APPLICATIONS OF POLYMERS IN MINERAL PROCESSING

P. Somasundaran, Y.H.C. Wang and S. Acar
School of Engineering and Applied Science
Columbia University
New York, N.Y. 10027, U.S.A.

Polymers are being recently used in mineral processing for flocculation of fines, selective flocculation-flotation for beneficiation of finely dispersed ores and thickening. There is also developmental work for their use as grinding aids. While in majority of cases bulk flocculation is sufficient, polymers which interact selectively with desired minerals are required in flocculation and flotation. Interaction of polymers with minerals is a complex function of system variables such as pH, ionic strength and mode of addition. In addition in heterogeneous mineral systems it is also influenced by the presence of dissolved mineral species. In this paper the principles governing these interactions will be discussed along with recent applications in the processing of various minerals.

INTRODUCTION

Polymers are being increasingly used in recent times in various mineral processing operations including flocculation and dewatering, effluent treatment and selective flocculation and flotation. They have even been shown to have significant effect in the grinding of minerals. In many of these operations, their performance is governed to a large measure, by their adsorption on mineral surfaces. Adsorption of polymers on minerals itself is governed by a multitude of system properties such as pH, ionic strength,
temperature, zeta potential and surface hydration of the solid, and molecular weight and nature and charge of the functional groups of the polymer. In natural mineral systems, in addition, the interaction of polymers with mineral surface is also influenced by the presence of dissolved mineral species. The effect of a few of the above parameters has been studied for a limited number of systems (1-21) but there is not enough information on the mechanisms by which all the relevant variables determine either their adsorption on minerals or the flocculation that results from it.

In this paper, some of the major applications of polymer adsorption in mineral processing will be discussed along with problems involved reviewing material presented elsewhere (22-29).

Need for Polymer Use

In mineral processing, more and more fine and ultrafine mineral matter is being currently mined and beneficiated. Considerable amount of fine waste is also produced during the processing of such mineral matter. These wastes in the form of slimes and sludges are not easily disposed and contain a large amount of valuable minerals in it. For example, 5 billion tons of phosphate values have been estimated to be lost in phosphatic clay wastes till now and every year about 40 million tons of slimes is discarded. In addition to the values lost in the slimes, a serious environmental problem results from this since the slime cannot be dewatered to an acceptable solid content. Many methods have been tried to dewater these wastes, but techniques involving use of polymers appear to hold most promise.

Similar problems also occur in the processing of copper, tin, tungsten, coal and iron both in terms of values lost and the slimes and sludges produced.

Traditional techniques do not work efficiently for recovering values from ultrafine material and it has become necessary to develop new techniques. A technique that has been successfully used for at least two mineral systems is selective flocculation using polymers followed by flotation. However satisfactory polymer and processing schemes have not been found for use in other systems where the fine particle problem
exists. Successful application of selective flocculation in these cases will depend to a large extent on the development of polymeric flocculants with functional groups that will lead to selective adsorption of the polymers on one or more of the many minerals in the system. Development of such reagents will in turn depend on a full understanding of the mechanisms involved in polymer adsorption and resultant flocculation or dispersion.

**Polymeric Flocculation**

Physico-chemical interactions that are important in determining flocculation are composed of the Van der Waals attractive forces, electrical double layer forces that can be attractive or repulsive in nature, bridging forces between adsorbed polymer species and particle surfaces, and steric forces that arise from the overlap of the adsorbed layers which also can be attractive or repulsive in nature (26).

While Van der Waals forces arise from London dispersion forces, Keesom interactions between permanent dipoles and Debye interactions between permanent and induced dipoles and the electrical forces arise from the charging of the particles in solution, bridging forces result from the possibility that a long chain adsorbate with several active groups on it can induce aggregation by attaching itself to two or more particles. It has been considered that this type of aggregation can take place only when particles are partially covered with polymers. This hypothesis has not however been experimentally proven. In fact, bridging should be possible even when the particles are fully covered if some detachment and reattachment of the adsorbed polymer is possible. Even though polymers have been considered in the past to adsorb irreversibly, desorption has been achieved recently under special conditions (29). Steric forces arise from the overlap of the adsorbed layers and can be repulsive or attractive in nature depending on whether these layers prefer to be in contact with the solvent or not. If the solvent power of the surrounding fluid for the adsorbed layer is minimal, then the layers on different particles will show a tendency to interpenetrate into each other and thereby promote aggregation of the particles. On the other hand, if the solvent power is high, then the adsorbed layers will prefer to be in contact with the
medium and there will neither be interpenetration of the adsorbed layers nor any aggregation. The interpenetration of the layers will take place if the free energy of interpenetration of polymeric chains into each other is negative. For this condition to be met, the increase in entropy due to the release of solvent molecules upon any desolvation of the polymers should predominate over the loss of entropy of the polymeric chains themselves and the increase in enthalpy due to the desolvation. Since this process is an entropic phenomenon, it is clear that the temperature will have a major role to play. The ionic strength level will also have a great influence. Ions due to their hydration will make fewer water molecules available for solvation for the polymers and this will essentially impart a tendency to the polymer to precipitate and to interpenetrate. On the basis of considerations of the above forces, one can derive conditions for flocculation and means for controlling the extent of it.

The most common method used for flocculation involves use of polymers. Such large molecules when adsorbed on the particles can, essentially shift the surface of contact between them so that the electrical nature of the interfaces, which might not have been originally conducive to aggregation, assumes a secondary role. It can be seen from Figure 1 that the zeta potential of both the positively and negatively charged hematite fines is reduced to a small value that is characteristic of the polymer. Under this condition, the coated particles will not repel each other and hence can be expected to flocculate. Indeed, the efficiency of polymeric flocculation can be expected to depend on, in addition to the extent of the adsorption of polymers, also the configuration of the adsorbed species.

Polymer adsorption on minerals itself is a very complex process since it is influenced by a number of polymer properties, mineral properties and solution properties. Forces responsible for polymer adsorption arise mainly from electrostatic, hydrogen and covalent bonding.

**Polymer Charge**

In the case of a polymer with a large number of charged units, electrostatic bonding can be a major
factor. The role of electrostatic forces in determining adsorption and flocculation is clearly seen in Figures 2 and 3 (30). It can be seen that both the adsorption and flocculation as determined by settling rate decrease with increasing anionicity of the polymer. The effect of the anionicity on adsorption is as expected for this since the negative charge on the copolymers should produce a reduction in this adsorption of the negative kaolinite particles. Flocculation under constant dosage conditions used here also decreased with increase in anionicity but it should be noted that the optimum dosage and the flocculation under such conditions can be different for each polymer.

**Ionic Strength**

The explanation based on the electrostatic interactions between the similarly charged polymer and the mineral particles is supported by the ionic strength effects seen in Figure 4. When the ionic strength of the solution is increased, the adsorption of the anionic polymer increases and becomes equal to
that of the nonionic polymer at 1 kmol/m$^3$ NaCl. The adsorption of the nonionic polymer itself is not affected to any significant extent by the ionic strength increase. Evidently under the high ionic strength condition, the electrostatic repulsion is eliminated by the compression of the double layer and the adsorption of the nonionic and the anionic polymers becomes identical to each other.

**pH**

On the basis of the electrostatic consideration pH also can be expected to have a larger effect on the adsorption of the anionic polymer. This is indeed found to be the case of the adsorption of the polyacrylamide and its sulfonated copolymer. (See Figure 5). Under alkaline and high temperature conditions, adsorption of the nonionic polyacrylamide was found to be reduced and as suggested by the observed increase in viscosity of the polymer solutions, this effect is considered to be due to the hydrolysis of the polymer.
In addition to the chemical variables, hydrodynamic conditions can also be expected to affect flocculation. The type of mixing used can be critical owing to the effect of the resultant 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, flocculation and even subsequent break-up of the flocs.

As indicated earlier, the nature of the flocculation of fines obtained in polymer solutions is dependent upon a number of factors including polymer characteristics, solid and solvent properties as well as the hydrodynamic conditions used during the flocculation and preflocculation stages. It is to be
Figure 4. Equilibrium adsorption of polyacrylamide (PAM) and sulfonated polyacrylamide (PAMS) on kaolinite as a function of ionic strength (31).

Figure 5. Comparison of the pH effect on the adsorption of polyacrylamide (PAM) and sulfonated polyacrylamide (PAMS) on kaolinite (22).
Figure 6. Various flocculation responses together with adsorption obtained with Na-kaolinite at pH 4.5 as a function of polyacrylamide (PAM 0.4-0) dosage (23).

noted here that different properties of the flocculated systems can be the determining criterion in different processes. For example, whereas supernatant clarity will be important when water is to be recycled, it can be the sediment volume or the settling rate that will be important in effluent treatment. For filtration, on the other hand cake strength and cake moisture content can be the important parameters. Different factors (see Table 1) can be manipulated in the system depending on which property is to be optimized.
For example, in a recent study (23) of the flocculation of kaolinite clay using polyacrylamides it was clearly seen that optimum polymer concentration and anionicity depended on the flocculation property studied (see Figure 6-8). Both the settling rate and the supernatant clarity with the nonionic polyacrylamide flocculent showed at pH 4.5 a marked increase to a maximum at about 25 mg/kg, whereas with the anionic polymer settling rate and supernatant clarity showed maxima at 10-25 mg/kg, but the system was totally dispersed at high concentrations. Sediment volume did not show any measurable change over the entire concentration range of nonionic polymer. In contrast, with the anionic polyacrylamide

\[ \text{Figure 7. Various flocculation responses together with adsorption obtained with Na-kaolinite at pH 4.5 as a function of 33\% hydrolyzed polyacrylamide (HPAM 0.4-33) dosage. (23)} \]
Table 1. Factors in Flocculation

Polymer Type
- Polymer Dosage
- Polymer Concentration
- Temperature
- pH
- Ionic Strength
- Use of Two or More Polymers and Order of Addition
- Method and Speed of Mixing of Polymer with Suspension

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Polymer Dosage</th>
<th>Polymer Concentration</th>
<th>Temperature</th>
<th>pH</th>
<th>Ionic Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLYACRYLAMIDE (MW = 0.4 x 10^6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-KAOLINITE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl = 10 mg/L</td>
<td>I = 3 x 10^{-4} mmol/mL NaCl</td>
<td>pH = 4.5 ± 0.2</td>
<td>S/L = 0.025</td>
<td>COND. TIME = 10 min</td>
<td></td>
</tr>
<tr>
<td>T = 24 ± 2°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8. Diagram illustrating the effect of polymer charge density on various flocculation responses of Na-kaolinite at pH 4.5 (23).
(33% hydrolyzed) both the sediment volume and the
slurry viscosity showed increases with polymer
concentration in the 0 to 50 and 25 to 50 mg/kg ranges
respectively. Viscosity and sediment volume, however,
remained at the highest levels up to the highest
tested concentrations of anionic polymer. The
different effects of polymers on the above responses
were discussed in terms of various characteristics of
flocs and floc-aggregates. While settling rate and
percent solid settled can be expected to be governed
essentially by the coarser region of the particle size
distribution, by the density and compressive strength
of the flocs, and by the structure of any three
dimensional networks that can trap the fluid, the
supernatant clarity will depend on any shift in the
fine region of the size distribution and on the
ability of the polymers and the network to capture the
ultrafines and colloids. Sediment volume and slurry
viscosity on the other hand can depend on, in addition
to the floc size distribution and the compressive
strength of the flocs, also the thickness of the
adsorbed layers of the polymer on the particles.

All the measured responses were sensitive to the
anionicity of the polymer used as the flocculent.
Settling rate showed a maximum with 0% hydrolysis and
the supernatant clarity exhibited a maximum in the 0
-20% hydrolysis range. While the anionicity did not
have a significant effect on the viscosity in the 0 -
20% range, further increases in anionicity produced a
measurable decrease in viscosity. These effects were
accounted for in terms of electrostatic interactions
between the polymer layers on the particles and
alterations in the configuration of the adsorbed
polymers due to the presence of the charged groups.
In this study, flocculation was correlated also with
both adsorption density and estimated surface coverage
for the nonionic and 33% hydrolyzed polyacrylamides.
Maximum settling rate was obtained with the nonionic
floculent at 0.1 and with the hydrolyzed sample at
0.2 surface coverage. Supernatant clarity showed a
maximum at a surface coverage of Na-kaolinite by the
hydrolyzed polyacrylamide of 0.1. At higher surface
coverages (such as 0.5) considered in the past to be
optimum for flocculation, complete dispersion was
obtained with both the nonionic and the anionic
polymer.
Clearly, the polymer properties have a major effect on the type of flocculation obtained. Additional work is indeed needed to establish the effect of many other types of cationic, nonionic and anionic co-polymers as well as block-polymers.

Selective Flocculation or Dispersion

The extent of selective flocculation or dispersion that can be achieved with minerals depends on the selective adsorption of flocculants on one or more, but not all, mineral types followed by their aggregation (24). Separation of the flocculated particles from the others can then be achieved by using conventional techniques such as flotation or sedimentation. In the case of flotation, it is necessary to take into account the interactions of flocculants with flotation agents.

Flocculant 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 illustrated in Figure 9 which gives data for settling of flocculated silica in the presence of an anionic and a cationic polymer. It can be seen that only the cationic polyelectrolyte 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 (32-34) 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 carboxylate 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 (35-40). 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 10). Results of tests with synthetic mixtures of these minerals are shown in Figure 11 as a function of concentration of the xanthate (41). 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.
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 (42). Similarly, flocculation of heavy minerals has been depressed by the addition of sodium sulfide, polyphosphates and polyacrylates (43).
Applications of Polymers in Mineral Processing

Separation index achieved in selective flocculation of chalcopyrite-quartz mixture as a function of concentration of hydroxypropylcellulose xanthate (41).

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 pelleting. Selective flocculation has been successfully used recently on a commercial scale for the beneficiation of low grade iron ore. This process uses starch which flocculate the hematite leaving the quartz and silicates dispersed. The commercial use of this technology is, however, currently limited to beneficiation of the Tilden iron ore and to that of potash in a Cominco...
plant in Saskatchewan, where clay flotation is achieved by the joint use of a synthetic flocculant and a cationic collector. Even though the process appears to hold potential for other ores, various problems existing both at the basic and applied level will have to be solved before this potential can be fully realized. For example, a major problem is that most of the currently available long chain polymers are bulk flocculants and lack the desired specificity. As mentioned earlier, specificity can, however, be introduced by incorporating active groups into the polymers. However, past work on selective flocculation using such modified polymers deals mostly with binary mineral systems in which the valuable mineral was a metal sulfide (galena, pyrite or sphalerite), or a metal or its oxide (hematite, chromite, iron and titanium) and the other component was a gangue minerals. Kitchener et al. (44,45) have claimed selective flocculation of sulfide minerals with mercaptan substituted polyols (xanthates). However, use of high molecular weight polymers with substituted mercaptan groups or other specific metal chelating groups as selective flocculants appears to be limited. One such use is that of Claus and et al. (46) who reportedly obtained selective flocculation of cassiterite from quartz-cassiterite mixtures under certain conditions using hydroxamic acid substituted polyacrylamide. Mechanisms involved in such processes are, however, largely unestablished.

Reports of separation by selective flocculation of multi-component natural ores themselves are scant. Commercial applications mentioned earlier, Carta et al (47) reported a study on the beneficiation of ultrafine fluorite from latium. For most systems, however, selective flocculation is not easily achieved even under conditions when excellent selectivity is expected. This fact becomes easily evident upon examining, for example, the results obtained by Usoni et al. (48) during their investigation of the selective properties of anionic, cationic and nonionic polymers as flocculants for several minerals individually and then in combination with each other. They observed the prediction of selective flocculation on the basis of the results from single mineral tests to agree fairly well with the results obtained for pyrite-quartz and sphalerite-quartz mixtures using nonionic separan but to fail for mixtures of galena-quartz and sphalerite-quartz using anionic
Aerofloc or Hercules CMC and for the mixture of Smithsonite-quartz even with separan which had worked for all other mixtures. Nature of such interactions between minerals is an important problem that deserves a detailed study.

Another problem of major importance on which almost no basic work has been reported, is the effect of addition of reagents such as flocculants on subsequent operations such as flotation, filtration, and possibly even pelletizing. Usoni et al. have in fact shown that polymers can enhance or depress flotation depending on the nature, concentration and duration of contact of the polymers with the mineral. With regard to effects of flocculants on filtration, major setbacks can result if the yield strength of the flocculated product is not maintained at a level that can prevent deterioration of permeability during filtration.

Concluding Note

Evidently, the potential of the selective aggregation flocculation using polymers is enormous, but the above discussion clearly shows also the enormous gap in our basic understanding of them. Extensive research on interactions between polymers and different type of minerals can prove very fruitful in realizing this potential.

ACKNOWLEDGEMENT

The author acknowledges the support of the Thermodynamics Multiphase and Particulate Processing Program of the National Science Foundation (CPE-83-18163).

REFERENCES


3. Tadros, T.F., J. Colloids Interface Sci. 6 (1978), 36


Somasundaran, P., J. Colloids Interface Sci. (1969), 557


Heller, W., Pure Appl. Chem., 2, (1966), 249


Wang, Y.H.C. and Somasundaran, P. Unpublished Results


Tilton, R.C., Murphy, J., and Dixon, J.K., The Flocculation of Algae with Synthetic Polymeric Flocculants, Water Research, 6, (1972), 155


