Controlled Adsorption of Surfactant and Polymer–Surfactant Mixtures for Enhanced Separation/Beneficiation of Minerals

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Surface characteristics of solids are often complex due to changes during particle preparation as well as interactions with the surrounding environment. The key to their separation and beneficiation lies in manipulation of the surface characteristics by treatment with selected reagents. Controlled adsorption of surfactants, polymers or a combination of both can modify the surface of the mineral to achieve the desired results. Alteration of surface properties of phosphate ores and metal oxides using such methods as adsorption and dissolution is discussed in this paper. Responses to these treatments are examined using flotation, dissolution and fluorescence spectroscopic techniques.

INTRODUCTION

A continuously increasing demand for high purity minerals and high performance materials with the concomitant decline of high quality raw materials has led to the need for developing means for exploiting low grade and complex ore deposits as well as wastes. Complex minerals such as phosphates and clays, unlike simple sulfide and oxide minerals, consist of multi-element components with complicated structure and consequently exhibit unusual surface properties. Usually, controlled adsorption of surface modifying reagents, such as polymers and surfactants, has been used in a number of mineral-surfactant systems to design separation techniques for the recovery of mineral values. These schemes and processes, which have been very successful for simple minerals, often fail when applied to complex mineral systems. In complex mineral systems the behavior of the constituent minerals is often very different from that predicted based on their distinct individual properties. For example, it has been shown that the surface chemical, electrokinetic and dissolution properties of the constituent minerals in phosphate ores become similar and hence the predictions for separation based on single mineral tests are often not realized. The fact that many of the major minerals are semi-soluble further complicates the matter. The resultant dissolved mineral species in solution undergo reactions such as hydrolysis, complexation, adsorption and even surface or bulk precipitation. It
Figure 1 Adsorption of Ethoxylated Sulfonate on and the Resultant Flotation of Francolite (A) and Dolomite (B)
identically, interactions between ethoxylated sulfonate and potassium oleate at the solid-liquid interface play a major role in determining the recovery and selectivity of francolite/dolomite. Even though the mechanisms involved are not fully understood, it is also clear that elimination of non-selective precipitation leads to higher and more selective recoveries.

Microflotation of 1:1 binary mixtures of dolomite and francolite using oleic acid and ethoxylated sulfonate at pH 5 resulted in 92% dolomite recovery with 77% grade in the float fraction. The francolite recovery was only 28% and thus, unlike the case when potassium oleate alone was used, the selectivity predicted from single mineral flotation studies was realized in mixed mineral flotation.

Surfactants with phosphorus containing anionic pendant groups are also used as flotation reagents for phosphate minerals. Since ethylene oxide groups on sulfonate surfactants were effective in selectively floating dolomite from francolite, the effect of ethoxylation on phosphate surfactants was next studied. The surfactant selected was di-(poly ethylene glycol p-nonyl-phenyl)-phosphate.

The adsorption of this ethoxylated phosphate on francolite and dolomite is given in Figure 4. The corresponding flotation of the single minerals is shown in Figure 5. Adsorption of ethoxylated phosphate on dolomite is higher than that on francolite and as a result of the flotability of dolomite is greater than that of francolite. At
an ethoxylated phosphate concentration of 20 μm and a pH value of 6.0, it should be possible to selectively float dolomite from francolite. Flotation of a binary mixture of dolomite and francolite using ethoxylated phosphate showed that 85% dolomite recovery with 81% grade can be achieved, suggesting that ethoxylated phosphate has great potential as a collector for the beneficiation of dolomitic phosphate ores. Analysis of dissolved ionic species indicated that Ca and Mg levels remained constant over the entire concentration range studied.

The results presented illustrate the fact that selective flotation of complex minerals can be achieved by preventing non-selective precipitation of surfactant complexes on mineral surfaces. Ethoxylation of sulfonates and phosphates raises the salt tolerance of the surfactants and also selectively floats dolomite from francolite/dolomite mixtures.

POLYMER–SURFACTANT INTERACTIONS

So far, the discussion has centered on complex minerals, but surface modification has also many other related applications in several fields. Poly (ethylene oxide) has served as an effective flocculant in several systems because of its phenomenal characteristics with respect to water solubility and availability in a wide range of

FIGURE 4 Adsorption of Ethoxylated Phosphate on Francolite and Dolomite

\[ \text{pH} = 6 \text{ to } 7 \]
\[ \text{I.S.} = 0.002 \text{ M} \]
molecular weights. It has been reported that poly (ethylene oxide) is ineffective as a flocculant for hydrophilic materials such as rutile, quartz and alumina. Attempts were made in this study to modify the surface of alumina in order to render it compatible with poly (ethylene oxide). Fluorescence spectroscopy was used as the in-situ probing technique. The polymer was end-labeled with a fluorescent probe, pyrene. The excimer formation tendency of pyrene was exploited to study the conformation of the polymer. If the polymer is stretched, the pyrene molecules at the ends of the polymer chain will be too far apart to interact and form an excited dimer (or excimer) and the emission will be only from the excited monomer. On the contrary, if the polymer is coiled, the two pyrene molecules will be close to each other and significant excimer formation will be observed in addition to emission from the monomer. The ratio of the excimer intensity, $I_e$, to the monomer intensity, $I_m$, is used as an indication of the extent of coiling of the polymer and will be called here as the coiling index. By maintaining a dilute polymer solution, intermolecular excimer formation can be avoided; all excimer formation is then intramolecular and a true indicator of polymer configuration.

It is well established in literature that sodium dodecylsulfate adsorbs strongly on alumina and that there can be significant interactions between poly (ethylene oxide) and sodium dodecylsulfate in bulk solution. It remains to be seen as to what effect the interactions between poly (ethylene oxide) and sodium dodecyl-
of soloids (hemi-micelles) has altered the conformation of the adsorbing polymer. It was also found that there was near complete adsorption of poly (ethylene oxide) once soloids (hemi-micelles) were formed at the interface. The amount of poly (ethylene oxide) adsorbed should be determined in order to further understand the processes involved. The above observation is significant for achieving the adsorption of polymers onto solids where they otherwise may not adsorb. In addition, this can have important application in controlling the stability of colloidal dispersions. It has been shown that maximum flocculation of alumina dispersions can be achieved by forcing the conformation of the adsorbed poly (acrylic acid) to change from coiled to stretched. Earlier studies have shown that interactions between a cationic polymer and an anionic surfactant can be used for the flotation of anionic quartz using an anionic surfactant. A similar study was undertaken to determine the effect of preadsorbed poly (ethylene oxide) on the adsorption of sodium dodecylsulfate on silica. Poly (ethylene oxide) adsorbs strongly on silica, but sodium dodecylsulfate does not adsorb on silica above pH 3.1. The adsorption of poly (ethylene oxide) on silica is of the high affinity type and is shown in Figure 8. Up to an initial concentration of 100 ppm all the polymer was adsorbed and no residual polymer was left in solution. In the present investigation, increasing amounts of sodium dodecylsulfate

FIGURE 7 Conformation of Pyrene-labeled Poly (ethylene oxide) on Alumina in the presence of preadsorbed Sodium dodecylsulfate (----SDS Adsorption)
SUMMARY

The results discussed clearly show that the natural surface properties of a mineral need not be a limiting factor in its separation from its associated minerals. By judicial control of the adsorption of polymers and/or surfactants, it is possible to manipulate the surface of the mineral to achieve the desired properties and results. Surface modification of complex minerals such as francolite and dolomite as well as simple minerals such as alumina and silica has been demonstrated by using reagent schemes made up of selected combinations of surfactant and polymers.

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References