

Principles, Techniques and Recent Advances in Fine Particle Aggregation for Solid-Liquid Separation

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Introduction

Waste water discharged from various chemical and nuclear processing operations contains dissolved metal species that are highly toxic and, in some cases, radioactive. When the waste is acidic in nature, neutralization using reagents such as lime is commonly practiced to reduce both the acidity and the amount of waste (Kuyucak et al. 1991). The sludge that results from the neutralization process contains metal oxide or hydroxide precipitates that are colloidal in nature and is highly stable. Destabilization of colloidal suspensions can be achieved by aggregation of fines into larger sized agglomerates. Aggregation of fines is a complex phenomenon involving a multitude of forces that control the interparticle interaction. In order to understand the colloidal behavior of suspensions a fundamental knowledge of physico-chemical properties that determine the various forces is essential. In this review, a discussion of basic principles governing the aggregation of colloidal fines, various ways in which interparticle forces can be manipulated to achieve the desired aggregation response and recent advances in experimental techniques to probe the interfacial characteristics that control the flocculation behavior are discussed.

Basic Principles of Colloidal Aggregation

Particles in a colloidal suspension collide due either to Brownian motion or to external forces induced by agitation, magnetic field, etc. The probability of adhesion upon collision will be determined by the net energy of interaction which is the result of attractive and repulsive energies

between the colliding particles. To achieve aggregation, the conditions should be manipulated such that the net energy of interaction between the colliding particles is attractive.

Attractive Interactions

The attractive interactions between the particles arise from London-van der Waals forces, Keesom forces and Debye forces, and also from the compatibility between the adsorbed layers of surfactants or polymers. The London-van der Waals attraction depends mainly on the Hamaker constant, which in turn depends on the density and the polarizability of the dispersed phase, and the radii of the colliding particles. For a given solid-solution system the above parameters are fixed and, therefore, the van der Waals attraction energy cannot be manipulated externally by varying the experimental conditions. The attractive interaction between the adsorbed layers of surfactants or polymers, on the other hand, can be manipulated by appropriately selecting the reagents that have higher affinity between themselves than towards the solvent medium.

Repulsive Interactions

The repulsive interactions arise from either the electrostatic repulsion caused by overlapping of similarly charged electrical double layers or the steric repulsion between the adsorbed layers of surfactants or polymers. Electrostatic repulsion can be minimized by decreasing the zeta potential which is a direct function of both the surface charge and the thickness of the electrical double layer. Zeta potential, and hence the electrostatic repulsion, can be decreased by reducing the surface charge on the particles and/or the thickness of the electrical double layer. Surface charge on the solids can be reduced by a) adsorption of inorganic or organic reagents carrying appropriate

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charge and b) appropriately modifying the suspension pH. Electrical double layer thickness, on the other hand, can be reduced by increasing the dielectric constant or the ionic strength of the medium.

Various Mechanisms of Colloidal Aggregation

Aggregation by Minimization of Electrostatic Repulsion

As mentioned earlier, aggregation of particles can be brought about by decreasing either the surface charge or the thickness of the electrical double layer. The aggregates produced by this mechanism are generally small and dense.

Control of Surface Charge

The surface charge can be reduced by the addition of either inorganic or organic species. Manipulation of surface charge by inorganic species involves addition of salts containing either *potential-determining ions* or *specifically adsorbing ions* (Stumm and Morgan 1981). *Potential-determining ions* are defined as species of ions which by virtue of their equilibrium distribution between the solid and the liquid phases determine the potential difference. The examples in this class are H^+ and OH^- ions (or pH) for oxide surfaces such as alumina and quartz, $Ca(NO_3)_2$ for calcite and $AgNO_3$ or KI for silver iodide. *Specifically adsorbing ions* are co-ordinatively bound to solid surfaces such as attachment of Zn^{2+} to MnO_2 surface. The effect of pH on the zeta potential of alumina and the corresponding flocculation response (plotted as amount settled solids) is shown in Figure 1. It can be seen from this figure that the zeta potential of alumina can be changed by adding potential-determining H^+ and OH^- ions (or pH) and that maximum flocculation occurs around the isoelectric point (the pH at which zeta potential is zero).

Surface charge may also be controlled by the adsorption of ionic surfactants and polymers. Manipulation of surface charge of alumina by sodium dodecylsulfonate (anionic surfactant; Somasundaran and Fuerstenau 1966) and polyacrylic acid (anionic polymer; Tjipangandjara and Somasundaran 1990) are typical examples in this class. Figure 2 shows the effect of polyacrylic acid

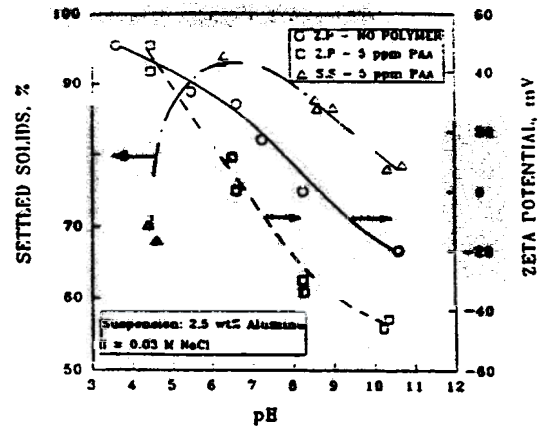


Figure 1. Effect of pH on Particle Zeta Potential and Flocculation Response of Alumina Suspension

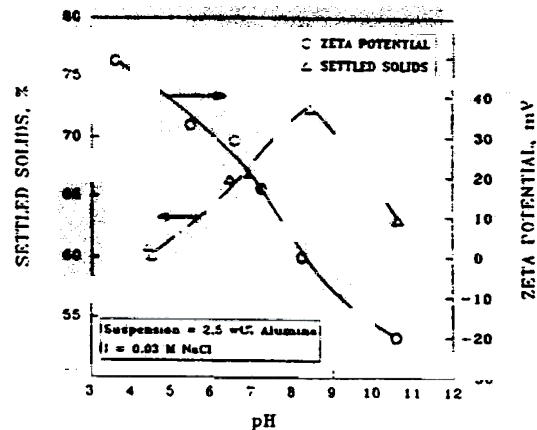


Figure 2. Effect of pH on Particle Zeta Potential and Flocculation Response of Alumina Suspension in the Presence of Polyacrylic Acid

addition on the zeta potential of alumina and the corresponding flocculation response. Here again, a good correlation between the zeta potential and flocculation response can be seen with the maximum in settled solids corresponding to the isoelectric point.

Compression of the Electrical Double Layer

Reduction of the zeta potential by electrical double layer compression can be achieved by adding inorganic electrolytes, for example, KNO_3 , $CaCl_2$, $AlNO_3$ for quartz, silver iodide, alumina, etc. (Somasundaran 1980).

Aggregation by Association of Adsorbed Surfactant Layers

As discussed earlier, attractive interaction between particles can arise from the compatibility of adsorbed surfactant layers. Flocculation of alumina by sodium dodecylsulfonate (Somasundaran and Fuerstenau 1966) and hematite by potassium oleate (Yap et al. 1981) are examples of this type of aggregation. Figure 3 shows the relationship among adsorption density, electrophoretic mobility (a measure of zeta potential) and flocculation response for an alumina-sodium dodecylsulfonate system. In this figure, the sharp increase in the adsorption density around 10^{-4} moles/liter has been attributed to lateral association of adjacent hydrocarbon chains of the adsorbed surfactant ions. It can be seen from Figure 3 that the settling index does not pass through a maximum at zero mobility, indicating that increased interparticle attraction due to compatibility of adsorbed surfactant layers is a major mechanism of aggregation in this case.

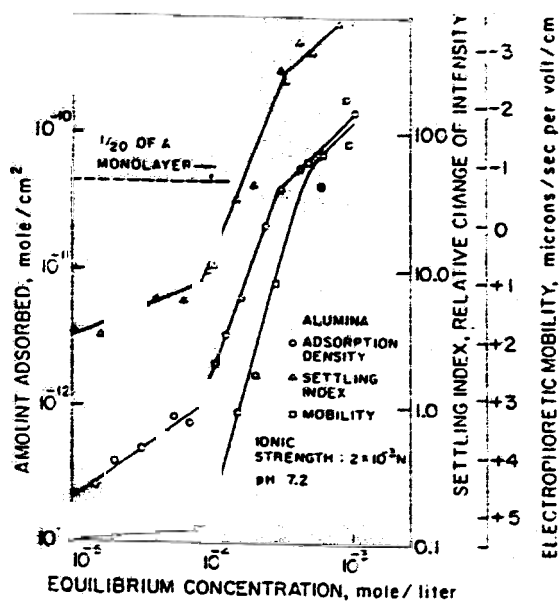


Figure 3. Relationship Among Adsorption Density, Particle Zeta Potential (Electrophoretic Mobility) and Flocculation Response in Alumina Sodium Dodecylsulfonate System

Aggregation by Bridging Forces

A macromolecule with specific functional groups can anchor on to two or more particles and thus induce aggregation by bridging. Aggregates produced by this mechanism are called flocs and are generally large and porous. The effectiveness of a polymer for a given system depends on the amount of polymer adsorbed, the particle zeta potential resulting from polymer adsorption and, more importantly, the conformation of the polymer at the solid-liquid interface. Figure 4 shows the flocculation response of an alumina suspension in the absence and presence of polyacrylic acid. It can be clearly seen from this figure that enhanced flocculation is obtained due to the addition of polyacrylic acid.

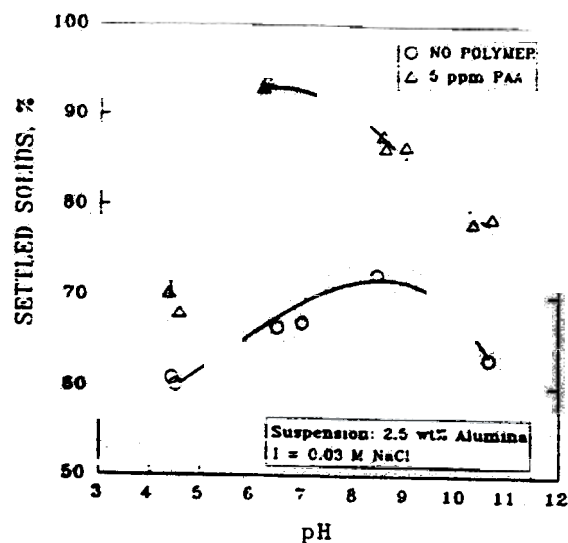


Figure 4. Flocculation of Alumina in the Presence and Absence of Polyacrylic Acid

Recent Advances in Polymer Flocculation Research

As discussed above, although there are several techniques for inducing aggregation of fines, flocculation using polymers remains the most widely applied method among them. This can be attributed to the fact that flocs with a wide variety of characteristics to suit different needs can be produced using polymers (Moudgil and Vasudevan 1989).

Conformation of polymers at the solid-liquid interface plays an important role in determining the flocculation response (Sato and Ruch 1980) of a colloidal suspension. Recently, several techniques such as small angle neutron scattering (Cosgrove et al. 1984), photon correlation spectroscopy (Gramain and Myard 1981; Kato et al. 1981) and ultracentrifugation (Garvey et al. 1976) have been attempted to estimate the conformation of polymer at the particle-solution interface. However, experimental correlation between conformation and flocculation has not been attempted since the above techniques are not easily amenable for use concurrently with flocculation response measurements. Recently, we developed a technique based on fluorescence spectroscopy for the *in situ* determination of polymer conformation in flocculation systems (Huang et al. 1990; Tjipangandjara and Somasundaran 1990). This technique consisted of labelling the polymer with a fluorescent probe such as pyrene which is attached either at the two ends of the polymeric chain or randomly along the length of the polymer chain (Turro and Arora 1986). When the probe is excited using an incident radiation some of the molecules of the probe, pyrene in our case, reach the excited state (P^*) and the rest remain in the ground state (P).

When the polymer is in a stretched conformation there is less probability for the excited molecule to be in the vicinity of the ground state molecule (Figure 5a). In this case, when the excited molecule returns to the ground state it emits fluorescence which is characteristic only of the pyrene monomer. However, when the polymer is coiled there is a high probability for the excited molecule and the molecule at its ground state to be in the vicinity of each other, which will result in the formation of an excimer (PP^*). The fluorescence emitted by the excimer is of different wavelength (480 nm) than that of the monomer (379 nm; Figure 5b). The ratio of intensities of the excimer to monomer peaks (I_e/I_m) will thus be a measure of the degree of coiling with a high ratio representing a coiled polymer and a lower ratio representing a stretched one. This technique has enabled experimental correlation, for the first time, between the polymer conformation and various flocculation responses such as settling rate, amount settled and supernatant clarity (Huang et al. 1990; Tjipangandjara and Somasundaran

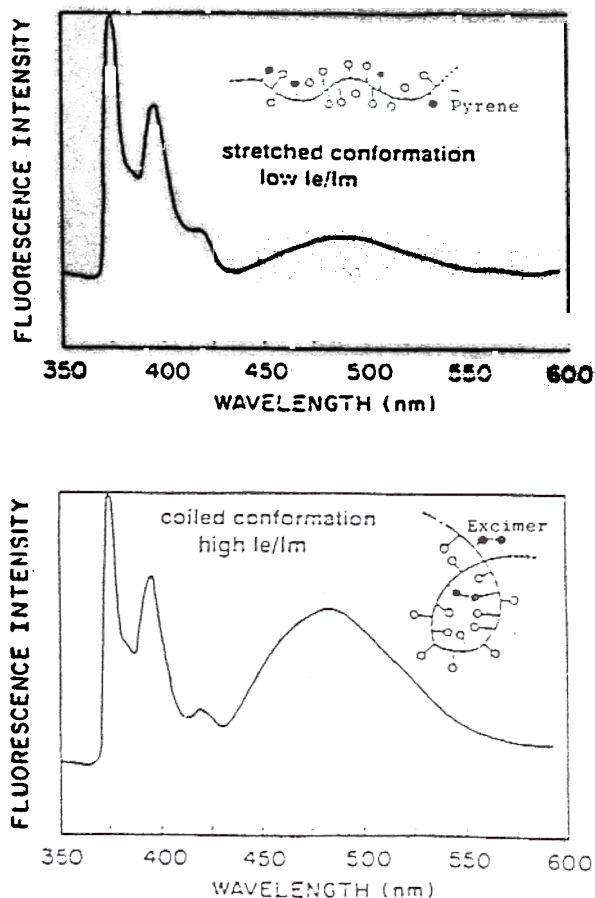


Figure 5. Fluorescence Emission Spectrum of Polymer in a) Stretched and b) Coiled Conformation

1990). The relationship between the amount of solids settled and the excimer to monomer ratio is shown in Figure 6 for alumina-polyacrylic acid system. It can be seen from this figure that the stretched polymer conformation (low excimer to monomer ratio) promotes flocculation for this system.

Conclusions

Aggregation of colloidal fines can be brought about by manipulating interparticle interactions such that attractive forces outweigh the repulsive ones. This can be achieved by minimizing electrostatic repulsion using inorganic and organic species, enhancing the compatibility of adsorbed surfactant layers or by using macromolecules to

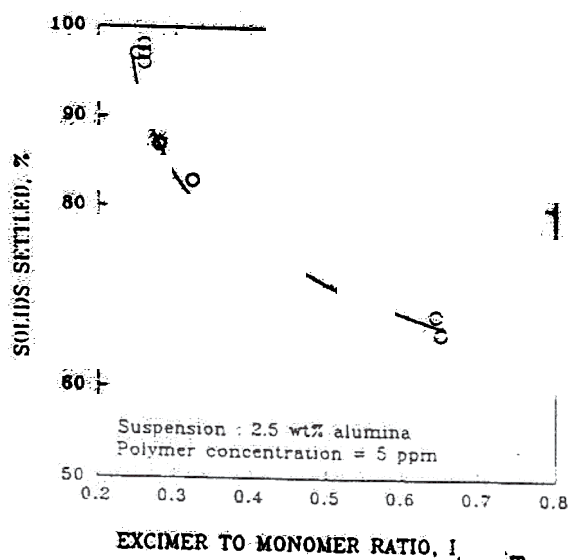


Figure 6. Relationship Between Excimer to Monomer Ratio (an Index of Polymer Conformation) and the Amount of Solids Settled (a Measure of Flocculation Response)

bridge the colloidal fines. Polymer flocculation remains the most widely used solid-liquid separation technique since flocs of desired characteristics can be formed using this technique. Polymer conformation plays a predominant role in flocculation, and a fluorescence technique can be used effectively to monitor the conformation of the adsorbed polymer concurrently with flocculation.

Acknowledgments

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