

73

WASTEWATER TREATMENT: THE ELECTRICAL CONNECTION

Normally, suspended solids carry a negative charge which must be addressed if unit operations are to be optimized

James F. Grutsch
Standard Oil Company (Indiana)
Chicago, Ill. 60601

Optimization of unit operations and a sequence of unit operations constitutes the staff of life for refinery engineers. Therefore, it is not unexpected that when new and restrictive wastewater treatment goals were imposed on the petroleum industry in the U.S., researchers with refinery background experience would bring a different perspective to bear on the problems of wastewater treatment. Using the refinery engineer's approach to achieve the best quality effluent in the most cost-effective manner has led to new perspectives in the understanding of the principles involved in, and the performance of, the basic water purification unit operations.

A significant improvement in wastewater purification using conventional unit operations is achieved when the overall treatment sequence is approached from the "systems optimization" point of view. All the individual unit operations are optimized, using for guidance an intrinsic property of solids in water, called zeta potential, which is defined later.

Systems optimization involves recognition that each unit operation in the end-of-pipe treatment sequence has a principal function. For example, obtaining maximum effluent purification involves maximum removal of soluble organics. The removal of soluble organics in the treatment sequence is by a biological process, the activated sludge process (ASP) being favored. Therefore, a systems optimization of a wastewater purification sequence

points to optimization of the ASP as the key element.

The ASP is generally used to achieve major reductions in suspended and colloidal material, as well as dissolved substances. When the refiner is almost wholly dependent on the ASP to achieve end-of-pipe treatment objectives, this operating mode may achieve the best overall reduction in contaminants.

Now, however, the refinery is confronted with very restrictive effluent limits on suspended solids, BOD, COD, ammonia, and some bioresistant materials, as well as variability limits for each parameter, as conditions for obtaining a National Pollution Discharge Elimination System (NPDES) permit. Under these conditions, the ASP becomes only one of a series of process steps required to meet the objectives.

When viewed in this context, the ASP can be optimized to achieve further control of process variability and increased removal of soluble contaminants. This is achieved by reversing the historic workhorse role of the ASP, and using the process only for the removal of essentially soluble contaminants.

Particle charges

Investigations into the optimization of each unit operation revealed that zeta potential (ZP) considerations provide a heretofore ignored basis of optimizing operation of essentially all unit operations used for purification of wastewaters. They include granular media filtration, dissolved air flotation (DAF), induced air flotation, clarification, and—surprisingly—the activated sludge process.

The suspended constituents of sewage and industrial wastewater, including microorganisms, dispersed oily colloids, inert suspended matter such as inorganic sulfides, silt, coke fines, and the like, have a negative electrical surface charge. The stability of colloidal and very slightly flocculated suspensions relates to the fact that the individual particles carry like electrical charges causing their mutual repulsion.

It is of utmost importance to recognize the impact of colloid scientists' work, when optimizing unit operations used in wastewater purification. Application of basic principles established by colloid scientists has led to a better understanding of fundamentals operative in wastewater processes, and yielded improved operating results. Fortunately, the principles can be utilized qualitatively, and are not limited to particles of colloid size.

The electric double layer

The electric double layer may be regarded as consisting of two regions:

- an inner region, which may include adsorbed ions
- a diffuse region in which ions are distributed according to electrical forces and thermal motion.

Stern proposed a model in which the boundary of the inner region (Stern layer) was located by a plane (the Stern plane) about a hydrated ion radius from the surface. Adsorbed ions attached to the surface by electrostatic or van der Waals' forces may be dehydrated in the direction of the surface. A certain amount of solvent will also be bound to the charged surface in addition to the adsorbed ions. The

shear plane, therefore, is probably located farther from the surface than the Stern plane. Ions with centers beyond the Stern plane are considered to be in the diffuse part of the double layer.

Electrokinetic potentials relate to the mobile part of the particle; therefore, the electrokinetic unit consists of the volume enclosed by the shear plane, which is rather inexactly known. The potential difference between the surface of shear and the solution is called the zeta potential (ZP).

DLVO theory

Unit operations used for wastewater purification essentially all involve solids in water. The DLVO theory quantifies particle stability in terms of energy changes when particles approach one another. The total energy is determined by summation of the attraction (London-van der Waals' forces) and repulsion (overlapping of electric double layers) energies in terms of interparticle distance. The general character of the resulting interaction energy-distance curve illustrates the very significant conclusions:

- attraction will predominate at small and large distances
- repulsion may predominate at intermediate distances, depending on the actual values of the two forces.

An important purpose of the chemicals used for destabilization is to reduce or eliminate the repulsion force at intermediate distances, so that attractive forces will predominate, and the particles will aggregate. This is a key consideration in optimizing physical separation operations. The reason that the negative ZP of waterborne solids brings about natural repulsion by negative surface charges of granular filter media, such as sand and coal, and those of the gas-liquid interface of dissolved air and induced air flotation systems.

Colloid destabilization mechanisms

Destabilization of the waterborne suspended solids may involve four mechanisms:

- colloid entrapment or removal via the sweep floc mechanism
- reduction in surface charge by double-layer repression
- charge neutralization by adsorption
- bridging by polymers.

Colloid entrapment involves chemical treatment with comparatively massive amounts of primary coagulant. The amount of coagulant used is typically so great in relation to the amount of colloidal matter, that the nature of the colloidal material is not

relevant. The amount of primary coagulant used may be 5-40 times as much as is used for charge neutralization by adsorption. The rate at which the primary coagulants form hydrous metal oxide polymers is relatively slow, and depends chiefly upon water temperature and pH.

Coupled with the high concentration used, all negatively-charged colloidal material is initially exposed to charge neutralization by the transient cationic species. The polymer matrix is three-dimensional and voluminous, providing for entrapment of solids. As the polymer contracts, freeing solvent water molecules, and settles, the suspended solids remain enmeshed in the settling floc and appear to be swept from the water; hence, the description of the process as a "sweep floc" mechanism.

However, this destabilization mechanism can result in the generation of large amounts of wet alum (or iron) sludges, which are difficult and costly to dewater. Even though it is by far the most widely used mechanism for water clarification, it is not recommended, because of the sludge problem, and because the use of other mechanisms result in significantly lower operating and capital costs.

Double-layer repression

Reduction in surface charge by double-layer repression is caused by the presence of an indifferent electrolyte which, in refineries, is chiefly so-

Advantages of using the ASP only for soluble contaminant removal

- Sludge-settling characteristics of the activated sludge mass are excellent at very high sludge ages; for example, over 40 days.
- Process control is greatly simplified through operation at a greater than 40-day sludge age.
- Using a very high sludge age for process operation eliminates the need for many process control tests.
- Operating at a very high sludge age produces an exemplary effluent very low in total organic carbon and other contaminants.
- A very high sludge age provides a remarkably low cell yield.
- At a very high sludge age, the population dynamics of the sludge mass improve.
- Maximum ASP capacity for purification is achieved through operation at high sludge ages.

dium chloride from brackish water usage, or saltwater ballast. For double-layer repression of colloid surface charge in brackish waters, the sodium ions of the indifferent electrolyte, which surrounds the colloid particles in order to balance their negatively-charged surfaces electrically, have less tendency to diffuse away from the colloid surface as the salinity increases. Some salt concentration may eventually be reached so that the thickness of the double layer may be small enough that two colloids approach each other so closely that van der Waals' forces cause aggregation.

An important aspect of double-layer repression is that the quantity of colloidal charge itself is not significantly reduced, but just that extent to which it extends outward from the colloid surface. This relates to the nature of the destabilizing chemical (salt) and its mode of action; i.e., the sodium ions remain free in the solvent, and cause rapid dissipation of the charge, as the distance from the colloid surface increases.

For demineralized water, there are not many ions available; therefore, the charge on the particle surface is not reduced much by adsorbed ions in the Stern layer, or counter ions in the diffuse layers. As a result, the zeta potential is high, and extends for a considerable distance into the solvent; in other words, the double layer is thick.

Fresh water (not demineralized), on the other hand, comparatively may contain many salts. The presence of counter ions may lead to some adsorption and potential drop across the Stern layer. The concentration of counter ions in the diffuse layer is much greater than the demineralized water example, and causes the charge to dissipate more rapidly. The double layer is much thinner than in the case of demineralized water.

For brackish or saltwater, the comparatively high concentrations of sodium ions discourage their diffusion away from the particle surface. The counter ions occupying the Stern layer cause an apparent reduction in potential but are not strongly absorbed and, therefore, do not permanently alter the surface potential charge to the much lower charge of the Stern potential, and the charge actually measured, the zeta potential. The high electrolyte concentration causes any residual charge to dissipate rapidly; in other words, the double layer is very thin.

Charge neutralization and bridging

Charge neutralization by adsorption of the destabilizing chemical to the

colloid is a key mechanism for optimizing removal of waterborne solids from waters. The colloidal charge may not only be reduced to zero, but actually beyond zero; that is, reversed. Charge neutralization by adsorption infers that the colloid-water interface is changed, and thus, so are its physiochemical properties.

It does not require much extension of one's imagination to see how this destabilization mechanism can explain those cases in which optimal chemical dosages were found, and overdosing that resulted in a deterioration in, or failure of, direct filtration. This phenomenon is more typically experienced with very low molecular weight polyelectrolytes, or surfactant-type molecules with little bridging properties.

Bridging by organic and inorganic polymers describes the destabilization mechanism by which the molecules of the added chemical attach onto two or more particles, causing aggregation. There are two kinds of bridging. These comprise polyelectrolyte bridging between dissimilarly, and similarly charged materials. Bridging of negatively-charged colloids by high molecular weight cationic and anionic polyelectrolytes are examples of the first and second kinds, respectively.

Double-layer repression can improve solids removal by direct filtration, but this mechanism does not achieve the best results. Indeed, it can conceal the definition of optimal chemical pretreatment to achieve best filtration results, if the interference of this destabilization mechanism is not recognized. Refinery experience indicates that the colloidal aggregates destabilized by double-layer repression appear analogous to loose flocculation by the secondary minimum; the aggregates are readily redispersed by hydraulic forces, as if the net binding forces are very weak.

Polyelectrolytes

Polyelectrolytes used as water-treating chemicals are macromolecules having many charged groups. They may be classified as cationic, anionic, and nonionic, depending upon the residual charge on the polymer in solution.

In solution, the polyelectrolytes are dissociated into polyvalent macro-ions and a large number of small ions of opposite charge (counter ions). The macro-ion is highly charged, which is the cause for the characteristic properties of the polyelectrolytes. Most of the macro-ions are long, flexible chains. Their size and shape depend upon the macro-ion charge, and interaction with counter ions. With in-

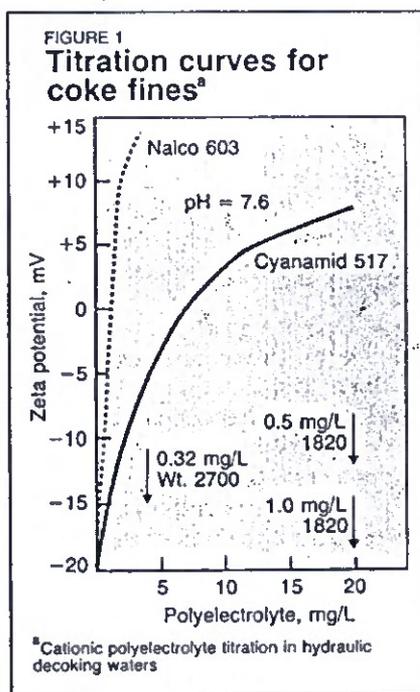
creasing charge, the macro-ion extends; with decreasing charge, the macro-ion assumes a contracted random coil.

The source of the charge is illustrated by the polyacrylates, widely used polymers. In distilled water, polyacrylic acid's carboxylic functional group is only slightly dissociated. The addition of sodium hydroxide (NaOH) reacts with the carboxylic acid groups, causing them to dissociate, leaving a charge on the macro-ion, and producing sodium counter ions.

In the case of polyelectrolytes, some counter ions at high concentrations screen the charged functional groups with an ionic cloud. Salinity, hydroxide, phenolics, and sulfides, are examples of the kinds of counter ions found to affect various cationics. Each wastewater application of cationics must address the contaminants present, if the most cost-effective polyelectrolyte is to be used.

Titration curves

A comparison of polyelectrolyte performance and determination of antagonisms and synergisms is conveniently and quantitatively determined by use of ZP titration curves. Because the stability of a suspension is determined by the balance between the short-range (van der Waals) attractive forces and the repulsive coulombic forces between the particles, the objective of ZP-cationic polyelectrolyte titration curves is to quantify the amount of polyelectrolyte needed to reduce the repulsive coulombic forces to levels that permit total destabilization by attractive forces.



Consider the refinery problem of the aggregation of coke fines in hydraulic decoking water, so they are readily removable. As shown in Figure 1, coke fines are originally stabilized by a negative ZP, but the negative charge is readily neutralized and reversed by cationic polyelectrolytes. One might think that too much cationic polyelectrolyte would simply restabilize the system as a positive colloid. However, the use of a cationic that has good bridging properties, in addition to charge neutralization, causes most of the solids to be enmeshed by the polymer.

The larger size aggregates are more readily separable even though comparatively highly charged. Addition of a small amount of high molecular weight weakly anionic polyelectrolyte to the positively-charged cationic-treated coke particles will once again reverse the charge.

Rather than redispersed the particles, however, the weakly anionic polymer efficiently "collects" the positively-charged particles into massive aggregates easy to separate. Once the high molecular weight weakly anionic polymer establishes bonds with the solids and forms aggregates, the aggregates are bound together with strong enough forces to resist redispersion by hydraulic forces in a clarifier, filter, or DAF unit.

Electrical models

Anionic polyelectrolytes are frequently used to flocculate negatively-charged colloidal systems. Even better appreciated is the capability of the activated sludge process to flocculate negatively-charged sewage, and industrial colloidal systems. An extreme case is the Contact Stabilization variation of the activated sludge process. Because the activated sludge mass and the anionic polyelectrolytes are both negatively charged, both of these destabilization examples seem to be counter to theory. However, a possible explanation for these extremely valuable properties lies in their electrical characteristics, and the environment in which they operate.

As discussed previously, ionizable groups of the polyelectrolyte are the source of an electric field. There are potential maxima in the region of the charged functional groups. There is a lesser potential field, outside the region of potential maxima, that might be described as a "potential tunnel." This is illustrated isometrically in Figure 2. When the polyelectrolyte is in the random coil conformation, as shown in Figure 3, there is an additional weak potential region (B) in the polyelec-

polyelectrolyte's sphere of influence. A fourth potential region is the solution in which there is no potential effect caused by the polyelectrolyte.

Each potential region has a different effect on counter ions. In the three potential regions within the polyelectrolyte's sphere of influence, counter ions can be considered as being bound to the polyelectrolyte. In the region of potential maxima, the bound counter ion may be localized at charged functional groups forming ion pairs. In the potential tunnel region, the bound counter ions are mobile, as they are in the weak potential region. Mobile counter ions establish an equilibrium, therefore, between the potential tunnel, weak potential field in the sphere of influence, and the solution.

A specially unique property of

polyelectrolytes is that the bound counter ions in the potential tunnel area can move parallel to the polyelectrolyte molecule in the apparent volume occupied by the potential tunnel. Thus, counter ions can "flow" in the potential tunnel areas, analogous to water in a garden hose. Polyelectrolyte solutions, therefore, show an extremely large dielectric constant.

The dielectric constant, or polarizability of polyelectrolytes, is determined by the volume of polyelectrolyte in which counter ions are retained (not by the charge density of the polyelectrolyte), as long as a region of bound but mobile counter ions is formed. The dielectric increment depends on the geometry of the polyelectrolyte; extended polyelectrolytes give much larger dielectric increments than do

polyelectrolytes in the random-coil conformation. Furthermore, the dielectric increment of polyelectrolytes in the extended (or helix) conformation increases rapidly with increasing length. Uniform and continuous distribution of charged groups, and the mobility of bound counter ions, are essential for large polarizability.

Polyelectrolyte destabilization

The means of negatively-charged polyelectrolytes to destabilize negatively-charged colloids is hypothesized to lie in the electrical properties of the polyelectrolyte. The proposed model in Figure 4 illustrates, approximately to scale, the colloid, its electrical double layer, the anionic polyelectrolyte, and its potential tunnel. Counter ions are cations in both cases.

FIGURE 2
Potential maxima and potential tunnel fields

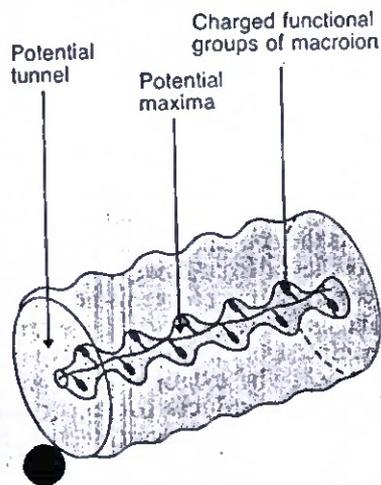
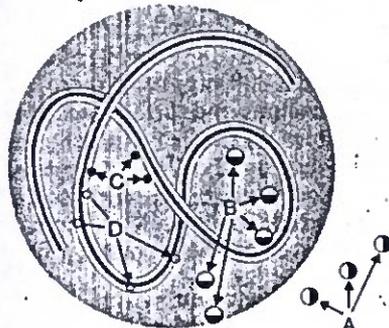
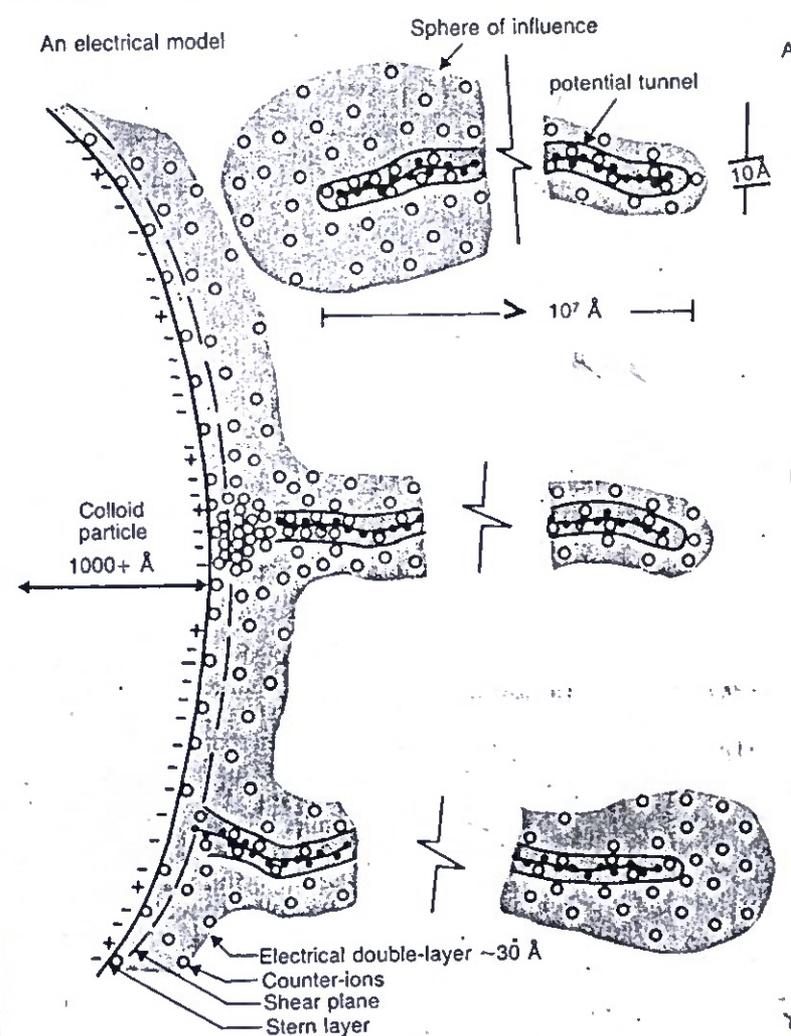


FIGURE 3
Macroion in random coil conformation, showing four potential regions



- A = No potential effect (the solution)
- B = Weak potential in the macroion's sphere of influence
- C = Potential tunnel
- D = Potential maxima near charged functional groups

FIGURE 4
Destabilization of negative colloid with anionic polyelectrolyte



- A = Polarizing anionic polyelectrolyte, showing potential tunnel, sphere of influence, and mobile counter-ions
- B = Polyelectrolyte flooding double-layer with counter-ions
- C = Bound polyelectrolyte

Cations in the double layer are subject to at least two opposing electrical forces, one being the coulombic attraction to the colloid particle. They are also attracted to the solvent, to maintain an electrically balanced system.

When the sphere of influence of the anionic polyelectrolyte approaches the electrical double layer of the colloid, repulsion, caused by encountering like charges, might be expected. However, in this instance, apparently:

- The polarizing polyelectrolyte's electrical sphere of influence shields the counter ions in a localized area of the colloid double layer from the attractive, electrical solvent forces.

- The resulting electrical imbalance results in an increase in the negative coulombic potential in the localized area on the colloid.

- The increase in negative coulombic potential attracts the mobile counter ions from the potential tunnel region of the polyelectrolyte.

- The potential tunnel of the polyelectrolyte serves as a conduit for counter ions, which neutralize the surface charge in the localized area of the colloid surface.

- The charge neutralization achieved reduces the energy of repulsion at the localized site sufficiently so that the sum of the energy of repulsion and energy of attraction curves yields an interaction energy of attraction at the localized site.

- The positive interaction energy at the localized site permits attractive London-van der Waals' forces at the primary minimum between the polyelectrolyte and colloid to react.

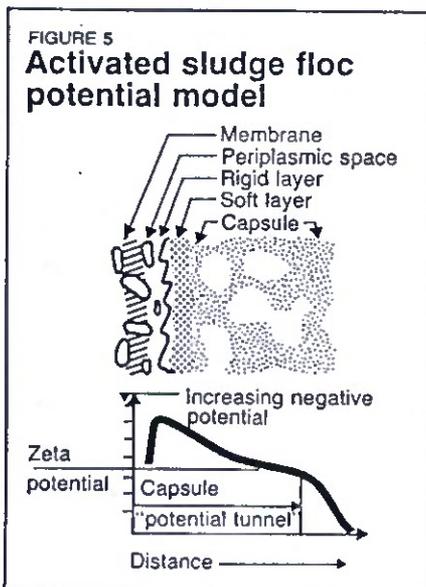
The key to this hypothetical model is the mechanism by which the anionic polyelectrolytes implement the initial shielding action of the colloid surface from the electrical solvent forces. This capability lies in the special properties of the polyelectrolyte. These include polarizability; bound, but mobile counter ions in the potential tunnel; the equilibria between counter ions in the potential tunnel, and spheres of influence established by coulombic forces.

This model also suggests why anionic polyelectrolytes do not effectively stabilize the very small colloid particles. The reason is that as the polyelectrolyte sphere of influence approaches the small colloid, the mass of the small colloid is so little that the repulsion forces predominate, and the particle moves away before the polarizing polyelectrolyte can shield the colloid from the solvent electrical forces. For these very small colloid particles, destabilization by the charge

neutralization, using cationic polyelectrolytes, is required.

"Bugging" a sludge system

The microorganisms constituting activated sludge also have a negative zeta potential. Glucuronic acid has been proposed as the source of the electrical charge (Figure 5).



The outermost surface of most bacteria is a slimy capsule varying in thickness up to 100 000+ Å. The capsule composition varies with species, and may consist of polymers of glucose or other sugars, amino and acid sugars, or polypeptides. Capsules generally consist of about 98% water. The function of the capsular layer is proposed as serving the microorganisms as an osmotic barrier; that is, a mechanism for guarding against too rapid an influx or efflux of water. It is proposed that the capsular layer performs an equally if not more important function of providing the potential tunnel region.

As previously stated, the zeta potential is the charge difference between the plane of shear and the solution. In the case of microorganisms, the shear plane is some small but indeterminate distance beyond the outer boundary of the capsule. It is hypothesized that the region beyond the shear plane is analogous to the diffuse layer of counter ions in the colloid double-layer model, whereas the capsule on the capsule side of the shear plane serves a function analogous to the potential tunnel region of polyelectrolytes. In other words, it provides for a region of bound but mobile counter ions.

The acidic polysaccharides in the outer layer of the soft layer are at least partially responsible for the negative, electric charge on the bacteria surface.

As in the polyelectrolyte example, mobile counter ions establish an equilibrium between the capsule layers (potential tunnel) and the solution, and the bound counter ions in the capsule layer can move parallel to the cell wall of the microorganism. The chief difference between the polyelectrolyte potential tunnel and the biological potential tunnel (capsule) is the comparatively large volume of the capsule—a desirable property.

Biological destabilization model

As for polyelectrolytes, the means for negatively-charged microorganisms to destabilize negatively-charged colloids also is hypothesized to be found in the electrical properties of the microorganisms. The model proposed for polyelectrolytes is analogous to the model for the biological system. Once again, cations are counter ions, in both cases. Dimensionally, the activated sludge floc and the capsule volume are larger than the comparative volumes occupied by the polyelectrolyte and its potential tunnel at the very low concentrations of polyelectrolyte used (frequently less than 1 mg/L).

As the diffuse counter ion layer of the double layers overlap, compared to polyelectrolytes, the massive size of the microorganisms floc more readily shields the counter ions in the colloid double layer from coulombic solvent forces. The microorganisms supply counter ions to satisfy the electrical imbalance from their potential tunnel (capsule). The localized increase in counter ions reduces the energy-of-repulsion curve analogous to anionic polyelectrolytes, and the particles flocculate into the biomass.

Once again, this model suggests why biopolymers (microorganisms) are more effective for destabilizing the very small colloids than anionic polyelectrolytes are. The polyelectrolytes are used in the range of 0.2–0.5 mg/L, whereas the activated sludge floc is usually at least 1000 mg/L, and may be up to 10 000 mg/L, or more. The massive volume and surface area of the biopolymer do not leave much space for the very small colloid to move into when electrical repulsion forces are encountered. Indeed, it is virtually encapsulated by the biomass.

Design consideration

Activated sludge has a bimodal floc size distribution. A good flocculating and settling sludge has a preponderance of large floc mass, compared to the fine particle fraction. The large floc mass is, in essence, a biopolymer analogous to a weakly anionic polyelectrolyte-type polymer. Thus, the

large floc mass is a biopolymer flocculant, and the fine particles represent the phase to be flocculated.

Qualitatively, when the ratio of the two phases overwhelmingly favors the biopolymer, as illustrated by the solid line in Figure 6, a good flocculating sludge results. When the fine particles predominate, their surface area overwhelms the capacity of the biopolymer for flocculation, and "arms and legs" (turbidity) are observed in the supernatant.

Inert and slowly biologically-oxidized colloids and suspended matter contribute to increasing the amount of fine particles in the sludge mass. Increasing sludge age increases their accumulation, thereby contributing to the deterioration in sludge flocculating properties. Removing colloids and suspended matter before ASP treatment results in an excellent activated sludge at very high sludge age.

ZP tells the story

There is another way of looking at the settling properties of activated sludge and the impact of the fine particle fraction on the settling properties that is much more enlightening in terms of understanding why solids are lost over an ASP final clarifier weir. That is to examine the zeta potential probability distribution of the activated sludge particles.

Zeta potentials are typically reported as averages, which are always misleading, particularly in the case of activated sludge. For example, the median ZP values of a good settling sludge could be -11 mV, and those of a poorly settling sludge can be -12 mV (Figure 7).

This difference is not only difficult to measure but is really insignificant. What is significant is the slope of the distribution curve, and the ZP of the highest-charged particles.

If, for example, a ZP of -14 mV or more negative provides enough repulsive force that the fine particles will not flocculate, fully 8% of the solids in the poorly settling sludge mass resist flocculation and settling. On the other hand, essentially all the particles in the rapidly settling sludge are well below -14 mV ZP, and flocculate well. Limiting the accumulation of colloids in the activated sludge by effective phase removal in pretreatment facilities is a principal means of controlling the ZP probability distribution of activated sludge.

Additional reading

Verwey, E. J. W., Overbeek, J. Th. G., *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.

FIGURE 6
Activated sludge bimodal floc size distribution

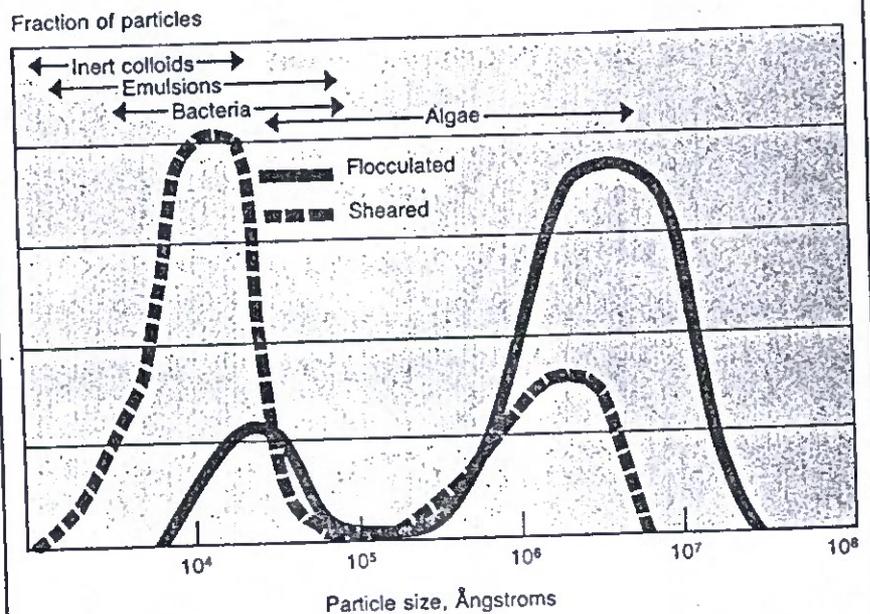
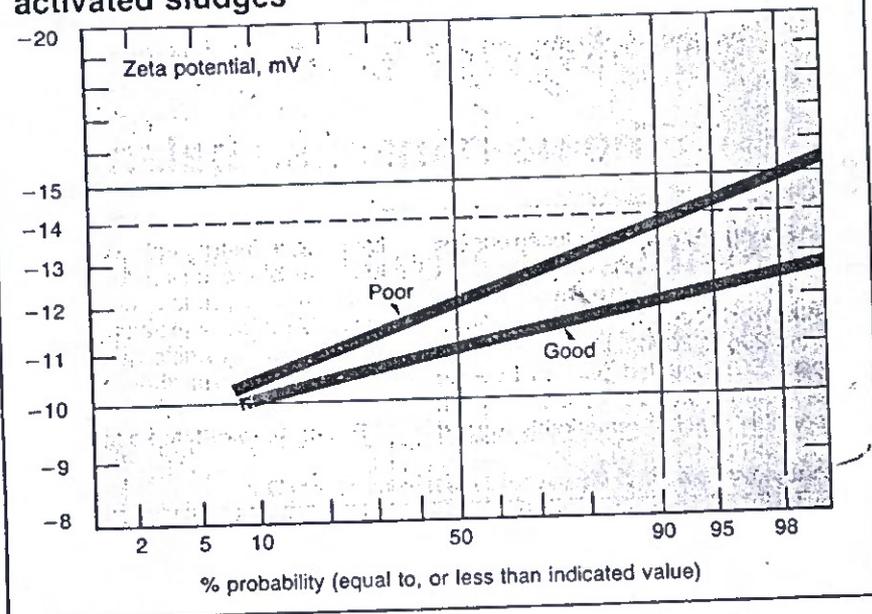


FIGURE 7
Probability curves for poor- and good-settling activated sludges



Overbeek, J. Th. G., *Colloid Science*, Vol. II, Elsevier, Amsterdam, 1952.

Grutsch, J. F., Mallatt, R. C., A New Perspective on the Role of the Activated Sludge Process and Ancillary Facilities, First Open Forum on Management of Petroleum Refinery Wastewaters, USEPA, API, NPRA, University of Tulsa, Tulsa, Okla., 1976.

Grutsch, J. F., Mallatt, R. C., Optimizing Granular Media Filtration of Refinery Waters Requires that the Electrical Charge Phenomena Operative be Addressed, *Chem. Eng. Prog.* 73 (4), 57 (1977).

Oosawa, F., *Polyelectrolytes*, Marcel Dekker, Inc., New York, 1971.



James F. Grutsch is director, Environmental Technology for Standard Oil Co. (Indiana). He has been involved in water pollution research for 25 years, in addition to technical service for refinery process units. Grutsch also participates in environmental projects sponsored by the American Petroleum Institute.

Coordinated by JJ