EFFECfS OF DISSOLVED MINERAL SPECIES ON THE ELECTRO-KINETIC BEHAVIOR OF CALCITE AND APATITE

J. OFORI AMANKONAH and P. SOMASUNDARAN
School of Engineering and Applied Science, Columbia University, New York, NY 10027 (U.S.A.)
(Received 7 May 1984; accepted in final form 22 March 1985)

ABSTRACT

The interfacial behavior of salt-type minerals such as calcite and apatite is governed to a large extent by their electrochemical properties which in turn are governed by pH and concentration of dissolved mineral species. In mixed mineral systems, the interfacial behavior of various minerals is often quite different from what might be expected on the basis of their individual properties. Predictions for flotation separation based on single mineral tests often fail in these systems mainly owing to the interactions between dissolved mineral species.

The effect of dissolved mineral species of the calcite—apatite system is investigated in this study using the electrokinetic technique. The electrochemical, dissolution and spectroscopic properties of each mineral were markedly altered by the supernatants of the other mineral. Most interestingly, under the test conditions, the isoelectric point of each mineral in the supernatant of the other was observed to be similar to the supernatant mineral source. It is clear that, under these conditions, a flotation separation scheme designed on the basis of the surface properties of the single minerals is not likely to perform satisfactorily. Tests in inorganic solutions have shown that surface reaction and/or bulk precipitation could be responsible for the observed shifts. Surface chemical alterations predicted from theoretical considerations using species distribution diagrams are correlated with the experimental results.

INTRODUCTION

Separation of phosphates from carbonitic gangues by flotation has been a major problem in the phosphatic industry for years. Direct application of various processes described in the literature to phosphate ores has often failed to reduce the carbonate content of the final product to an acceptable level [1, 2]. Furthermore, a previous investigation [3] has shown predictions of selective flotation on the basis of single mineral tests to fail even for synthetic mineral mixtures.

The difficulties encountered in the separation of calcite—dolomite type impurities from phosphates have been attributed to the similarities in the surface chemical, electrokinetic and dissolution properties of these minerals
as a result of which both the carbonates and phosphates respond similarly to anionic and cationic collectors [4, 5].

The dissolution characteristics of the minerals can be expected to play a major role in determining the nature of the interactions taking place in the bulk solution or in the interfacial region and hence the efficiency of such interfacial processes as flotation and flocculation. In salt-type mineral systems where the solubility is markedly higher than in most other systems such as oxides and silicates [6], this role is expected to be even more significant.

Effects of dissolved species in various mineral systems have been reported by several investigators. Healy [7] observed drastic changes in the point of zero charge of magnetite when stored in glass containers. The observed changes were attributed to the silicate species released from the glass container. In a similar manner, the dissolved species can cause significant activation or depression of flotation under certain solution conditions. These effects have been correlated with both the specific adsorption of hydroxy complexes of the cations as well as the stronger tendency of multivalent ions over monovalents to compete with the surfactant ions for the adsorption sites [8–14]. Fuerstenau and Miller [15] have obtained good correlation between the pH range in which quartz flotation, using anionic surfactants, is activated by cations and the pH range in which the first hydroxy complex of the cation is formed. This illustrates the role of the specific adsorption of these complexes. The high adsorption affinity of partially hydrolyzed ions on charged surfaces has been recognized by Wolstenhamme and Schulman [16]. Dissolved ferric and other metallic species have been reported to activate the flotation of silica using fatty acid as the collector [11, 12, 14, 15]. This suggests that the dissolved species from hematite can affect silica flotation in hematite-silica systems. It should prove useful to study the effect of hematite supernatant itself on silica flotation. In a separate study by Iwassaki and Soto [17], the effect of calcium and magnesium species released into the solution by the impurities associated with hematite have been shown to have a significant effect on the selective flocculation of hematite from quartz. This study clearly shows that the water in equilibrium with the ore can contain sufficient amounts of calcium and magnesium ions to significantly alter the surface properties of silica. As has been shown by several investigators [18–21], surface precipitation of a different form of the mineral than its original one from a solution that is supersaturated is also possible. This fact has been considered in detail by Parks [22] for alumina systems and by Brown and co-workers [19, 20, 23] for phosphates.

Due to the complex nature of salt-type mineral systems, much controversy exists in the literature on the role of polyvalent ions. Polkin [24] considers the polyvalent ions to be essential for the formation on hydrophobic multilayers on calcite. Sun et al [25] and Eigeles [26] consider such ions to be harmful due to precipitation as metal soaps in the pulp.
Surface or bulk precipitation of a more stable phase is perhaps one of the major effects due to dissolved species. For example, in the presence of $10^{-4}$ kmol m$^{-3}$ calcium, MacKenzie and Mishra [27] observed that the apatite surface closely resembled that of the calcite. This could be due to the precipitation of calcium carbonate on the surface of the apatite. The implication of this observation is that a separation scheme based on the interfacial properties of the individual minerals is not likely to perform satisfactorily for beneficiation of ores. The observation by Le Bell and Lindstrom [28], and Calara and Miller [29] on the electrokinetic behavior of fluorite after various treatments must be noted. These authors observed drastic changes in the point of zero charge of fluorite when it was conditioned in carbonate solutions.

The effects of dissolved mineral species of calcite and apatite on the flotation of these minerals has been shown recently in our laboratory to be drastic under certain solution conditions [6]. Flotation of calcite and apatite in mineral supernatants was drastically depressed due to the presence of dissolved species.

The electrokinetic behavior of calcite and apatite in water and in mineral supernatants is discussed in this work. Experiments have also been conducted in various electrolytes containing mineral constituent ions in order to identify their role when present in mineral supernatants. The observed changes in the electrokinetic behavior have been correlated with thermodynamic predictions.

EXPERIMENTAL MATERIALS AND METHODS

Materials

Calcite
The calcite of 10-micrometer size was prepared during an earlier investigation by Somasundaran and Wang [4, 30] and was used in this study.

Apatite
Synthetic hydroxyapatite was used in this study. It was prepared by the precipitation technique described by Moreno et al. [20] and modified by Somasundaran and Wang [4, 30]. The method involves mixing appropriate amounts of K$_2$HPO$_4$ in a KOH solution and Ca(NO$_3$)$_2$ in water and boiling the reaction products under appropriate solution conditions to avoid the formation of octa-calcium phosphate as a precursor. To avoid the possible precipitation of CaCO$_3$ in the system or the formation of carbonate species in the crystal lattice of the apatite, the experimental set-up was constantly flushed with purified and dried nitrogen gas. Settled crystals were washed and then freeze-dried and characterized using electron spectroscopy for chemical analysis (ESCA).

The stoichiometry of the samples was determined by measuring concentrations of dissolved species in the mineral supernatants. In these tests,
the conditioning of the minerals was done in a nitrogen glove box to mini-
mize the interference by atmospheric carbon dioxide. The molar ratios of
calcium/phosphorus (Ca/P) and calcium/carbonate (Ca/Ct) were 1.59 and
0.93 for apatite and calcite, respectively, and their calculated thermo-
dynamic solubility products were $10^{-11.5}$ and $10^{-5.345}$. ESCA was used to
determine the surface chemical composition of the freshly prepared (un-
treated) mineral surfaces. Comparison of the ESCA spectra with standards
provided by the Physical Electronics Division of Perkin—Elmer [31] showed
the samples to be pure calcite and apatite. Surface areas of the calcite and
apatite samples as determined by the BET technique using Quantasorb
were found to be 0.71 and 30.3 m$^2$ g$^{-1}$, respectively.

Inorganics

All inorganics such as KNO$_3$, KOH, K$_2$CO$_3$, K$_3$PO$_4$, Ca(NO$_3$)$_2$, HNO$_3$ etc.
were of certified ACS grade purchased from Fisher Scientific Company.

Methods

Reactions at the mineral—solution interface were studied in this work by
measuring the zeta potential as a function of pH under various conditions.
The zeta-potential values were measured by the electrophoretic technique
using the Lazer Zee Meter and the Zeta-Meter manufactured by Pen Ken Inc.
and Zeta-Meter Corp., respectively. The equilibration of the mineral for zeta-
potential measurements was done by stirring for 30 min 0.1 g of the mineral
with 100 ml of triply distilled water containing the required amount of KOH
or HNO$_3$. Thirty minutes conditioning time was selected on the basis of
kinetic studies. Depending on the initial pH, significant changes in pH and
zeta potential were observed only within the first 10—20 min of conditioning.
Furthermore, the data in the literature indicate that conditioning times for
flotation tests do not often exceed 10 min [6]. It is to be noted, however,
that several hours of conditioning are required for complete equilibrium [32,
34]. The equilibration as well as electrokinetic measurements were conducted
in the presence of atmospheric carbon dioxide.

Zeta-potential measurements were conducted in mineral supernatants
as well as in water. The supernatant was prepared by stirring the mineral
with water at the desired pH for 30 min followed by centrifugation. The
supernatant obtained was checked under an optical microscope to ensure
the absence of solid particles. The pH was then readjusted and the solutions
used for conditioning of the mineral prior to zeta-potential measurements.
To check for possible effects of variations in ionic strength, experiments
were conducted also in $2 \times 10^{-3}$ kmol m$^{-3}$ KNO$_3$.

Additional measurements were made in mixed supernatants prepared
by combining 50 ml each of the supernatants of calcite and apatite pre-
pared at about the same pH.
Fig. 1. Zeta potential of calcite and apatite in: (a) water, (b) $2 \times 10^{-3}$ kmol m$^{-3}$ KNO$_3$. 
Fig. 2. Effects of calcite supernatant on the zeta potential of apatite: (a) water, (b) $2 \times 10^{-3}$ kmol m$^{-3}$ KNO$_3$.
Fig. 3. Effects of apatite supernatants on the zeta potential of calcite: (a) water, (b) $2 \times 10^{-3}$ kmol $m^{-3}$ KNO$_3$. 
RESULTS AND DISCUSSION

Results obtained for the zeta potential of apatite and calcite in water, and in $2 \times 10^{-3}$ kmol m$^{-3}$ KNO$_3$ solutions are given in Figs 1(a) and 1(b), respectively. It can be seen that the isoelectric points of calcite and apatite in both water and KNO$_3$ solutions are about 10.5 and 7.4, respectively. This is in agreement with the results reported in the literature [27, 32, 33].

The effect of the supernatant of calcite on the zeta potential of apatite is shown in Figs 2(a) and 2(b). Examination of the results shows that the apatite surface is more positively charged in calcite supernatant than in water over the entire pH range investigated, and that the isoelectric point has shifted from 7.4 to about 11, towards that of calcite. Similarly, the zeta potential of calcite in apatite supernatant was measured as a function of pH. The results given in Fig. 3 show the zeta potential of calcite to be reduced drastically by the supernatant of apatite, and the isoelectric point to shift from 10.5 to 6.5. The decrease in the magnitude of the zeta-potential values in KNO$_3$ solutions from those in water alone could be attributed to the compression of the double layer under high ionic strength conditions [34].

![Graph showing zeta potential vs pH](image)

Fig. 4. Illustration of the effects of supernatants on the IEP of calcite and apatite.
Fig. 5. Zeta potential of: (a) calcite in calcite supernatant, (b) apatite in apatite supernatant.
In order to identify clearly the effects of supernatants, the results in Figs 2(b) and 3(b) (experiments under controlled ionic strength conditions) are replotted in Fig. 4. The results show calcite and apatite to interchange approximately their isoelectric points in the supernatants of each other. The observation of Ananthapadmanabhan and Somasundaran, reported in Ref. [6], for the effect of the supernatants of calcite and apatite on their flotation behavior must be noted here. These effects are obviously due to the dissolved mineral species present in the supernatants. It is interesting to note that the flotation of these minerals was found to be affected also by their own supernatants. However, the zeta potential of a mineral is not expected to be affected to any appreciable extent by its own supernatant if similar conditions are maintained since the equilibrium concentration of the potential determining ions on the surface should be identical whether treated in water or in their own supernatants. Figure 5 showing the results of the zeta potential of calcite and apatite in their own supernatants indicates that, indeed, the zeta potentials are only slightly affected.

Fig. 6. Illustration of the similarity in zeta potentials of calcite and apatite in mixed supernatants.
The results of the zeta-potential measurements in mixed supernatants, presented in Fig. 6, further show the effects of dissolved species; if calcite and apatite are present as a 1:1 mixture (weight basis), the two minerals have identical surface-charge characteristics in the basic pH region.

Evidently, these effects are due to some or all of the dissolved mineral species. In order to identify the species actually responsible, zeta-potential measurements of calcite and apatite were conducted in inorganic solutions containing each species. The results obtained in the presence of Ca(NO₃)₂, K₂CO₃ and KH₂PO₄ are given in Figs 7 to 9. Data given in Fig. 7 for the zeta potential of apatite in Ca(NO₃)₂ solutions of several concentrations show that the surface of the mineral is more positively charged in Ca(NO₃)₂ solutions at all pH and levels of concentration tested. This is in agreement with the results in the literature [4, 30, 34].

The effect of K₂CO₃ on the zeta potential of apatite (Fig. 8) is found to be minimal in the concentration range studied in accord with the fact that the carbonate will be present mostly in the HCO₃⁻ form in the pH range where apatite is negatively charged and, therefore, cannot be expected

\[ \text{Fig. 7. Effect of Ca(NO}_3)_{2} \text{ addition on the zeta potential of apatite.} \]
to produce any specific effects. On the other hand, high concentrations of 
$K_2CO_3$ can be expected to cause the precipitation of $CaCO_3$ on the surface 
of apatite to produce more positive zeta-potential values. However, relatively 
higher concentrations of carbonate are required for the calcite precipitation. 
While the concentrations of $K_2CO_3$ used in the experiments ($10^{-3}$ and $10^{-1}$ 
kmol m$^{-3}$ $K_2CO_3$) would be insufficient for this process, calcite supernatants 
could contain enough carbonate to effect the precipitation. The possibility 
of surface conversion processes from a thermodynamic point of view is 
discussed later in this section.

The effect of $K_3PO_4$ addition shown in Fig. 9 indicates that the surface 
of apatite has become more negatively charged in the pH range examined 
in agreement with past results [27, 35]. This decrease is mainly due to the 
role of phosphate as potential determining ions for apatite.

Figures 10 and 11 present results for the zeta potential of calcite in 
the above inorganic solutions. As can be seen from Fig. 10, the effect of 
$Ca(NO_3)_2$ addition is to make the surface of calcite more positively charged. 
In the concentration range tested, only positive potentials were recorded 
over the entire pH range.

![Fig. 10. Effect of $Ca(NO_3)_2$ addition on the zeta potential of calcite](image)
Similar to the effects on apatite, \(K_3PO_4\) addition reduces the zeta-potential values of calcite (Fig. 11). It must be noted that zeta-potential values obtained for calcite in \(10^{-3}\) kmol m\(^{-3}\) \(K_3PO_4\) closely agree with those obtained for apatite in water. As shown later, even less than \(10^{-9}\) kmol m\(^{-3}\) total phosphate can cause precipitation of apatite from calcite supernatants under neutral pH conditions. The observed changes in zeta potential can therefore be attributed to the precipitation of apatite on the calcite surface.

Analysis of the zeta-potential results presented above show the observed shifts in the isoelectric point of calcite and apatite in the supernatants of each other to be the result of many complex surface processes. The mechanism of surface charge generation for these minerals has been examined in detail during an earlier investigation [4, 5, 34, 35]. The electrokinetic behavior of apatite and calcite in various inorganic solutions has also been determined [32, 35]. These properties, however, have not been studied for heterogeneous mineral systems. In a recent investigation [36] we have shown from theoretical considerations that, depending on the solution conditions, apatite surface can be converted to calcite, and vice versa through surface reaction or bulk precipitation of the more stable phase.
The observed changes in the electrokinetic properties of calcite and apatite can therefore be examined on the basis of the mineral—solution chemical equilibria involving dissolved mineral species.

From studies of solubility isotherms for apatite and calcite at 25°C [19, 23, 37], the singular point for these minerals is identified to be 9.3. Above this pH calcite is more stable than apatite. The implication is that, if apatite is brought in contact with alkaline solutions (pH > 9.3) previously equilibrated with calcite, calcite can precipitate on the surface of apatite. From similar considerations, the conversion of calcite to apatite is also possible below the singular point. We have shown theoretically [36] that, if calcite supernatants are prepared above pH 9.3, the total carbonate present in these solutions can exceed the amount required for the conversion of apatite to calcite as illustrated in Fig. 12(a). As shown in Fig. 12(b), the total phosphate in equilibrium with apatite below the singular point can also convert calcite surface to apatite under appropriate conditions. As mentioned earlier, much lower phosphate concentrations are required in this case. Our investigation on the solubility behavior of these minerals based on supernatant analysis under various solution conditions [38] has

Fig. 12(a). Illustration of the conversion of apatite to calcite.
also shown that, indeed, the precipitation of these minerals is quite possible.

The surface conversion of calcite and apatite is further illustrated by the results of recent spectroscopic investigations in our laboratory using ESCA [39]. The minerals were conditioned under solution conditions similar to those used for zeta-potential studies. The data given in Fig. 13 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. This behavior is attributed to the precipitation of calcite on apatite.

On the basis of the electrokinetic, spectroscopic, flotation, dissolution and precipitation behavior of these minerals in heterogeneous systems, as well as the analysis of the mineral—solution chemical equilibria governing them, conditions for selective flotation have been discussed in detail in a recent publication [40].

Fig. 12(b). Illustration of the conversion of calcite to apatite [36].
SUMMARY AND CONCLUSIONS

Dissolved mineral species play a major role in the interfacial behavior of sparingly soluble minerals such as calcite and apatite. Electrokinetic studies were conducted on the calcite–apatite heterogeneous system to develop an understanding of the manner in which dissolved species affect this behavior. The isoelectric points of calcite and apatite in both water and KNO₃ solutions are 10.5 and 7.4, respectively. When the minerals are conditioned in the supernatants of each other, they approximately

Fig. 13. ESCA spectra of C(1s) peak of apatite conditioned in calcite supernatant at pH ~ 12 [39].
interchange their points of zero charge; when apatite is conditioned in the supernatants of calcite, its isoelectric point shifts from 10.5 to about 6.5 (8.0 in the presence of $2 \times 10^{-3}$ kmol m$^{-3}$ KNO$_3$) towards that of apatite. Similarly, the isoelectric point of apatite is shifted from 7.4 to about 11.0 towards that of calcite. If calcite and apatite are present as a 1:1 mixture (weight basis), the two minerals have identical surface-charge characteristics in the basic pH range. These effects are discussed on the basis of mineral—solution equilibria controlling these systems. Thermodynamic considerations indicate that the apatite surface can be converted to calcite in the supernatant of the latter and vice versa. Based on the results of the electrokinetic, spectroscopic, flotation, dissolution and precipitation studies, the observed shifts in isoelectric points are attributed to the precipitation of one mineral on the surface of the other.

ACKNOWLEDGEMENTS

Support of the National Science Foundation (CPE-83-04059) and Florida Institute of Phosphate Research is greatly acknowledged. We wish to thank K.P. Ananthapadmanabhan and Kenneth Wong for helpful discussions.

REFERENCES