CHAPTER 12

Role of Surface Chemistry of Phosphate in Its Beneficiation

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ABSTRACT

The beneficiation of phosphate is complicated due to its sparingly soluble nature. The surface properties of phosphate and associated minerals are determined, in addition to the ionic composition of the solution, by the dissolution of the lattice ions of the minerals and subsequent complexation, hydrolysis, adsorption, and precipitation of the dissolved species. These, in turn, are influenced by the pretreatment of the mineral. These complex interactions determine the interfacial properties of phosphate and associated minerals and thereby the efficiency of beneficiation processes such as flotation and flocculation. Understanding of the chemistry involved in such systems is helpful to develop the optimum beneficiation schemes. It is shown that desired selectivity can be achieved by controlling the chemistry of the systems. More important, the need to conduct development tests under plant conditions is clearly demonstrated.

INTRODUCTION

Phosphate is one of the most important minerals processed by techniques such as flotation and flocculation/dispersion, which rely heavily on differences in the surface chemical properties of the minerals in the system. For example, flotation is efficient for the benefication of phosphate ores with silicate gangues, but those with carbonaceous gangues are not as easily separated by flotation techniques. The poor selectivity in the latter case has been attributed to the similarities in the surface chemical properties of the constituent minerals. The surface properties of phosphate are affected not only by phosphate's own solution chemistry but also by the dissolved species from other salt-type minerals present such as calcite and dolomite. Furthermore, these properties are influenced by the water chemistry of the reagents involved.

In this paper, the surface chemistries of phosphate and associated minerals is discussed followed by their influence on the reagents adsorption and phosphate beneficiation by flotation and flocculation.

SURFACE CHEMISTRY OF PHOSPHATE AND ASSOCIATED MINERALS

Adsorption of surfactants and polymers on solids is dependent on, among other factors, the interfacial properties of the solids, which in turn are governed to a larger extent by their surface chemistries. Solid particles, when contacted with water, will undergo dissolution and develop a surface charge. The extent of dissolution is dependent on the type and concentration of the chemicals in the solution.

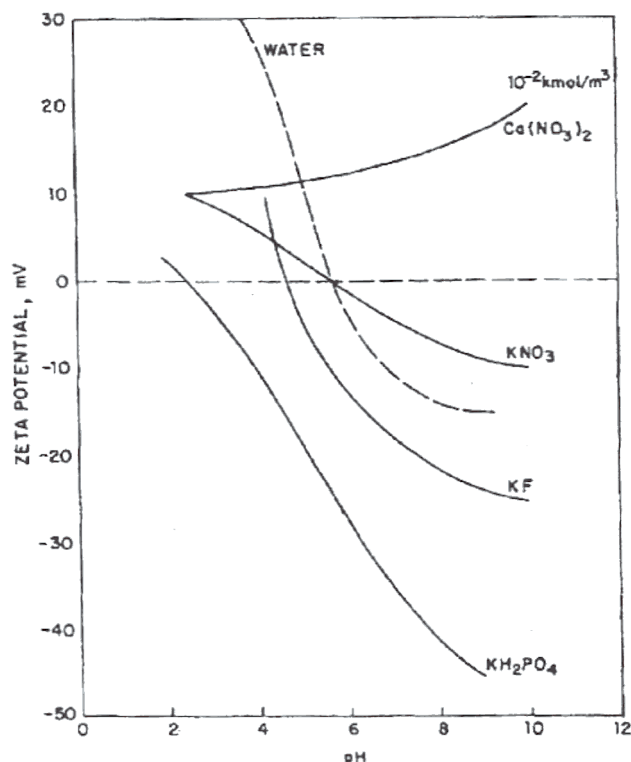* NSF IUCR Center for Surfactants, Henry Krumb School of Mines, Columbia University, New York.

FIGURE 1   Effect of Ca, PO_4, and F on the zeta potential of natural apatite as a function of pH

The dissolved mineral species can undergo further reactions such as hydrolysis, complexation, adsorption, and precipitation. The complex equilibria involving all such reactions govern the interfacial properties of the minerals as well as their flotation and flocculation behavior.

Electrochemical Properties

The zeta potential of a natural apatite $(Ca_{10}(PO_4)_6(F, OH)_2)$ sample in water and various uni- and multivalent salt solutions is illustrated in Figure 1 as a function of pH. Clearly, hydrogen and hydroxyl are (surface) potential determining ions. KNO_3 does not shift the isoelectric point, so K^+ or NO_3^- have no potential determining role in the case of apatite. The effects of $Ca(NO_3)_2$, KF, KH_2PO_4 on the isoelectric point of apatite can thus be attributed to Ca^{2+}, F^-, and PO_4^- ions and their complexes. Under all pH conditions, phosphate addition makes the apatite more negatively charged while

calcium makes it more positively charged. Fluoride is found to make the mineral more positively charged under acidic conditions and more negatively charged under alkaline conditions. It can be concluded that solution pH and concentrations of calcium, phosphate, and fluoride have a profound influence on the electrochemical properties of apatite.[1,2]

Effects of Pretreatment

It is to be noted that pretreatment such as cleaning and storing can have marked effect on the electrochemical properties of these minerals.[3,4] The isoelectric point of apatite has an initial value of 4.5, which shifts to about 5.5 upon equilibrium. When the mineral was treated with a concentrated fluoride solution (1 mol/liter) for a prolonged time (8 hours), the zeta potential of apatite became more positive (or less negative) throughout the pH range studied[5] (Figure 2).
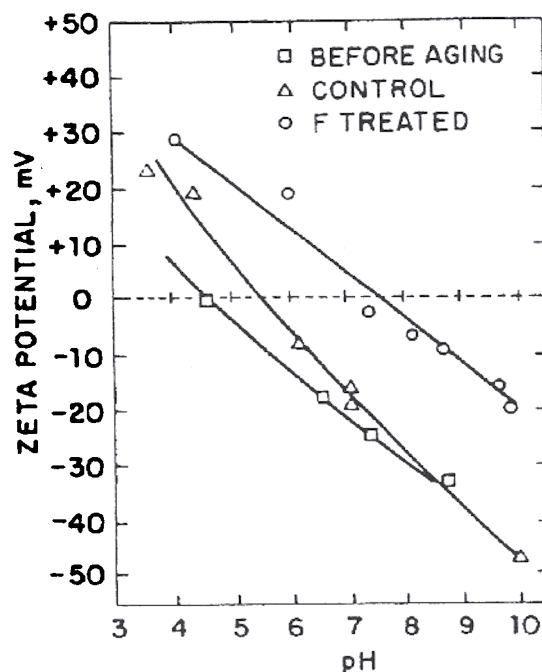
FIGURE 2 Effect of prolonged fluoride contact on the electrochemical properties of natural apatite (Zeta potential in 2×10^{-3} *M* KNO_3 solution of freshly cleaned apatite, cleaned and aged apatite, and F-treated [using 1*M* KF following cleaning and aging] apatite.)

Surface Conversion

During the processing of carbonaceous phosphate ores, apatite, calcite, and dolomite will dissolve in water followed by pH-dependent hydrolysis and complexation of the dissolved species. These dissolved species can have a marked effect on their interfacial properties. From theoretical considerations, depending on the solution conditions, the apatite surface can be converted to calcite and vice versa through surface reactions or bulk precipitation of the more stable phase. The equilibrium governing the conversion of apatite to calcite can be written as[6]:

$$Ca_{10}(PO_4)_6(OH)_2 \text{ (S)} + 10CO_3^{2-}$$
$$= 10CaCO_3 \text{ (S)} + 6PO_4^{2-} + 2OH^-$$
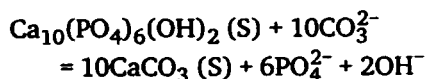
It can be seen from this equation that, depending on the pH of the solution, apatite can be converted to calcite if the total carbonate in solution exceeds a certain value. In fact, the amount of dissolved carbonate from atmospheric CO_2 does exceed that required to convert apatite to calcite under high pH conditions.

Surface conversion due to the reaction of the dissolved species with the mineral surface can be predicted using stability diagrams for heterogeneous mineral systems.[7,8] This is illustrated in Figure 3 for the calcite–apatite–dolomite system under open conditions (open to atmospheric CO_2). The activity of Ca^{2+} in equilibrium with various solid phases shows that the singular point for calcite and apatite is 9.3. Above this pH apatite is less stable than calcite and hence conversion of apatite to that of calcite can be expected in the calcite–apatite system. Similarly, apatite is more stable than calcite below pH 9.3. For calcite–dolomite and apatite–dolomite systems the singular points occur at pH 8.2 and 8.8, respectively. It is also to be noted that Ca^{2+} in equilibrium with calcite–dolomite–apatite in an open system could be significantly different from that in a closed system.

The surface conversions in a calcite–apatite system have been confirmed experimentally. Electrokinetic data obtained for a calcite–apatite system in water and in the supernatant of each other are shown in Figure 4. When apatite is contacted with
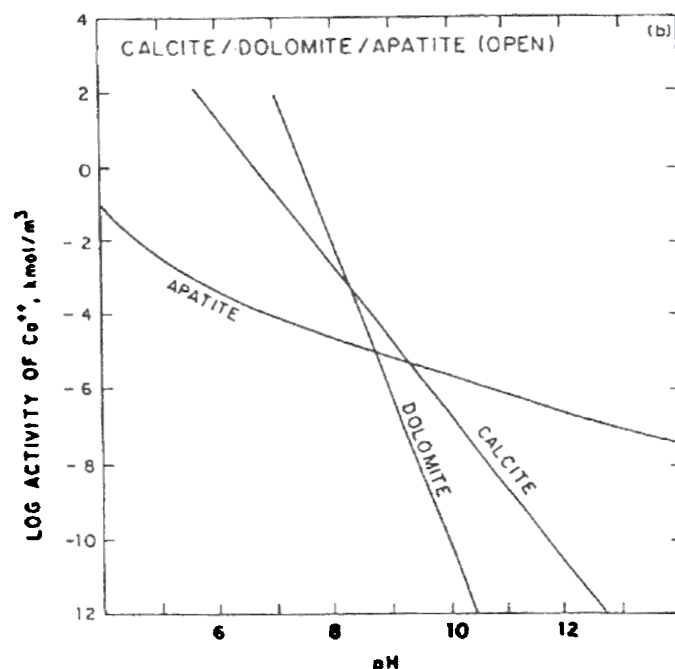
FIGURE 3 Stability relations in calcite–apatite–dolomite system open to atmospheric carbon dioxide at 25°C ([Mg^{2+}] = 5.0×10^{-4} *M*)

the calcite supernatant its zeta potential is seen to shift to that of calcite and vice versa, suggesting surface conversion of apatite to calcite and calcite to apatite, respectively.[9]

The zeta potential data obtained in mixed supernatants of calcite and apatite also show the effect of dissolved mineral species. If supernatants of calcite and apatite are combined as a 1:1 mixture, the two minerals have almost identical surface charge characteristics in the basic pH range (Figure 5).

The surface conversion of apatite and calcite is further supported by ESCA measurements. The results in Figure 6 show that when apatite is conditioned in the supernatant of calcite at pH ~12, its surface exhibits spectroscopic properties characteristic of both calcite and apatite.[9] This behavior is attributed to the precipitation of calcite on apatite. Note the implication of such conversions on the efficiency of processes such as flotation and flocculation, which depend on the differences in the surface properties of component minerals in the system.

Surface Chemistry of Phosphatic Slimes

In the beneficiation of Florida phosphoric clay waste by selective flocculation to recover francolite from clay minerals (montmorillonite), the surface chemistry of phosphate as well as associated minerals was found to play an important role. Polyacrylic acid (PAA) was used as a flocculant for francolite since there is specific interactions between the carboxylate group on PAA and the calcium sites on francolite. While high separation efficiency could be obtained with artificial mixtures of francolite and montmorillonite using polyacrylic acid as a flocculant, the efficiency for natural phosphate slimes was very low. This is attributed to the fact that polyacrylic acid interacts also with montmorillonite when there are calcium species on its exchangeable sites. In the case of natural phosphate slimes, dissolved calcium species from francolite can adsorb on the exchangeable sites of the clay surfaces and activate polyacrylic acid adsorption on the clay, which in turn leads to a decrease in separation efficiency.[10]
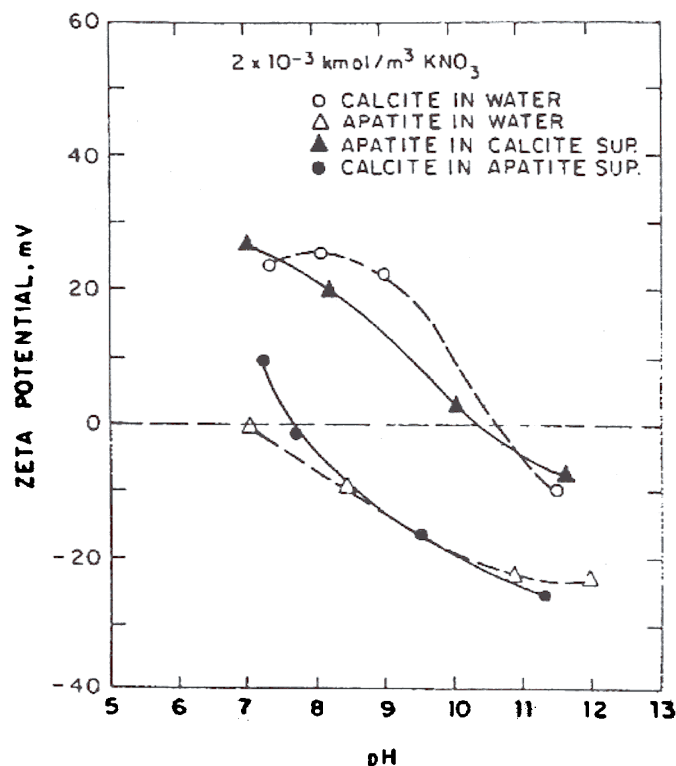
FIGURE 4   Effect of supernatants on the zeta potential and isoelectric point of calcite and apatite

Furthermore, with aging of the slime, there is an additional drop in the separation efficiency. Thermodynamic calculations of the stability of minerals in phosphate slimes suggest that a mixture of fluorapatite with common clay minerals is not stable under conditions prevailing in the slimes studied. It was found that millisite, a calcium-aluminum phosphate, is the stable phosphate phase. Formation of this compound at the clay-water interface leads to loss of separation efficiency by selective flocculation.[11]

From the above discussion, it can be concluded that the surface properties of phosphate are a function of various salt concentrations, pH, species from the dissolution of the minerals, as well as pretreatment. These factors will play a major role in determining the adsorption of reagents on them and selectivity in subsequent flotation or flocculation.

SURFACE CHEMISTRY OF PHOSPHATE MINERAL PROCESSING

Adsorption of reagents at the solid–liquid interface is greatly affected by the surface charge characteristics of the minerals. In addition to reagent adsorption, interactions among dissolved mineral species and various reagent species can also be expected. Chemical equilibria in aqueous solutions containing both the minerals and the reagents can be expected to be much more complex than in either of the individual systems (reagents–solution equilibrium and minerals–solution equilibrium). All of these interactions can affect the surfactant adsorption and subsequent beneficiation processes.
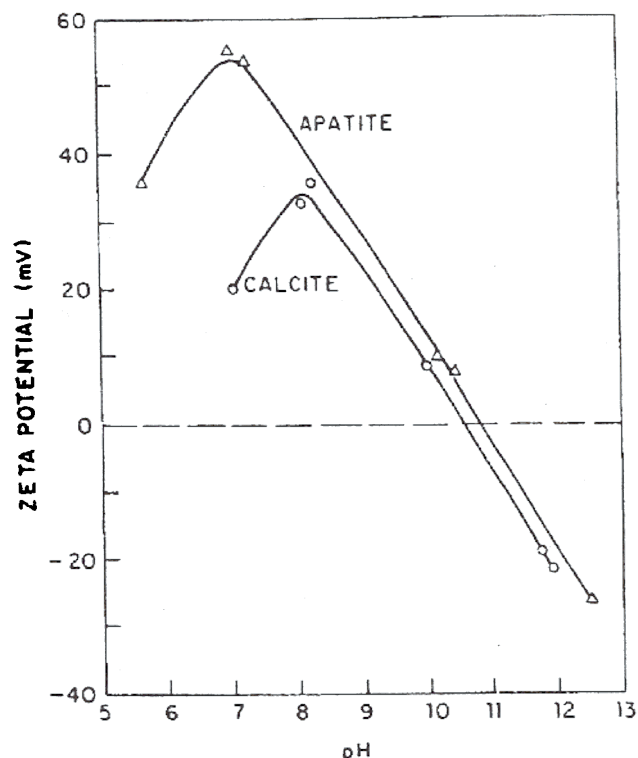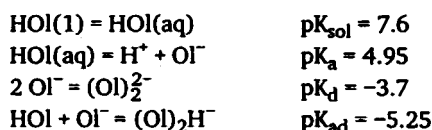
FIGURE 5   Illustration of the similarity in zeta potentials of calcite and apatite in mixed supernatants

Oleic Acid Solution Chemistry

Long-chain fatty acids such as oleic acid are among the commonly used reagents for flotation of phosphates. Flotation using fatty acids is markedly affected by solution properties such as pH, as weakly acidic fatty acids can undergo special associative interactions that influence their adsorption and flotation properties.[12] For example, oleic acid species will undergo dissociation to form ions (Ol$^-$) at high pH values and exist as neutral molecules (HOl) at low pH value. In the intermediate region, the ionic and the neutral molecular species can associate to form ion–molecule complexes ((Ol)$_2$H$^-$). As the surfactant concentration is increased, micellization or precipitation of the surfactant can occur in the solution. In addition, surfactant species can associate to form other aggregates, such as the dimer (Ol$_2^{2-}$), in premicellar solutions. Also, long-chain fatty acids such as oleic acid have very limited solubility, which is a sensitive function of pH.[13–15]

The solution equilibria of oleic acid (HOl) are expressed as follows:

HOl(1) = HOl(aq)	pK$_{sol}$ = 7.6
HOl(aq) = H$^+$ + Ol$^-$	pK$_a$ = 4.95
2 Ol$^-$ = (Ol)$_2^{2-}$	pK$_d$ = –3.7
HOl + Ol$^-$ = (Ol)$_2$H$^-$	pK$_{ad}$ = –5.25

The species distribution of oleic acid as a function of pH based on the above equilibria at a given concentration is shown in Figure 7. It can be seen from this figure that:

1. pH of the precipitation of oleic acid at the given concentration is 7.45.

2. Activities of oleic monomer and dimer remain almost constant above the precipitation pH and decrease sharply below it.

3. The activity of the acid-soap (Ol)$_2$H$^-$ exhibits a maximum in the neutral pH range.

It is important to note that the surface activities of various surfactant species can be markedly different from those of each other. It has been estimated that the surface activity of the acid-soap (Ol)$_2$H$^-$ is five orders of magnitude higher than that of the neutral molecule (HOl) and
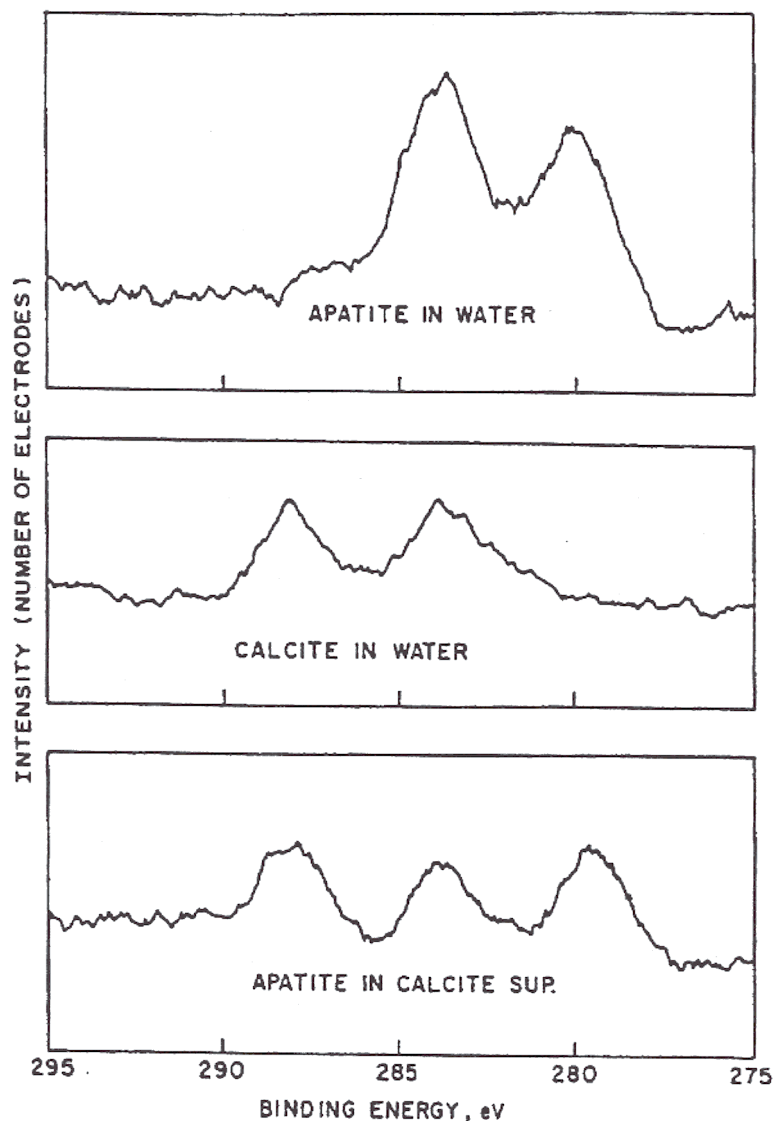
FIGURE 6 ESCA spectra of C(1s) peak of apatite conditioned in calcite supernatant at pH ~12

about seven orders of magnitude higher than that of the oleate monomer Ol⁻.[16]

Adsorption and Precipitation of Oleate in Mixed Mineral Systems

As a result of the low solubility of oleic acid, the adsorption of oleate on solid, in some cases, is in fact due to precipitation of the surfactant in the interfacial region.[17] If, at any stage, activity of Ca^{2+} in solution is greater than that in equilibrium with Ca^{2+}-oleate, Ca^{2+}-oleate can be expected to precipitate. Adsorption isotherms of oleic acid on

both francolite and dolomite has been observed to be a two-region linear isotherm with a change of slope at about 10^{-4} kmol/m^3 [18] (Figure 8). Simultaneous analysis of the dissolved mineral species in the supernatants of the samples used in the adsorption experiments (Figures 9a and 9b) shows a sharp decrease in the concentrations of both Mg and Ca species when oleate concentration exceeds 1.0×10^{-5} kmol/m^3 in the case of francolite and 3.0×10^{-5} kmol/m^3 in the case of dolomite. This suggests that bulk precipitation of calcium and magnesium species can also occur
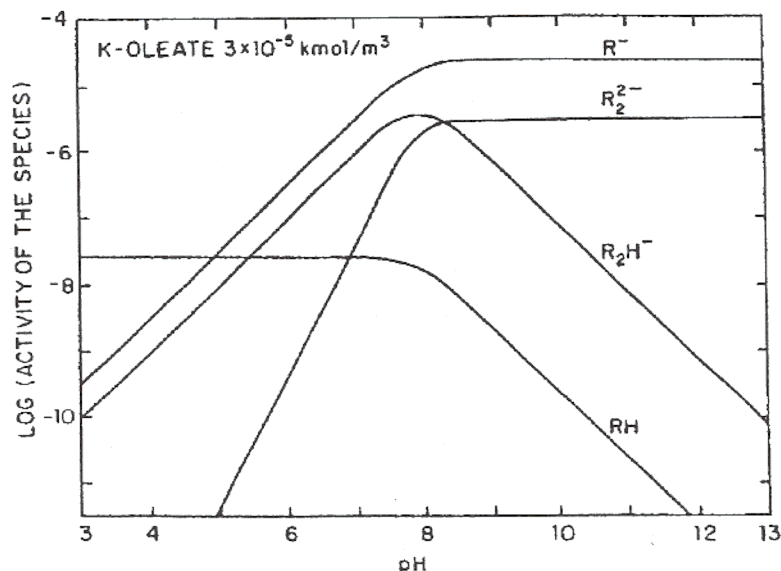
FIGURE 7   Oleate species distribution diagram as a function of pH (Total oleate concentration = $3 \times 10^{-5}M$.)
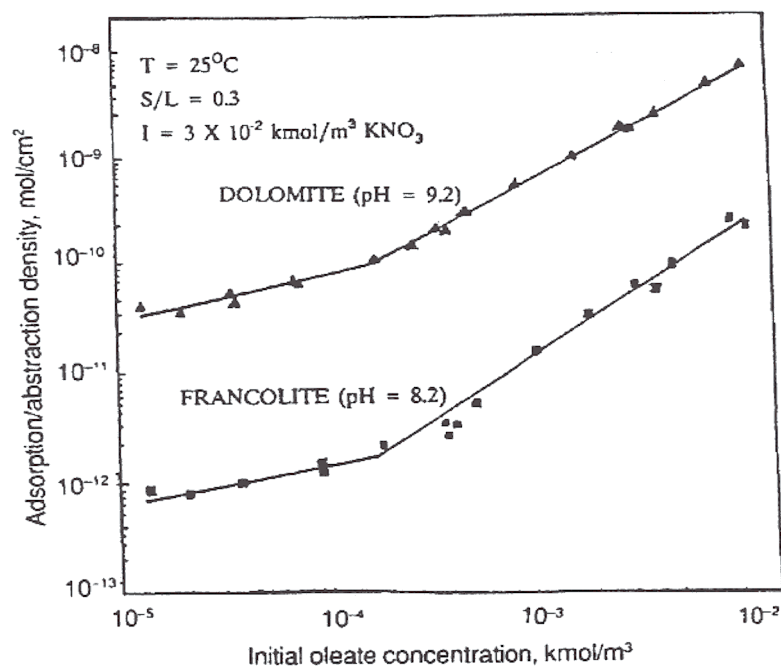

FIGURE 8   Adsorption isotherms of C_{14} labeled oleic acid on francolite and dolomite

under such conditions. Bulk precipitation can cause depletion of valuable reagents and retard their full utilization for processing. Bulk precipitation can also coat the mineral particle and change its colloidal behavior. It is to be noted that coating of particles by surfactant precipitate does not necessarily make the particles hydrophobic and floatable. For example, we did not find calcium oleate to act as a collector when we added it to mineral suspensions in several cases.[19]
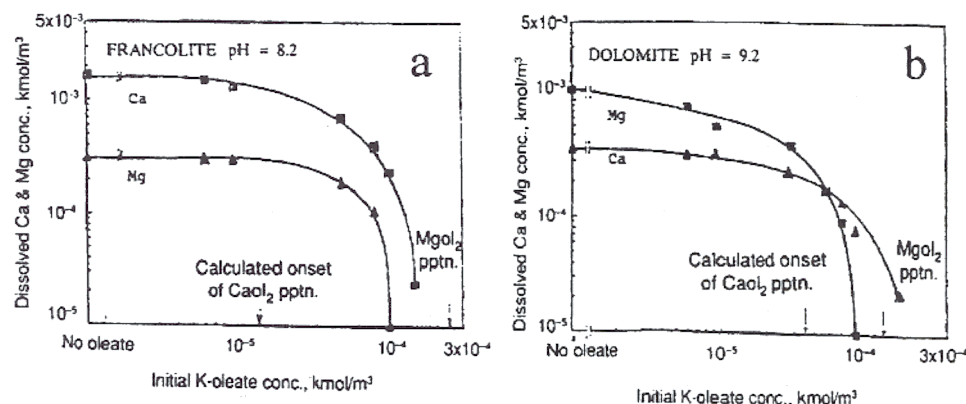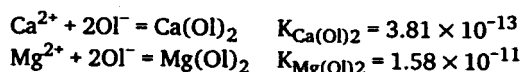
FIGURE 9 Dissolved Ca and Mg levels from: (a) francolite and (b) dolomite suspensions as a function of oleate concentration

Major chemical equilibria for the precipitation of Ca and Mg species by oleate can be given as follows:

$$Ca^{2+} + 2Ol^- = Ca(Ol)_2 \quad K_{Ca(Ol)2} = 3.81 \times 10^{-13}$$
$$Mg^{2+} + 2Ol^- = Mg(Ol)_2 \quad K_{Mg(Ol)2} = 1.58 \times 10^{-11}$$

The onset of the precipitation of $Ca(Ol)_2$ and $Mg(Ol)_2$ is calculated from the solubility products given above and marked in Figure 9. The calculated oleate concentrations at the onset of precipitation are in good agreement with experimental observations.

It is postulated that, in the case of oleate adsorption on dolomite and francolite, different mechanisms govern the adsorption process. In the low concentration range ($<10^{-4}$ kmol/m³), the adsorption of oleate on both minerals occurs mainly due to chemical bonding on surfaces without any precipitation. At an intermediate concentration of about 10^{-4} kmol/m³, the solubility limit of Ca and Mg oleate can be reached in the interfacial region but not in the bulk solution, suggesting surface precipitation of oleate on both minerals. In the high concentration range ($>5 \times 10^{-4}$ kmol/m³), oleate depletion may be dominated in the case of both minerals by its precipitation with Ca and Mg in the bulk solution.

From the above discussion, it is clear that a flotation separation scheme designed on the basis of the surface properties of single minerals is not likely to perform satisfactorily due to various interactions among the dissolved minerals species, surfactants, and the particles, leading to significant surface alterations. The effect of dissolved species of calcite and apatite on fatty acid flotation of both minerals has been studied using mineral supernatant solutions containing various dissolved species, and typical flotation results are given in Figure 10. Both supernatants of calcite and apatite are found to depress the calcite flotation by oleic acid in the tested pH range, with apatite supernatant exhibiting a larger depression effect. Similar results have also been obtained for apatite flotation. The supernatants of calcite and apatite depressed the apatite flotation under all tested pH conditions.[7]

Studies on the dissolved species responsible for the observed effect revealed that for calcite flotation, the depression role of apatite supernatant results from the combined effects of calcium and phosphate species in solution. The depression role of calcite supernatant is mostly that of the calcium and possibly some carbonate. The depression due to calcium is caused by the depletion of reagent owing to the precipitation of calcium oleate. In the case of apatite flotation, the depression was due to phosphate and carbonate species in solution. We proposed the competition between oleate and phosphate/carbonate for the surface calcium site to be the main reason for the depression of apatite flotation. Calcium-oleate precipitation, in this case, does not occur to a significant extent due to the low concentration of oleic acid used in flotation. It must be noted from the above discussion that water chemistry will play a crucial role in the flotation of apatite–calcite systems by affecting the surface chemistry of the solids.
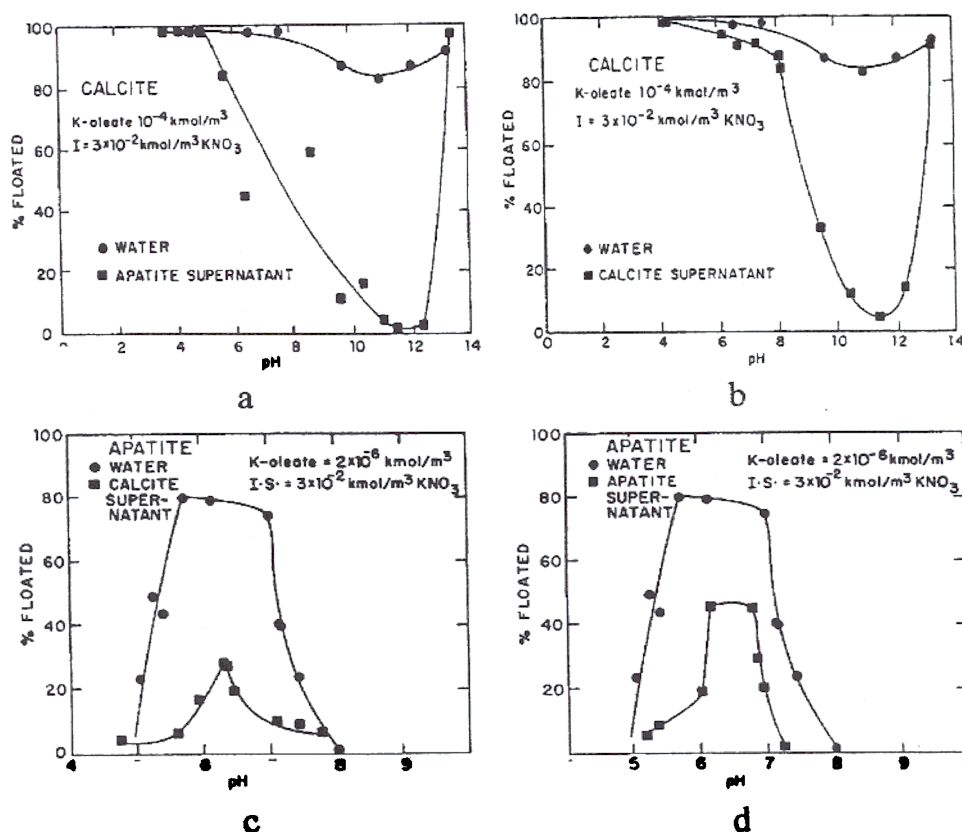
FIGURE 10   a. Effect of apatite supernatant on calcite flotation; b. Effect of calcite supernatant on calcite flotation; c. Effect of calcite supernatant on apatite flotation; d. Effect of apatite supernatant on apatite flotation

TABLE 1   Comparison of laboratory and plant conditions

	Laboratory Conditions	Plant Conditions
		Lightnin Labmaster L1U08, four-bladed cruciform propeller operating at 350 rpm
pH	9.1 to 9.5	9.1 to 9.5
Water	Distilled and plant water	Plant water
Solid, %	10 (2 g sample)	72 (1,000 g sample)
Time, min	120 (except for kinetics)	3 (except for kinetics)

Adsorption Kinetics Under Laboratory and Plant Conditions

A major factor that usually does not receive much attention in fundamental investigation of the flotation process is that flotation is a dynamic process. Another important factor that is invariably ignored in basic research is the possible differences between the performances of an operation in the laboratory and the plant. Adsorption kinetics of

surfactants and particularly differences in kinetics of adsorption on different minerals during conditioning can be the single overriding factor controlling the efficiency of an industrial flotation operation. Kinetics of surfactant adsorption on solids can indeed be expected to be affected by their solution chemistry. Anionic conditioning is a unit operation that precedes rougher flotation and skin flotation of phosphates in Florida flotation plants. The effect of solution chemistry on the oleic acid
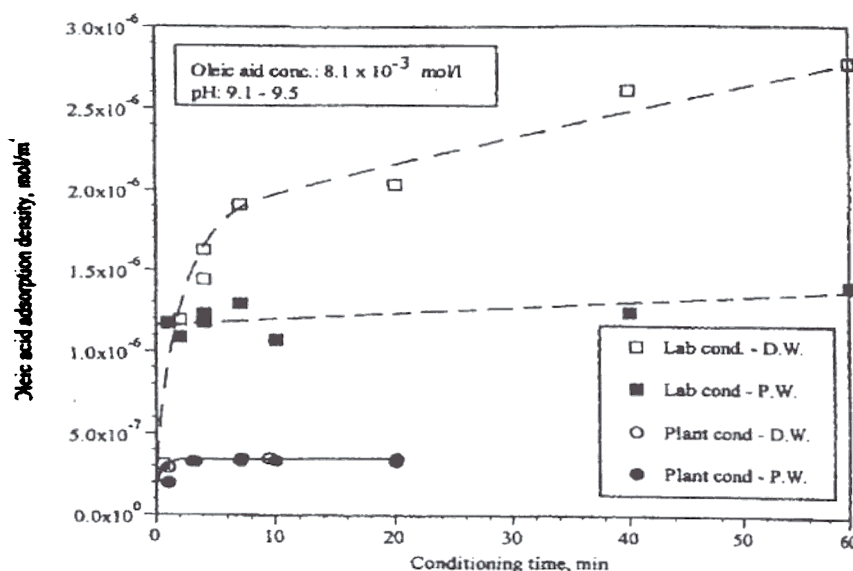
FIGURE 11   Kinetics of oleic acid adsorption on francolite in distilled water (D.W.) and plant water (P.W.) under plant conditions

adsorption on francolite during anionic conditioning has been recently studied in detail.[20] In order to identify the effect of process variables on the adsorption, the experiment was carried out under both laboratory and plant conditions. The laboratory and plant conditions are compared in Table 1.

The kinetics of oleic acid adsorption on francolite under both laboratory and plant conditions, using distilled water and plant water, is shown in Figure 11. The adsorption density and kinetics are clearly quite different depending on the conditions and the water. Under laboratory conditions, the adsorption in the plant water is significantly lower than that in the distilled water. This was proposed to be due to reagent loss resulting from oleic precipitation by the dissolved species in plant water. In contrast, under the plant conditions, adsorption behavior of oleic acid in plant water and distilled water is similar and adsorption densities are lower than those under laboratory conditions. The lower adsorption density is due to the intense agitation under plant conditions that can remove some of the bound oleate. The similar adsorption behavior under plant conditions for both the plant water and the distilled water is due to the high solids loading in the process. The high solid/liquid ratio under plant condition reduces

the amount of dissolved species and thus reduces the reagent loss due to precipitation.

The adsorption isotherms of oleic acid on francolite under laboratory and plant conditions are compared in Figure 12. Adsorption is markedly higher under the laboratory conditions than under the plant conditions. On the other hand, under the plant conditions the adsorption is similar in the distilled water and the plant water. This suggests that the effect of dissolved species is reduced under plant conditions.

Use of Surface Chemistry Principles to Improve Phosphate Flotation

From the above discussion, it can be seen that the surface chemistry of phosphates and associated minerals plays a vital role in controlling the beneficiation processes. Understanding the chemistry involved in these systems offers opportunities to manipulate such processes by optimizing the contributing factors such as alteration of the surface properties; complexation of ions, which causes precipitation of the surfactant; prevention or enhancement of collector adsorption; and changes in the adsorption kinetics to achieve the desired selectivity in flotation and flocculation.

In the anionic flotation of phosphate, Ca^{2+} affects the grade of phosphate by activating the quartz
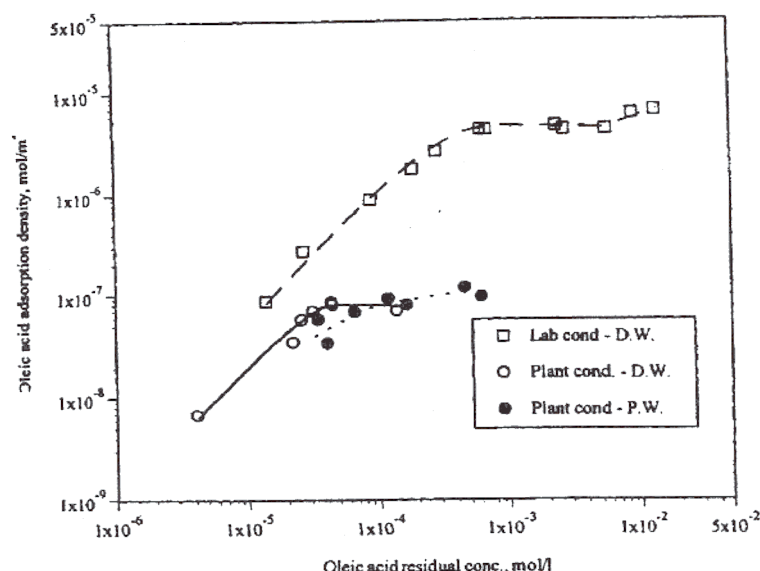
FIGURE 12   Adsorption isotherms of oleic acid adsorption on francolite in distilled water (D.W.) and plant water (P.W.) under laboratory and plant conditions

through formation of calcium-bearing precipitates at high pH. This detrimental effect can be prevented by adding sodium silicate, which can interact with Ca^{2+} and form calcium silicate. Since calcium silicate and quartz are negatively charged, detachment of calcium silicate from quartz can occur and thus quartz flotation can be depressed.[21]

It has been found that in carbonate/phosphate systems, with fatty acid as the collector, apatite is depressed in the acid media (pH 5.5–6.0) while carbonate is floated. The depression of phosphate at this pH is possibly due to the adsorption (or formation) of aqueous $CaHPO_4$ on its surface, preventing surfactant ions from approaching the surface of the phosphate particles. Free Ca^{2+} in solution can affect the formation of aqueous $CaHPO_4$. From thermodynamic considerations it can be predicted that the selective flotation of carbonates from phosphates in acid media can be enhanced by minimizing free Ca^{2+} in solution and by increasing HPO_4^{2-} in the system. This can be done by: (1) decreasing free Ca^{2+} concentration in the system to low values by adding suitable chemical reagents such as sulfuric acid or chelating agents such as oxalic acid, and (2) adding soluble phosphate salts to enhance the depression of the phosphate minerals. Results from experiments with natural phosphate ores are in agreement with the theoretical predictions.[22]

Based on the oleic acid solution chemistry, a two-stage conditioning process for the flotation of dolomite from apatite was proposed.[23] The mixed minerals were first conditioned at pH 10 with oleic acid collector. The system was then reconditioned below pH 4.5 where dolomite was floated. The selectivity of dolomite from apatite is attributed to two factors in this process: (1) high adsorption of oleate on dolomite during the first stage at pH 10, which is maintained after reconditioning at lower pH, and (2) oleate to oleic acid transformation upon reconditioning reducing its efficiency and this reduction being more severe for apatite than for dolomite. In the high pH range oleate adsorbs on apatite and calcite through specific interactions, while at low pH when oleic acid is the major species, the adsorption is through weaker physical interaction. Thus, oleic acid is a poor collector compared to oleate.

Modification of collector adsorption on minerals can be used to control their flotation response. In one study, alizarin red S, a dye that stains calcite, was tested as a modifying agent in a calcite–apatite system due to its preferential adsorption on these minerals. Even though alizarin red S adsorbs more on apatite than on calcite, it depresses the flotation of apatite using oleate as collector more than that of calcite (Figure 13). In the absence of alizarin red S, both calcite and
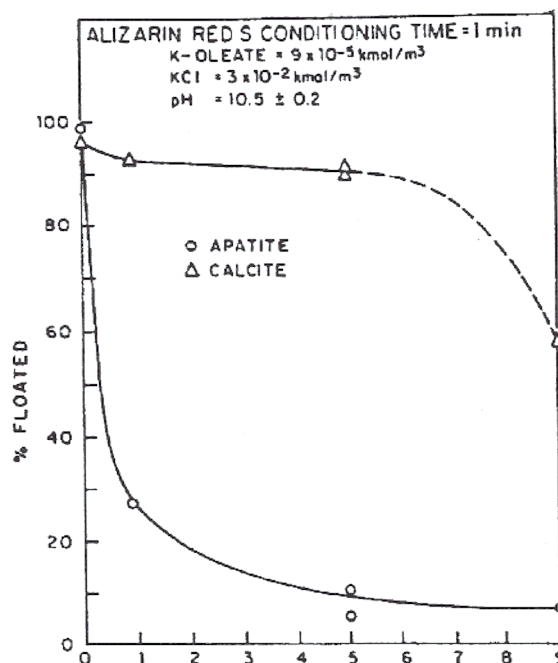
FIGURE 13 Flotation of calcite and apatite from their mixture (1:1) at pH 10.5 as a function of alizarin red S concentration

apatite float with oleate at pH 10.5. When alizarin red S concentration increases to 5×10^{-6} mol/m^3, the flotation of calcite is affected very little with a recovery of about 90%, while apatite flotation is depressed to 5–10%. Calcite flotation is affected only at higher concentrations of alizarin red S. Alizarin red S or its derivatives can hence be a promising reagent for the beneficiation of phosphate with carbonaceous gangues.[24]

SUMMARY

The surface chemistry of phosphates plays a primary role in determining reagent adsorption on the phosphates and hence their separation by processes such as flotation and selective flocculation. The complex interactions among solid surface species, dissolved species, and reagents species also have marked effects on the reagent adsorption as well as flotation/flocculation. Minerals can undergo dissolution, with the extent of dissolution depending on solution conditions such as pH, ionic strength, and concentration of constituent

ions. The dissolved mineral species can further interact with mineral solids leading to surface conversion of the minerals. Surfactant can exist in different forms in solution depending on the solution pH and the surfactant concentration. The dissolved mineral species can interact with surfactant species leading to surface and bulk precipitation. All of these processes can significantly affect the adsorption of reagents on minerals. A full understanding of various interactions in a surfactant-solid–solution system is essential for developing efficient separation schemes. Indeed, desired selectivity can be achieved by the use of appropriate additives to control dissolved species, modify surface chemistry of the solid, and optimize reagent adsorption and particularly the kinetics involved during the conditioning.

ACKNOWLEDGMENTS

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