PRINCIPLES OF FLOCCULATION, DISPERSION, AND SELECTIVE FLOCCULATION

P. Somasundaran

Henry Krumb School of Mines
Columbia University
New York, NY 10027

ABSTRACT

Processing of fine particles in suspension is markedly affected by their state of dispersion/aggregation. In addition, tendency for a given component of the system to undergo selective aggregation or selective dispersion is an important property which may be put to use for processing. In this paper, principles governing flocculation, dispersion, and selective flocculation of mineral fines are discussed and then the role of major solution properties such as pH, ionic strength, etc. is examined.

INTRODUCTION

Fines and ultrafines are invariably produced during various industrial processes. In certain processes it is the aim to produce as fine a material as possible and to have it in a totally dispersed state whereas in some other processes too fine a material than desired is often produced as a part of the overall process. In all cases the nature of dispersion or aggregation of fine particles affects significantly the performance of processes involving them as well as quality of products manufactured. Thus, in paints and varnishes it is necessary to have the particles in a dispersed state for long periods, whereas in waste water treatment it is the objective to get the particles in an aggregated and sedimented form. Because of the highly complex manner in which fine particles interact while in liquids, in order to achieve the desired dispersed or aggregated state it is necessary to have an accurate understanding of the physico-chemical properties that play a governing role in determining such interactions and of means by which one can control them. In this paper, a discussion of basic principles governing dispersion and aggregation of fine particles will be
presented after defining terms that are commonly used.

**TERMINOLOGY**

Following the IUPAC guidelines (1), *aggregation* refers to the process or the result of the formation of a group of particles held together in any manner. *Coagulation* refers to the specific type of aggregation that leads to formation of aggregates that are compact whereas *flocculation* refers to that which leads to aggregates that are loose or open. Usually addition of inorganic salts or acid or alkaly causes a *coagulum* to be formed and addition of polymers gives rise to the formation of *flocs*.

As far as the particles themselves are concerned, there are a variety of terms loosely used to indicate their size leading to considerable confusion between scientists and engineers in various disciplines. They include *fines*, *ultrafines*, colloids, *slimes*, *sludges*, *sediment*, *suspension*, oozes, slurries, mud, gel, suspensoid, and sub-sieve size and sub-micron size particles. The following definitions are offered here on the basis of their size. Major interactions such as van der Waals attraction, electrostatic attraction, and gravitational sedimentation are dependent on the size of the particles. The classifications given below are based on the magnitude of these interactions.

*Colloid*: colloid is composed of particles that are less than 1 micron in size.

*Ultrafines*: these are particles that are not separated by conventional non-gravity processes such as flotation and are less than 10 microns in size but greater than 1 micron in size.

It is recognized that for certain minerals such as coal, the minimum size for flotation might be much greater than that indicated above.

*Fines*: particles that are not easily separated by gravity processes and are less than 100 microns in size but not less than 10 microns in size.

*Coarse particles*: these are defined as particles that are larger than 1000 microns (16 mesh).

*Slime*: slime is defined as a mixture of colloidal and ultrafine size waste mineral matter generated during milling operations and has slow settling characteristics.

*Sludge*: this is colloidal mineral or non-mineral matter which has a tendency to form a highly porous three-dimensional network structure and has, as a result, very slow deliquorizing characteristics.
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BASIC PRINCIPLES

When fines are produced during mining or milling operations the particles gain energy in the form of surface energy and deformation energy which gets stored in the sub-surface region. The system can eliminate this increase in energy partly by permitting the new solid surface to undergo interactions with the solvent and solute molecules. In addition, most systems can also be expected to eliminate as much of the increase in energy by means of re-aggregation. The rate of this re-aggregation can however be extremely slow depending upon the nature of interactions between the particles as well as energy changes involved in, for example, the desolvation or desorption of any species in the interfacial region upon re-aggregation. It is mostly this rate that can be controlled in order to achieve the desired dispersion or aggregation of the system. In this paper therefore kinetic aspects of aggregation will also receive emphasis in addition to the equilibrium processes.

The rate of aggregation will depend essentially on probability of collisions between particles, probability of attachment during such collisions and probability of detachment of particles from the aggregates subsequently. While the probability of collision will depend on the Brownian motion determined essentially by the temperature of the system and on fluid flow motions determined by the viscosity of the pulp and external stirring, probabilities of adhesion and detachment are dependent on the type of physico-chemical interactions between the particles and, to some extent, on velocity gradients in the pulp.

Both Brownian and velocity gradient aggregations are described by Smoluchowski treatment that relates the rate of aggregation to the radius of the particle and the total number of particles in the system in the following manner. Aggregation due to Brownian motion, known as perikinetic aggregation, leads to a decrease of particles governed by the following second order equation if every collision is successful in creating an adhesion (2).

\[
\frac{dN_t}{dt} = -8\pi D r N_t^2
\]

where \( N_t \) is the total number of particles at time \( t \), \( D \) is the diffusion coefficient for the particle, and \( r \) is the radius of the particle. Integrated form of equation (1) is

\[
N_t = \frac{N_0}{1 + 8\pi D r N_0 t}
\]

This derivation takes into account formation of only doublets from original particles. In reality primary particles can also aggregate with multiplets. Solution for all particles aggregates containing \( i \) particles is given as
S Slow stirring can indeed promote aggregation. Such aggregation under the influence of velocity gradient is known as orthokinetic aggregation. Rate of orthokinetic aggregation is given by

\[
\frac{dN_t}{dt} = \frac{16Gr^3}{3} \sum_{k=1}^{p} \frac{N_k^2}{k}
\]

\(G\) is velocity gradient, \(N_k\) is number of \(k\) particles per unit volume, \(k\) is particles formed by aggregation of two particles, \(p\) is particle of limiting size in shear gradient \(G\). As mentioned earlier, above formulations assume that every collision is fruitful. In reality, only a fraction of the collisions might be effective and as a result the aggregation might be slow. The magnitude of this fraction is dependent upon the nature of interactions between particles and, to some extent, viscous properties of the liquid film between the particles. If \(V\) is the total energy of interaction between particles of radii \(r_i\) and \(r_j\) when they are separated by a distance \(d\) the fraction of effective collisions, \(\alpha\), according to Fuchs (3) is given by the following expression

\[
\frac{1}{\alpha} = 2 \int_{2}^{\infty} \exp \left( \frac{-V}{kT} \right) \frac{dS}{S^2} \]

\(k\) is Boltzmann constant and \(S\) is equal to \(\frac{2d}{r_i + r_j}\). As an example, for maximum \(V\) equal to 5, 15, and 25 kT, \(\alpha\) is \(2.5 \times 10^{-2}\), \(10^{-5}\), and \(10^{-9}\), respectively.

The interactions between particles that are important in determining \(\alpha\) are made up of London-van der Waals attractive forces \(V_a\), electrical double layer forces \(V_e\) that can be attractive or repulsive in nature, bridging forces \(V_b\) that are always attractive and steric forces \(V_s\) that arise from the overlap of adsorbed layers. Steric forces can be repulsive or attractive depending on the solubility properties of the adsorbed layer.

\[
V = V_a + V_e + V_b + V_s
\]

**Attractive Forces**

\(V_a\), the attractive interactions, arise from London dispersion forces, Keesom forces due to interactions between permanent dipoles and induced dipoles in the particles and Debye forces due to interactions amongst
induced dipoles. These forces vary as \( \frac{1}{d^6} \) where \( d \) is the intermolecular spacing. For macroscopic bodies, the forces when summed over all the molecules in the body vary as \( \frac{1}{d^n} \). \( n \) has a value less than 6, depending upon the shape of the interacting bodies. For example, for two flat plates \( n \) has a value of 2 and for between two spheres it has a value of 1. Thus

\[
V_a \text{ between two plates} = -\frac{A}{12\pi D^2} \tag{7}
\]

\[
V_a \text{ between two unequal spheres} = -\frac{A}{6D} \left(\frac{R_1R_2}{R_1 + R_2}\right)
\]

\[
V_a \text{ between a plate and a sphere} = -\frac{AR}{6D}
\]

\( A \) is a constant for a given system of materials and is known as the Hamaker constant. It is dependent essentially on the polarizing properties of the molecules comprising various components of the system. Hamaker constants have been compiled for a number of systems by Healy (4) recently and are given below.

<table>
<thead>
<tr>
<th>System</th>
<th>( A ) erg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/vacuum/water</td>
<td>3.6 - 6.3 x 10^{-13}</td>
</tr>
<tr>
<td>Water/hydrocarbon/water</td>
<td>3.4 - 7.0 x 10^{-14}</td>
</tr>
<tr>
<td>Hydrocarbon/vacuum/hydrocarbon</td>
<td>5.0 - 9.0 x 10^{-13}</td>
</tr>
<tr>
<td>Hydrocarbon/water/hydrocarbon</td>
<td>3.4 - 7.0 x 10^{-14}</td>
</tr>
<tr>
<td>Quartz/vacuum/quartz</td>
<td>8.0 -10.0 x 10^{-13}</td>
</tr>
<tr>
<td>Quartz/water/quartz</td>
<td>1.0 \ x 10^{-13}</td>
</tr>
<tr>
<td>Gold/water/gold</td>
<td>1.24 - 3.3 x 10^{-12}</td>
</tr>
</tbody>
</table>

All the above values refer to the case where the particles are fairly close to each other so that there is no real lag in the propagation of electro-magnetic waves between them. On the other hand, if they are
separated by a very large distance (5) the van der Waals attractive energy of interaction is retarded approximately by a factor of \( \frac{1}{D} \).

Hamaker constant has been experimentally determined recently for the mica/water/mica system and was found to be \((2.2 \pm 0.3) \times 10^{-13} \) erg for \(10^4 < D < 65^4\) in fair agreement with the value given above for quartz/water/quartz system (6). Interestingly, this value is found to be independent of salt concentration below 1 M, whereas other forces such as the electrical double layer force that will be considered subsequently, are very much dependent on ionic strength, particularly in the \(10^{-5}\) to 1 M range.

**Electrical Double Layer Forces**

Most particles in liquids are electrically charged, the nature and magnitude of which are dependent on the mechanisms responsible for the charge generation on their surfaces and the properties of solids and solution comprising the system. Predominating mechanisms of charge generation on the surfaces are preferential dissolution, or hydrolysis of surface species followed by pH dependent dissociation of surface hydroxyl groups (7 to 12). Alternate mechanisms that have been proposed include dissolution of lattice ions followed by hydrolysis in the bulk and subsequent adsorption of the resulting complexes. Adsorption of other charged species that are present in the system or impurities can also give rise to a charge on the surface. Thus, for simple salts such as silver iodide, preferential dissolution and adsorption of lattice ions, \(\text{Ag}^+\) and \(\text{I}^-\) are considered to be the governing mechanism. \(\text{Ag}^+\) and \(\text{I}^-\) ions that determine the surface charge are called potential determining ions. The surface will be positively charged under low \(p\text{Ag}\) conditions and negatively charged under high \(p\text{Ag}\) conditions. The \(p\text{Ag}\) (or \(p\text{l}\)) at which the net charge of the surface is zero is called the point of zero charge (pzc). The point of zero charge is an important experimentally accessible property of the system since its location with respect to solution conditions will essentially determine the repulsion or lack of it between particles and consequently the stability of a suspension of the particles. For oxides, the hydrolysis of the surface species followed by pH dependent dissociation is considered to be the major governing mechanism and hence \(\text{H}^+\) and \(\text{OH}^-\) are potential determining ions. For salt-type minerals such as calcite and apatite, preferential hydrolysis of surface species as well as preferential dissolution of ions which is often accompanied by reactions with the solution constituents and possible uptake by the solid have been proposed to be important for determining the surface charge (10,12-16). Thus for calcite, both \(\text{Ca}^{++}\), \(\text{CO}_3^{--}\), \(\text{H}^+\), and \(\text{OH}^-\) can be considered to be potential determining ions even though \(\text{Ca}^{++}\) has not been found to exhibit all the characteristics of such ions. In contrast to the above minerals, clay minerals exhibit charge characteristics that are dependent upon the special structural characteristics of these minerals. Most natural sediments have clays in them and it is often the properties of the clay components that determine the behavior of these sediments. Also, clay is present in most ore bodies and has a major influence on the processing of ores. Clay minerals, because of their unique structure consisting of sheets of \(\text{SiO}_4\) tetra-
hedra and AlO$_6$ octahedra with possible substitutions, for example of Si$^{4+}$ with Al$^{3+}$, exhibits a negative charge on the face of the mineral platelets that is pH independent, and charge on the edges that is pH dependent due to hydroxylation and ionization of the broken Si-O and Al-O bonds at the edges. The point of zero charge in such a case is determined approximately by the algebraic sum of face and edge charges. It is interesting to note that at the point of zero charge both the sides and faces of clays can be charged. Because of these interesting heterogeneous charge make-up of clays, they show peculiar flocculation properties. For example, clay minerals under appropriate solution conditions can adhere to each other by means of face to edge attachment and give rise to the so-called card-house structure.

The charge of the mineral/solution interface can indeed be modified for controlling the flocculation by adsorption of ionized chemical species or polymer. This is possible since it is not the surface potential that is directly controlling the interactions between particles, but an interfacial potential at some distance away from the surface that the particle will have to work against as they approach each other. Control of this potential, which can be assumed for convenience to be the potential at the shear plane, known as $\zeta$-potential, is possible by adjusting the ionic composition and pH of the medium and this will be considered further subsequently.

**Steric Forces**

Steric forces arise from the overlap of the adsorbed layers and can be repulsive or attractive in nature depending on whether or not the outermost layers on the particles prefer to be in contact with the solvent. If the solvent power of the medium for the exposed portions of the exterior layer, for example those of an adsorbed polymer layer, is satisfactory, they will be compatible with the medium and the suspension will remain stable. On the other hand if the solvent power for the adsorbed layer is minimal, there will be a tendency for the exposed portions of the adsorbed layer on one particle to interpenetrate into those of a layer on another particle and thereby promote aggregation.

Interpenetration and aggregation is possible only if the net change in Gibbs free energy due to interpenetration of the polymer chains is negative (17). The Gibbs free energy change is considered in such cases to be determined essentially by the change in entropy due to release of solvent molecules and due to the decrease in randomness of the polymer chain and by the enthalpy of desolvation of the polymer chains. Briefly, for flocculation to occur according to this mechanism, the increase in entropy due to the release of solvent molecules should outweigh the loss of entropy due to interpenetration of polymer chains and increase in enthalpy of desolvation (see Figure 1). It is clear that the desolvation characteristics of the adsorbed polymer species and the dependence of it on solution properties such as temperature and ionic strength will be important in determining aggregation by this mechanism.
Flocculation under complete coverage is possible only if the free energy of interpenetration of adsorbed layers, $\Delta G_I$, is negative.

Figure 1. Flocculation by polymers under complete coverage and partial coverage conditions.
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Bridging Forces

A long chain adsorbate with several active sites on it can induce aggregation by attaching itself to two or more particles. Polymers can provide such bridging between particles particularly under conditions where particles are not totally coated by the polymeric species (see Figure 1). If particles are already fully covered with polymers, bridging can take place only if there is either detachment of some portion of the polymer already on a particle to provide sites for attachment of polymer fractions adsorbed on other particles or polymer-polymer bonding itself. It has been suggested by various authors including Healy and La Mer that maximum flocculation and filtration rates occur when the fraction of particle surface covered by polymer molecules is close to 0.5 (18-20). It is to be noted that, to this author's knowledge, this hypothesis has not, however, been experimentally proven. As indicated earlier, bridging should be possible even when particles are fully covered if some detachment and reattachment of the adsorbed polymer is possible. Adsorption of polymers is in general found to be irreversible (21,22). But in the author's opinion, that is, except in the occasional case of polymers with functional groups that form covalent bonds with the surface species, only due to the cumulative effect of adsorption of a single polymer molecule on several sites. Detachment and reattachment of portions of such a polymer should, however, be possible and such a process should facilitate bridging. Absence of bridging might then be interpreted to suggest the presence of strong repulsive steric interactions between dangling portions of the adsorbed polymers.

AGGREGATION/DISPERSION AND ROLE OF ADSORPTION IN IT

As mentioned earlier, aggregation between particles can take place if the interparticle repulsive force does not exceed in magnitude the corresponding attractive force. As it is the electrostatic force that is most often responsible for the repulsion, one can achieve aggregation if solution properties could be adjusted to minimize such forces. On the other hand, if dispersion is desired one would need to maximize the electrostatic repulsive forces between particles. On the basis of these considerations, aggregation can be expected to occur under the conditions discussed in the following sections and dispersion under all other conditions.

A. Homocoagulation

As indicated earlier, the total interactions between the particles will be determined by the summation of forces that arise from the overlap of similarly charged electrical interfaces and from that of the adsorbed layers that prefer to be in contact with the solvent.

\[ V = V_a + V_e + V_b + V_s \]

Excluding \( V_b \) and \( V_s \), the following expression can be written for the total energy of interaction between two particles separated by a distance \( H_0 \) in terms of the average Hamaker constant \( A \) and surface potential \( \psi_1 \) and \( \psi_2 \) of two particles of radii \( r_1 \) and \( r_2 \) respectively (23).
\[ V = V_a + V_e = \frac{-A \pi r_1 r_2 \alpha}{6(r_1 + r_2)H_0} + \]

\[ \frac{r_1 r_2 \varepsilon}{4(r_1 + r_2)} \left[ \psi_1 \psi_2 \ln \frac{1 + \exp(-\kappa H_0)}{1 - \exp(-\kappa H_0)} + (\psi_1^2 + \psi_2^2) \ln \left(1 - \exp(-2\kappa H_0)\right) \right] \]  

(10)

\( \varepsilon \) is the dielectric constant, \( 1/\kappa \) is the double layer thickness and \( \alpha \) is a factor that takes into account retardation of London forces under conditions of aggregation in secondary minimum indicated in Figure 2 (24). It can be seen from the above expression that \( V \) will be attractive at large and small distances since exponential of \(-\kappa H_0\) will be smaller than the inverse power of \( H_0 \) for large and small \( H_0 \). Typical variation of \( V \) as a function of distance between particles is illustrated in Figure 2. The bottom curve is for a case with negligible electrical repulsion between particles and the upper curves for conditions with increasing repulsion. On the basis of this, it is clear that one can obtain aggregation by controlling the charge on the particles so that repulsive energy between them will be less than that of the attractive energy. Healy has recently summarized zeta potential conditions to meet the above requirements (4). It has been shown that aggregation can be obtained if \(|\zeta|\) is less than about 14 mV. Zeta potential of a mineral can be adjusted in a number of ways:

![Diagram illustrating variation of V as a function of distance from the surface.](image-url)

Figure 2. Diagram illustrating variation of \( V \) as a function of distance from the surface.
1) Control of the Surface Charge by the Addition of the Required Potential Determining Ions. ex: HCl or NaOH for titania, quartz, alumina and clays; AgNO₃ or KI for silver iodide.

This method is illustrated in Figure 3 where zeta potential and stability ratios of alumina are given as functions of pH (25). Stability is minimum near zero zeta potential conditions.

![Graph](image)

**Figure 3.** Comparison of stability of alumina suspensions with zeta potential of the particles at various pH values (8).

b) Compression of the Double Layer by the Addition of Required Amounts of Inorganic Electrolytes. ex: KNO₃, CaCl₂, AlNO₃ for quartz, silver iodide, alumina, etc. The effect of the compression of the double layer is illustrated in Figure 4 where results obtained by Wiese and Healy for the addition of KNO₃ to titania suspensions are given as functions of pH (26). Zeta potential of titania is shown in this
Figure 4. Zeta potential–pH isotherms for TiO$_2$ in $10^{-2}$, $10^{-3}$ and $10^{-4}$ KNO$_3$ solutions. pH values at which rapid coagulation was observed are also shown (26).
c) Addition of Ionic Surfactants

Th adsorb on mineral particles and

The pH and lead in

The adsorption of lead in

Aluminum Dosage mol dm$^{-3}$

\begin{align*}
\text{DISPERSED} & \quad \text{DISPERSED} \\
10 & \quad 10^{-4} \\
\text{7} & \quad 10^{-5} \\
\text{pH} & \quad 9 \\
\end{align*}
chain surfactants has been attributed to lateral association between adjacent hydrocarbon chains of the adsorbed surfactant ions. Such association to form two-dimensional aggregates is analogous to micelle formation and results from the favorable energetics of the removal of the alkyl chain partially from the aqueous environment. Mineral aggregation by surfactant is illustrated in Figure 6 with alumina/dodecylsulfonate system as the example. In this figure, stability ratio (which is inversely proportional to coagulation) for this system is given along with sulfonate adsorption density and electrophoretic mobility. Similarity of the adsorption isotherm to stability isotherm is clearly evident in this figure. It should be noted that the ionic strength of the system is maintained at a constant level of 2 x 10^{-3} M under all conditions and therefore the observed changes in electrophoretic and stability isotherms is not due to the double layer compression that one normally gets with the addition of a salt. The increased adsorption of the anionic sulfonate due to the two-dimensional aggregation and consequent reduction in zeta-potential of the particles is what is considered to be mainly responsible for the observed change in stability. It is however to be noted that alumina does not disperse even after the surface charge is reduced to zero and then becomes negative. In other words, maximum aggregation is not obtained at conditions corresponding to zero zeta potential. Continued increase in aggregation even after the system has undergone charge reversal was attributed to the fact that it may be possible for particles with their surface partially covered to be bridged to each other with the help of the adsorbed surfactant species. Such an aggregation would help to remove some of the hydrocarbon chains of adsorbed surfactant molecules out of the aqueous environment and thereby lower the free energy of the system further.

Inorganic electrolyte such as sodium silicate and sodium hexametaphosphate are added often to increase the dispersion of a system. The exact mechanism by which these reagents work is not known even though it is speculated that the charge of the particle does possibly increase with the addition of these ions.

B. Heteroaggregation

Heteroaggregation between two different types of particles will also be governed by equation 10 which relates the interaction energy between the two particles to their surface potential and the Hamaker constant. Hamaker constant $A$ in this case is the average for, say, particles 1 and 2 in medium 3 and is given by

$$A = A_{12} + A_{33} - A_{13} - A_{23}$$

The easiest way to get aggregation in this system is to select conditions such that one type of particles will be charged oppositely to the other type, i.e., $\psi_1$ will be opposite in sign to $\psi_2$. James et al (31) have tested this possibility by mixing titania and $\text{Al}_2\text{O}_3$ in one
Figure 6. Settling index, adsorption density and electrophoretic mobility of alumina-sodium dodecylsulfonate system as a function of the concentration of the sulfonate (28).
case and amphoteric latex colloids in another case at various pH values; maximum coagulation was obtained when equal amounts of the two colloids were mixed at a pH that is intermediate between their isoelectric points.

Indeed, if it is dispersion between the two types that is required (as in selective flocculation), then it is achieved by selecting a solution composition that will yield the same sign for both $\psi_1$ and $\psi_2$.

C. Polymer Flocculation

Large molecules when adsorbed on the particles can essentially shift the surface of contact between them away from the original charged surface so that the electrostatic forces which might not have been originally conducive for selective aggregation, assumes a secondary role. Polymers are widely used in this manner for clarification of effluents and filtration. Adsorption of polymers on mineral particles and the effectiveness of the adsorbed polymer in promoting flocculation is dependent to a large extent on polymer properties such as molecular weight, nature and concentration of functional groups, and configuration, mineral properties, solution properties such as ionic strength and solvent power for the polymer. The effects of pH, ionic strength, solid to liquid ratio and aging of the polymer solution on the adsorption of non-ionic polyacrylamide and anionic sulfonated polycrylamide on homo-ionic Na-kaolinite have been determined recently by Hollander, Gryte and Somasundaran (21) using labelled polymers. It was clearly shown in this work that while the above parameters had minimal effect on the adsorption of polyacrylamide (except for pH which showed decreased adsorption in the alkaline range), adsorption as well as viscosity of the anionic polymer was markedly affected by the ionic strength. Similar results have been obtained recently by Tadros and Vincent for the effect of electrolytes on the adsorption of poly vinyl alcohol on polystyrene particles (32). Fundamentals of adsorption of polymers and its role in flocculation have been recently reviewed by us and salient parts of this review are presented here (33-36).

Forces responsible for adsorption result mainly from three types of bonding, i.e., electrostatic, hydrogen and covalent bonding. The predominance of any of the above mechanism over the others depends on the particular mineral/polymer system and the properties of the aqueous medium. Under favorable conditions, more than one type of mechanism can be operative.

Electrostatic Bonding. In the case of a polymer with a large number of charged units on it, electrostatic bonding is the predominant mechanism by which the polymer adsorbs on particles. Such polymers can neutralize and even cause a reversal of surface charge at very low dosages (33,34). This effect is illustrated in Figure 7. Polystyrene sulfonate adsorption on positively charged hematite particles is found to reduce the charge on it to zero and then at larger additions to make it negative. Ability of the anionic sulfonate to adsorb in amounts higher than those needed for complete neutralization and to ad-
Figure 7. Zeta potential of hematite fines as a function of concentration of sodium polystyrene-sulfonate (39).

POLYSTYRENE SULFONATE CONC., PPM (DRY SOLIDS BASIS)

ZETA POTENTIAL, MV

PH = 3.7

PH = 7.8
sorb on even negatively charged hematite particles results from the fact that there are other mechanisms in addition to electrostatic mechanism that are operative in this case.

**Hydrogen Bonding.** As mentioned above, anionic polystyrene sulfonate is able to adsorb even on negative hematite particles. Also it is well known that even non-ionic polymers can adsorb in measurable amounts on mineral particles. This is attributed to the presence of $\text{-NH}_2$ and $\text{-OH}$ groups on the polymer that can hydrogen bond with the surface oxygen species of the mineral. Flocculation by interparticle bridging follows such adsorption if the electrical double layer repulsive force between the particles is not very strong. It is to be noted that adsorption by hydrogen bonding alone is relatively non-selective and polymers that adsorb due to hydrogen bonding are therefore ideally suited for bulk flocculation rather than selective flocculation.

**Covalent Bonding.** Selective adsorption of polymers can be achieved if adsorption is due to covalent bonding between the active groups of the polymer and the cations of the mineral surface. Such flocculation of kaolin by polyacrylamides owing to the formation of salt-type compounds by reaction between the polymer and the Ca$^{++}$ ions present on the kaolin has been reported by Michaels and Morelos (40). A good example in this regard is the flocculation of chalcopyrite that is obtained by the addition of hydroxypropylcellulose xanthate (see Figure 8) (33, 41). Xanthates are known to chemisorb on chalcopyrite and evidently the better performance of the cellulose xanthate on chalcopyrite than on quartz is due to similar chemical adsorption of the xanthated polymer on the chalcopyrite particles.

**Kinetics of Adsorption.** Rate of uptake of polymer by minerals is governed mostly by the diffusion of the polymeric species to the surface of the particles and its pores, which in turn is influenced by the molecular weight, structure, and configuration of the polymer molecule, polymer concentration, agitation, temperature, ionic strength, and pH (42). As can be expected, the rate of adsorption increases with increase in agitation and polymer concentration (42, 43). The increase in molecular weight of the polymer, on the other hand, has been reported to produce an increase in some cases and a decrease in rate of adsorption in others (44-46). In general, when the suspending medium is a poor solvent for the polymer, the rate of adsorption of the polymer is greater. Both the kinetics and the extent of adsorption are very much dependent on the porous nature of the particles. Equilibrium is attained of course only slowly if the particles are porous (47, 48). It is interesting to note that with porous particles, the extent of adsorption can vary also due to any change in configuration (coiling) that the polymer might undergo with changes in solution properties such as pH and ionic strength.
Figure 8. Percentage solids settled of chalcopyrite fines and quartz fines as a function of concentration of hydroxypropylcellulose xanthate (39).
As mentioned earlier, flocculation is dependent both on the probability of collision and the probability of adhesion. Some of the factors that govern the probability of adhesion have been discussed earlier. Probability of adhesion during collision can be enhanced also by providing sufficient kinetic energy by means of stirring, this effect being particularly dependent on the size of particles. For particles that are larger than 1 micron, kinetic energy provided by stirring can be high enough to overcome the electrostatic repulsion energy. This becomes evident upon examining the results of Warren given in Table 2 (4).

Table 2. - Energies of particles in suspension due to various interactions (4).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 μm</td>
</tr>
<tr>
<td>van der Waals attraction</td>
<td>-10 kT</td>
</tr>
<tr>
<td>Electrostatic repulsion</td>
<td>0-100</td>
</tr>
<tr>
<td>Brownian motion</td>
<td>1</td>
</tr>
<tr>
<td>Kinetic energy of sedimentation</td>
<td>10(^{-13})</td>
</tr>
<tr>
<td>Kinetic energy of stirring</td>
<td>-1</td>
</tr>
</tbody>
</table>

Under turbulent conditions, collisions can occur either due to diffusion while entrained in eddies or due to inertia. Levich's theory predicts the collision rate under turbulent conditions, \(J_{turb}\), to be

\[
J_{turb} = 12\pi \beta r^3 n_1^2 \left( \frac{\varepsilon_0}{\nu} \right)^{\frac{1}{2}}
\]

where \(\beta\) is a constant, \(n_1\) is the initial concentration of particles, \(\varepsilon_0\) is the energy loss per second per unit volume, and \(\nu\) is the kinematic viscosity. Interestingly, under conditions selected by Warren (49) on the basis of the above formula for equal collision rates between fines and fines and between fines and coarse, greater aggregation was observed by him between coarse and fines than between fines and fines. It was suggested that the probability of adhesion is larger for collision between a coarse and a fine particle than between two fine particles.

It is to be noted that the type of mixing and agitation can affect flocculation using polymers significantly also because of the effect of
agitation on the distribution of the polymer uniformly in the pulp. In this regard, the point of addition of the polymer, the concentration of the polymer solution and the manner of addition can be expected to have an influence on the polymer uptake and flocculation.

SELECTIVE AGGREGATION OR DISPERSION

The extent of selective aggregation or dispersion that can be achieved with minerals depends on the liberation of individual mineral particles from each other and adsorption of flocculants on one or more, but not all, mineral types followed by their aggregation. Separation of the flocculated particles from the others can then be achieved by using conventional techniques such as flotation, elutriation or sedimentation with care to produce minimum redispersion of flocs during such processes. In the case of flotation, it is also necessary to take into account the interactions of flocculants with flotation agents.

An examination of various particle-particle interactions discussed earlier suggests following criteria for selective interactions (aggregation or dispersion) between, say, particles of component in a mixture of 1 with many other component minerals (2, 3, etc.)

1. Particles of one should carry a charge similar to as many other major minerals as possible so that there will be no aggregation between them. The magnitude of the charge should be such that the repulsive energy will be larger than the attractive energy. As mentioned earlier, the zeta potential of the particles should be greater than 15-20 mV in magnitude. \( |\zeta_1| > 15 \) to 20 mV; \( \zeta_1/\zeta_2 = + \).

2. Charge on the particles to be aggregated, say, of component 1, should be such that the repulsive energy between them will be less than the attractive energy. For this zeta potential of these particles should be, at least after adsorption of the coagulants or flocculants, less than 15 mV in magnitude. \( |\zeta_1| < 15 \) mV. An apparent contradiction with requirement 1 is evident now since it requires \( |\zeta_1| \) to be greater than 20 mV. This requires, at least in principle, that \( |\zeta_1| \) be, say, near 10 mV and \( |\zeta_2| \), to counteract the reduction of potential on particle 1, be about 30 mV or so. It is interesting to note that in practice, however, selective aggregation is rarely obtained even when solution conditions meet the above requirements (35).

3. Adsorption of coagulants or flocculants should be selective. In this regard, it might even be sufficient to have differences in just the rate of adsorption of reagents on various minerals components. In such a case, the differences in kinetics have to be utilized by optimizing reagentizing times for different polymer concentrations.

Reagents that are used for inducing selectivity include polymers, dispersants and activators. Adsorption of polymers is usually not as
selective as that of surface active or inorganic reagents. Partly this is due to the hydrogen bonding nature of the polymer adsorption. Selective adsorption of polymer molecules can be achieved by adjusting the chemical composition of the suspending medium and thereby the surface potential on the mineral or by introducing into the polymer active functional groups that will form complexes or salts with the metal species on the surface of the desired mineral. In the former case the dependence of adsorption of ionic polymers on surface charge is exploited. The dependence of polymer flocculation on electrostatic interaction is clearly illustrated in Figure 9 which gives data for settling of flocculated silica in the presence of cationic Nalcolyte-610 and anionic Separan AP-30.

It can be seen that only the cationic Nalcolyte is able to produce any significant flocculation of the negatively charged quartz particles. Based on such a premise, selective separation of quartz from its mixtures with hematite, calcite, etc. has been achieved by several investigators (50-52) using, for example, anionic polyacrylamide.

As mentioned earlier, selective flocculation can also be obtained by incorporating groups that can form covalent bonding with the mineral surface species. It is well known that adsorption of collectors on minerals depends on the presence of functional groups such as carboxy-
late and mercaptan in them. It should be possible to obtain selectivity during flocculation by incorporating such groups that are already known to adsorb selectively. Such an approach has been successfully tested in the past by a number of workers (33,38,40,53-55). For example, tests with hydroxypropylcellulose xanthate containing mercaptan as the active group has been observed to produce good flocculation of chalcopyrite with practically no effect on quartz (see Figure 8). Results of tests with synthetic mixtures of these minerals are shown in Figure 10 as a function of concentration of the xanthate (39). An excellent separation index of 0.75 was obtained after a one-stage cleaning operation in which quartz particles that have been trapped in the bulk chalcopyrite flocs, particularly at high polymer concentrations, were washed away.

**Activators and Dispersants**

Selective flocculation or dispersion of natural ores is often made difficult owing to interference from the dissolved ions. Like in the case of flotation, additives that can complex with such dissolved ions or adsorb on mineral particles selectively to modify them can be used to enhance selectivity in such cases. Thus, separation of hematite-quartz mixtures using anionic polyacrylamide has been reported to be promoted by the addition of Calgon (principally sodium hexametaphosphate) and sodium fluoride (56). Similarly, flocculation of heavy minerals has been depressed by the addition of sodium sulfide, polyphosphates and polyacrylates (41). Polyphosphates and polysilicates are widely used also as bulk dispersants. Such dispersants are particularly effective when excessive slimes are present in the system since these colloidal particles do have a tendency to coat the mineral particles and thereby reduce the selectivity of a flocculation operation (57).

In this regard it is important to note that selection of any dispersant has to be made so that there will be minimum interference by these reagents on subsequent adsorption of flocculants. Indeed all these reagents including the flocculant itself should not interfere with any downstream process such as flotation, filtration or pelletizing.

An interesting new approach of activation has been recently developed by Rubio and Kitchener to induce selectivity in flocculation (58). Selective flocculation was obtained by these authors using 'hydrophobic polymers' on minerals that are preconditioned with surfactants to produce a hydrophobic surface.

**Spherical Agglomeration**

Minerals reagentized with surfactants can also be aggregated using oil. In this process, fines when tumbled in an aqueous solution containing oil aggregate due to the formation of capillary bridges between surfactant coated particles. Such aggregation has been obtained by Puddington et al (59,60) for graphite, chalk, zinc sulfide, coal,
Figure 10. Separation index achieved in selective flocculation of chalcopyrite-quartz mixture as a function of concentration of hydroxypropylcellulose xanthate (39).
iron ore and tin ore in aqueous solutions. Similarly good separation has been reported by Read and Hollick (57) for a lead/zinc ore where the slime fraction of the ore was dispersed by a combination of sodium silicate, sodium carbonate, and a polyacrylate and subsequently conditioned with copper sulfate and then potassium amylxanthate.

**Carrier Flotation**

A selective aggregation process, known as carrier flotation as well as ultrafloation and piggy-back flotation, has been successfully used for more than fifteen years for the removal of anatase impurity from kaolin (61). In this method an auxiliary mineral is used as a carrier for the fine particles to be separated. The carrier particles are coarser than the material to be floated. It is speculated that the fines form a coating on the carrier mineral and are then floated along with the coarser carrier particles. Recently Wang and Somasundaran (62) have obtained evidence that anatase can be floated without the carrier also even though to a lesser degree than in the presence of the calcite carrier. Carrier calcite particles activate the process apparently both due to the action of dissolved calcium and due to the enhanced size-dependent aggregation between the calcite particles and anatase particles (62).

**Closing Remarks**

In principle, bulk as well as selective flocculation and dispersion of almost all minerals should be possible by the control of the ionic composition of the pulp, pre-treatment and pre-conditioning of the mineral and by the use of properly modified polymers, activators and dispersants. While basic mechanisms governing such aggregation or dispersion in simple mineral systems are fairly well understood, very little is known on the behavior of complex natural ore systems. Major problems that exist in the area of aggregation, dispersion, and selective aggregation have been discussed in detail by the author recently (63,64,34). It has become very clear that interactions that are of serious consequences do occur in multi-mineral systems and that it is essential to fully develop our understanding of such interactions, particularly of minerals with dissolved mineral species as well as those of minerals and reagents with dissolved ions that are naturally present in plant water.

**Acknowledgment**

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Geologically the Indian coals belong to Gondwana formations. Being of drift origin, these coals contain high percentage of mineral matter distributed in finely disseminated form. Indian coal-preparation plants process prime coking and medium coking coals for use in steel plants. Limited resources of good quality coking coals (Table 1) could not keep pace with the rapid developments of the iron and steel industry in India. This resulted in the introduction of coal-preparation technology and the establishment of washeries in India in the last 30 years or so. The first four washeries were set up during the early fifties at West-Bokaro, Jamadoba, Lodna and Kargali. Next came the first non-coking coal washery at Morozabad set up by the Associated Cement Company. In 1961, following the recommendation of Central Coal Washeries Committee (1953-54), Hindustan Steel Ltd. had set up five central washeries at appropriate locations, viz. Durgapur, Duga (2 washeries), Fatherdih and Bhojpur, so that the raw coal feed having similar washability characteristics can conveniently come from a number of collieries to a particular washery. Subsequently, to meet the increasing demand of metallurgical coal by steel plants, two more central washeries (at Durgapur and Chasinal) and three pit-head washeries (at Kathara, Swang and Giddi) were installed by 1970. The prime objective of washing Indian coking coal is essentially to reduce the ash content.

All the washeries in India, taken together have an installed capacity of about 26 million tons of raw coal input per annum. Details of these washeries in respect of their annual capacity, main washing systems adopted and the nature and size of the products are given in Table 2. It can be observed from this table that (1) bulk of the coal is processed in units like jigs, HM baths and NH cyclones; (2) only two of the washeries have cleaning circuits for treatment of fines.