form the net interaction energy curve. At each distance, the smaller value is subtracted from the larger to get the net energy. The net value is then plotted — above if repulsive and below if attractive — and a curve is formed. If there is a repulsive section, then the point of maximum repulsive energy is called the energy barrier.

The height of the barrier indicates how stable the system is. In order to agglomerate, two particles on a collision course must have sufficient kinetic energy due to their velocity and mass, to “jump over” this barrier. If the barrier is cleared, then the net interaction is all attractive, and as a result the particles agglomerate. This inner region is after referred to as an energy trap since the colloids can be considered to be trapped together by van der Waals forces.

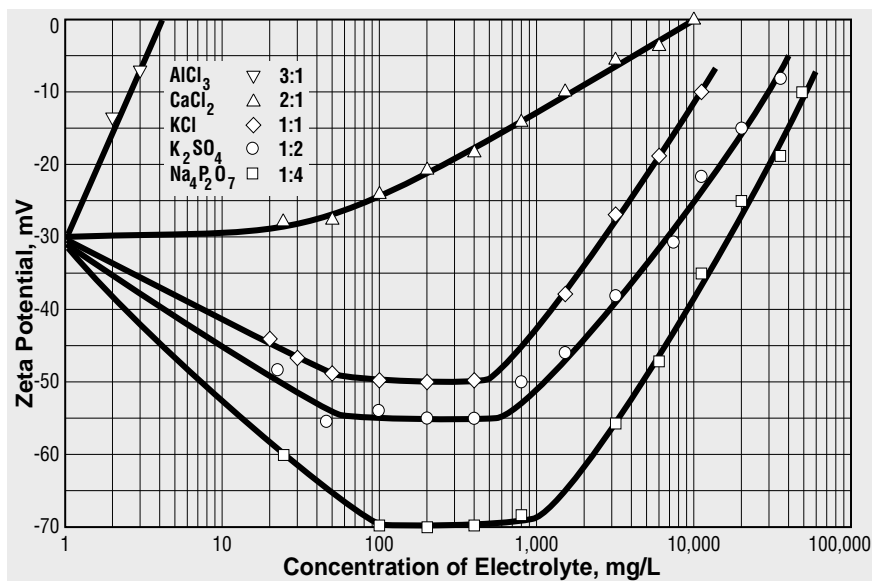
In many cases we can alter the environment to either increase or decrease the energy barrier, depending upon our goals. Various methods can be used to achieve this, such as changing the ionic



Interaction

The net interaction curve is formed by subtracting the attraction curve from the repulsion curve.

In many cases we can alter the environment to either increase or decrease the energy barrier, depending upon our goals.



Effect of Type and Concentration of Electrolytes

Simple inorganic electrolytes can have a significant impact on zeta potential. The effect depends on the relative valence of the ions and on their concentration. Relative valence can also be thought of as the type of electrolyte, with type being the ratio between the valences of the cation and the anion.

In this example, the zeta potential of a dilute suspension of colloidal silica was modified by adding different electrolytes. Aluminum chloride is a 3:1 electrolyte and its trivalent cations easily push the zeta potential toward zero. Contrast this with the effect of potassium sulfate, a 1:2 electrolyte. First the zeta potential becomes increasingly negative until a plateau is reached at about 50 mg/L. At about 500 mg/L, the zeta potential begins to decrease because the ions are compressing the double layer.

environment, or pH, or adding surface active materials to directly affect the charge of the colloid. In each case, zeta potential measurements can indicate the impact of the alteration on overall stability.

Nothing is ever as simple as it first seems. There are other effects that must be considered whenever you work with particle stability. Steric stabilization is the most significant one. Usually this involves the adsorption of polymers on particle surfaces. You can visualize the adsorbed layer as a barrier around each particle, preventing them from coming close enough for van der Waals attraction to cause flocculation. Unlike electrostatic stabilization, there are no long range repulsive forces and the particles are subject to attractive forces until the outer portions of the steric molecules contact each other.

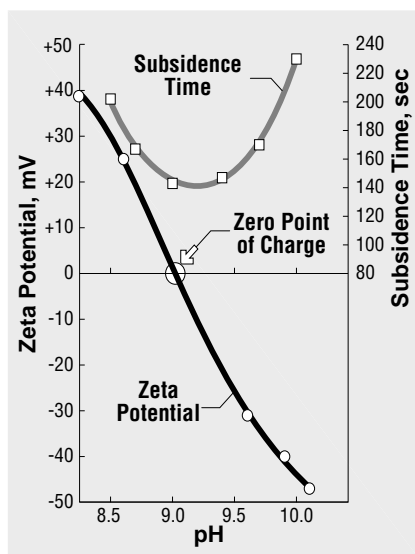
Mechanical bridging by polymers can be an effective flocculating technique. Some long chain polymers are large enough to adsorb to the surface of several particles at the same time, binding them together in spite of the electrostatic forces that would normally make them repel each other.

In practice, a combination of effects can be used to create stable systems or to flocculate them. For instance, stable dispersions can be created by a combination of electrostatic repulsion and steric hindrance. Electronegative dispersions can be flocculated using long chain cationic polymers which simultaneously neutralize charge and bridge between adjacent particles.

Zeta Potential Applications

Minerals & Ores

Many raw mineral ores such as those for copper, lead, zinc and tungsten are separated by first grinding the ore, mixing it with a collector and suspending it in water. The next step is flotation. Air is bubbled through the mixture and the collector causes the mineral particles to adhere to the bubbles so that they can be recovered at the surface. The efficiency of this process depends upon the degree of adsorption between the collector and the mineral and can be controlled by the zeta potential of the particles. In another interesting application, zeta potential studies have been used to minimize the viscosity of coal slurries.



Clays & Drilling Fluids

Clays are an essential part of paper, adhesives, ointments, rubber and synthetic plastics. In each of these systems, we have to deal with dispersions of clay in water or other fluids. Clay colloid chemistry helps us to tailor their characteristics to fit the task.

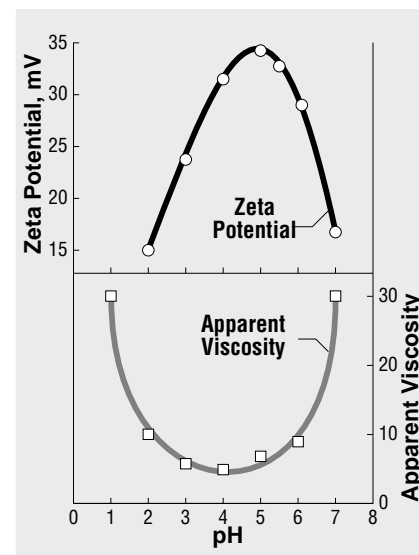
Clays are also used as drilling fluids in water well and petroleum well production. They are called drilling muds and are chemically conditioned to vary their properties during drilling. A highly charged suspension is desirable for the initial drilling operation. This keeps the clay colloids discrete, allowing them to penetrate into the porous wall of the drilled hole and clog the soil pores, forming a thin, impermeable cake which prevents the loss of drilling fluid. Later, the clay charge may be reduced to form a flocculated suspension in order to keep it from clogging the lower, pumping zone of the well.

Determining Point of Zero Charge

These experiments with alpha-alumina show good correlation between the point of zero charge as determined by zeta potential and the point of maximum subsidence rate. Subsidence rate is a measure of the degree of coagulation.

Ceramics

Slip casting is used in volume production of ceramic ware. A suspension of clay is prepared and poured into porous molds, which draw off the water from the clay particles by capillary action. A filter cake of clay forms as the water is drawn off. The structure of the clay layer depends on the degree of dispersion of the clay suspension.



Control of Slip Casting

Clay suspensions for slip casting must have their viscosity minimized so that they pour readily and release trapped air bubbles easily. The above figure shows the effect of pH on the apparent viscosity and zeta potential of thorium oxide (ThO_3). Note that a maximum zeta potential corresponds to a low apparent viscosity.

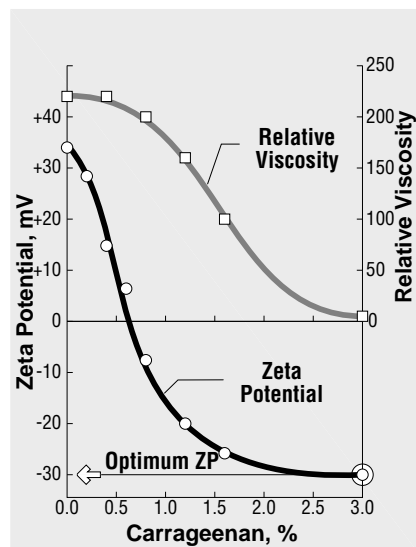
Coal
Dairy Products
Detergents
Dry Powder Technology

Dyestuffs
Emulsions
Fibers

Pharmaceuticals

The physical properties of a pharmaceutical suspension affect the user's response to the product. A successful suspension will not cake and will, therefore enjoy a long shelf life. With fine colloids this can be achieved by adding a suspending agent to increase the zeta potential, and produce maximum repulsion between adjacent particles. This highly dispersed system will settle very slowly, but any that do settle will pack tightly and aggravate caking.

Another, and sometimes more effective, approach is to formulate a weakly flocculated suspension. The suspended particles form light, fluffy agglomerates held together by van der Waals forces. The flocculated particles settle rapidly forming a loosely adhering mass with a large sediment height instead of a cake. Gentle agitation will easily resuspend the particles. Weak flocculation requires a zeta potential of almost zero.



Fluidization of an Antacid Suspension

Fluidization is an alternative to flocculation. A negatively charged colloidal polyelectrolyte is used as a "fluidizing" agent. The polyelectrolyte adsorbs onto the surfaces of insoluble particles and deflocculates them once the zeta potential exceeds the critical value.

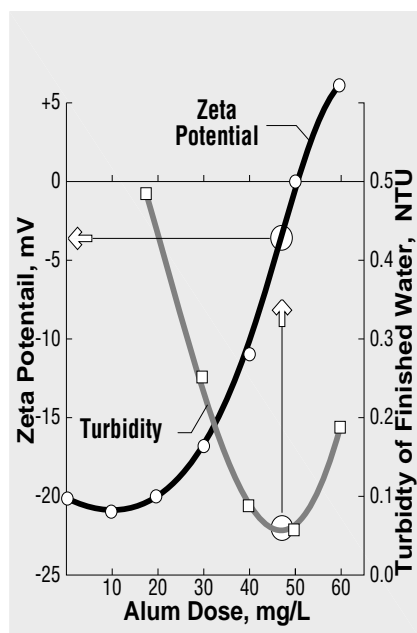
This graph illustrates the fluidization of an aluminum hydroxide suspension using carrageenan sodium as the "fluidizing" agent. The drops in zeta potential and viscosity of the suspension correlate quite well with each other and are produced by an increase in the concentration of carrageenan.

Paints

The pigments in paint must be well dispersed in order for the paint to perform successfully. If the pigment agglomerates, then the paint will seem to have larger pigment particles and may fail color quality. Gloss and texture are also affected by the degree of dispersion between the particles in the paint. Zeta potential measurements can be used in this application to control the composition of the paint and the dosage of additive required for an optimum dispersion.

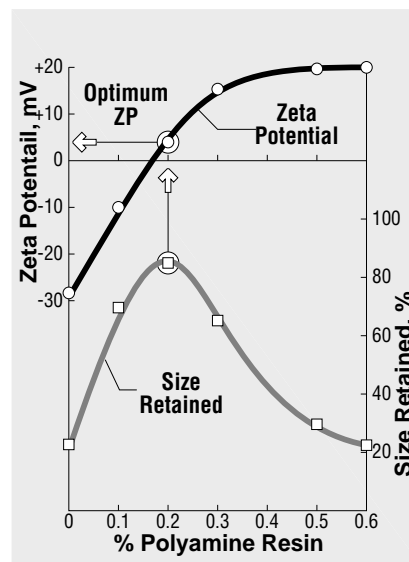
Water and Wastewater Coagulation

Zeta potential is a convenient way to optimize coagulant dosage in water and wastewater treatment. The most difficult suspended solids to remove are the colloids. Due to their small size, they easily escape both sedimentation and filtration. The key to effective colloid removal is reduction of their zeta potential with coagulants, such as alum, ferric chloride and/or cationic polymers. Once the charge is reduced or eliminated, then no repulsive forces exist and gentle agitation in a flocculation basin causes numerous successful colloid collisions. Microflocs form and grow into visible floc particles that settle rapidly and filter easily.



Papermaking

Retention of fines and fibers can be increased through zeta potential control. This reduces the amount of sludge produced by the wastewater treatment facility as well as the load on white water recycle systems. Zeta potential measurements also assist the papermaker in understanding the effect of various paper ingredients as well as the physical characteristics of the paper particles themselves.



Synthetic Size Retention in Papermaking

The point of maximum size retention corresponds to a zeta potential of +4, which can be considered the optimum ZP. More positive or more negative values of the zeta potential cause a drop in the percent of size retained. Operating at the optimum value results in titanium oxide savings, improved sheet formation, increased wire life, improved sizing, pitch control, and biocide reduction.

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. Just take a sample from the rapid mix basin and measure the zeta potential. If the measured value is more negative than the target ZP, then increase the coagulant dose (and vice-versa).

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

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