Electrokinetic Study of the Role of Modifying Agents in Flotation of Salt-type Minerals

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Introduction

The practical separation of slightly soluble salt-type minerals from one another by froth flotation is often difficult because of the similarity of the surfaces of the minerals (Hanna and Somasundaran, 1976). Further, because these minerals possess a small solubility in water, constituent ions dissolved from one of the minerals can adsorb onto the other minerals, rendering their surfaces even more similar in nature, (Hanna and Somasundaran, 1976; Smith and Steiner, 1980). In an important contemporary commercial flotation operation (Smith and Steiner, 1980; Pradip and Fuerstenau, 1983), the rare earth fluorocarbonate mineral bastnaesite is floated, using a carboxylate collector, from a number of gangue minerals, primarily barite and calcite. In the case of these three minerals, for example, rare earth ions can dissolve from bastnaesite, partly coating the other minerals with a rare-earth-rich surface.

Because of the similarity of the minerals' surfaces and the interactions among the minerals giving rise to even more alike surfaces, it is necessary in salt-type mineral flotation to add a number of modifying agents to the system that modulate the environment in which the collector functions. In the flotation of bastnaesite from calcite and barite using an anionic carboxylate collector, modifiers added include sodium carbonate, a lignin sulfonate, and sometimes sodium fluorosilicate.

The present investigation is an attempt to elucidate via an electrophoresis study the role of sodium carbonate and lignin sulfonate in this flotation separation. Also, an attempt is made to assess the role of rare earth ions potentially dissolved from the bastnaesite.

Materials and Methods

The bastnaesite used in the experimentation was handpicked specimens from Mountain Pass, California. The calcite was clear Iceland spar from Chihuahua, Mexico, purchased from Wards Natural Science Establishment. The barite was high-quality material from Potosi, Missouri. All reagents used, except for the sodium lignin sulfonate, were of reagent grade or of best purity obtainable. The sodium lignin sulfonate was of industrial grade. Water used was double-distilled in glass stills.

The minerals were prepared for experimentation by grinding in a clean environment. The barite and bastnaesite were ground dry; the calcite was ground wet to avoid conversion to aragonite, which is possible during dry grinding (Burns and Bredig, 1956; Lin and Somasundaran, 1972). Particle size used in the experimentation was <10 μm.

The zeta potential measurements were made in a Komline-Sanderson ZR-4 Zeta Reader, a commercially available electrophoresis apparatus. In the present work 0.6 gm of the minerals were placed in 100 mL of water prior to zeta potential measurements. The minerals were preconditioned in the water for 2 h, after which measured amounts of solutions containing the chemicals to be studied were added to the mineral suspensions and the pH was adjusted using either NaOH or HCl solutions. Electrokinetic measurements were then made using the zeta reader in a standard manner. Reported pH values were obtained just after the measurements.

Results and Discussion

Figure 1 shows the zeta potential of barite, bastnaesite, and calcite in pure water as a function of pH. Note that barite has the most positive surface of the three minerals and calcite the most negative. Bastnaesite thus lies between barite and calcite in electrostatic charge characteristics. Therefore, in a system without modifiers, based on coulombic collector-mineral interaction alone, it should not be possible to float bastnaesite from both of the other minerals. From the figure it can be seen that the pH of the isoelectric point in solution (pH_{iep}) of barite, under the conditions studied, lies at about pH 5.8 and that of bastnaesite at about pH 4.6. The pH_{iep} of calcite could not be realistically determined because of dissolution of the mineral at acid pH values and because it appeared that the calcite used in this

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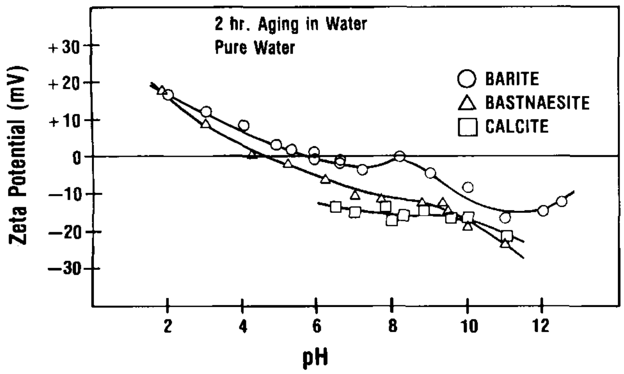

Figure 1. Zeta potential of barite, bastnaesite, and calcite in pure water as a function of pH.

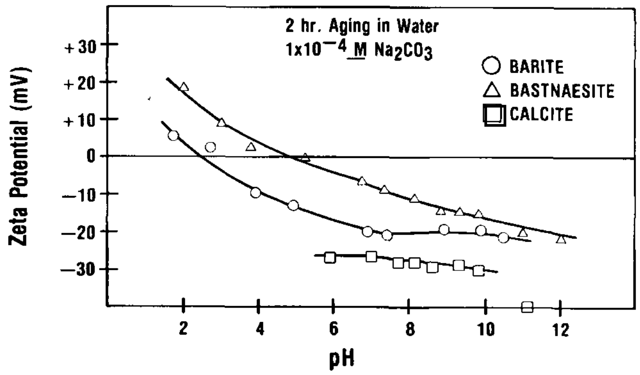

Figure 3. Zeta potential of barite, bastnaesite, and calcite in 1 x 10^{-4} kmol/m^3 Na_2CO_3 solution as a function of pH.

work had an acidic pH_{iep} value. It should be noted that various values have been reported for the pH_{iep} of calcite. For example, Hanna and Somasundaran list pH_{iep} or point of zero charge (PZC) values for the mineral ranging from 5.5 to 10.8. Marinakis and Shergold (1985) report calcite electrophoresis data similar in nature to that of the present experimentation.

Figure 2 shows the effect of addition of 1 x 10^{-4} kmol/m^3 sodium oleate, a carboxylate collector, on the zeta potential of the minerals. The figure illustrates the large effect of sodium oleate addition on the zeta potential of minerals, calcite being least affected and barite most affected. This means that barite adsorbs the greatest quantity of oleate, except at quite acid pH values. Therefore, barite should generally float most readily in the absence of activators. The phenomenon is consistent with the fact of the more positive barite surface. Overall, it is seen that modifiers are necessary for successful floatation of bastnaesite from the other minerals when using oleate as collector.

Figure 3 demonstrates the effect of addition of 1 x 10^{-4} kmol/m^3 sodium carbonate on the zeta potential of the minerals. The effect on barite and calcite is great, making both minerals more negative at all pH values studied. Bastnaesite is unaffected by the addition, and in the presence of sodium carbonate is much the more positive of the minerals. Sodium carbonate is obviously a crucial modifier added to the system.

Figure 4 shows the effect of lignin sulfonate addition on the zeta potential of the minerals studied. This substance creates a more negative surface on all the minerals at all pH values except for little effect on calcite at pH values above 9.3. Thus, there is adsorption of it onto all the minerals and it must function as a depressant for all the minerals. It functions least as a depressant for calcite, followed closely by bastnaesite at basic pH values. The most profound effect is that on barite. It appears, then, that the main function of the lignin sulfonate should be to strongly depress the barite.

Figure 5 shows the effect of addition of 1 x 10^{-4} kmol/m^3 $CeCl_3$ on the zeta potential of the minerals as a function of pH. Because cerium is the rare earth metal present in greatest amount in bastnaesite, Ce (III) ions were chosen for study as representative of the rare earth ions that could be derived from a small dissolution of bastnaesite. It is obvious from examination of the figure that the presence of Ce (III) produces profound effects on the mineral surfaces at pH values more acid than about pH 9.5–10. Indeed, all of the surfaces become much more positively charged. Thus, there should be promotion of flotation of all the minerals by anionic collectors such as oleate through an interaction of the minerals with each other and a slight disso-

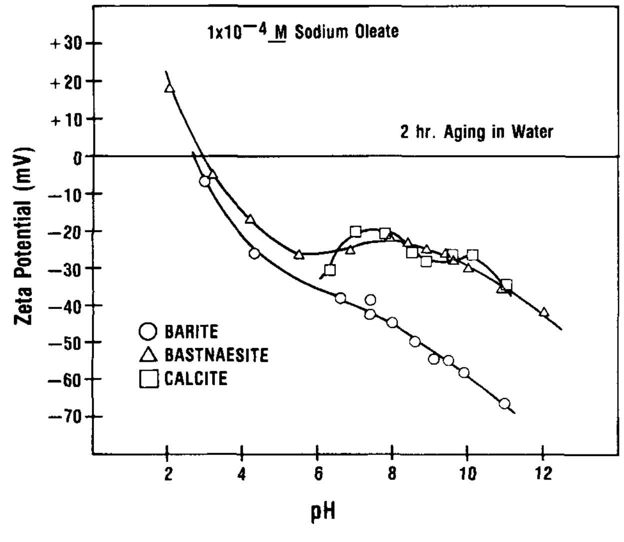

Figure 2. Zeta potential of barite, bastnaesite, and calcite in 1 x 10^{-4} kmol/m^3 sodium oleate solution as a function of pH.

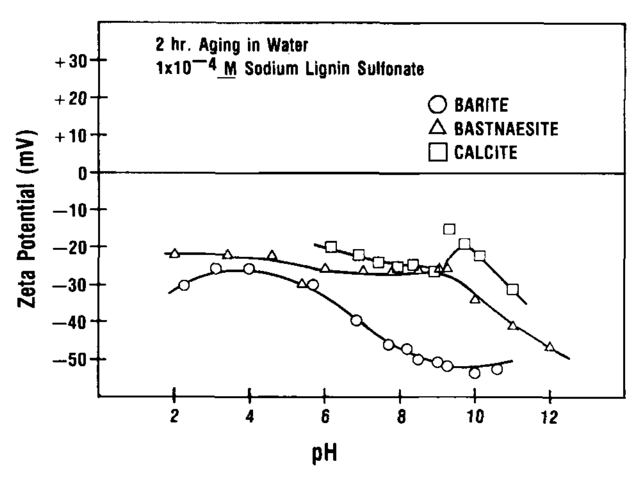

Figure 4. Zeta potential of barite, bastnaesite, and calcite in 1 x 10^{-4} kmol/m^3 sodium lignin sulfonate solution as a function of pH.

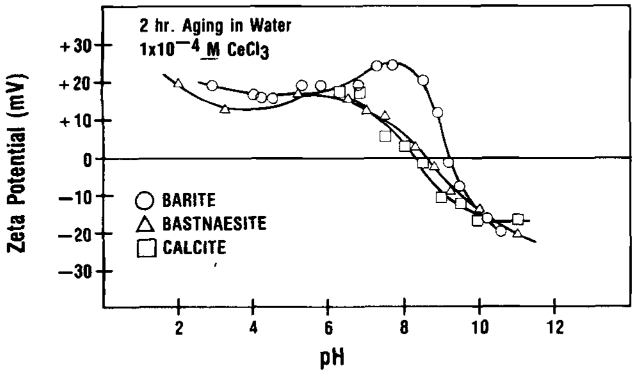

Figure 5. Zeta potential of barite, bastnaesite, and calcite in 1 × 10^{-4} k/mol/m^3 CeCl$_3$ solution as a function of pH.

lution of the rare earths from the bastnaesite. Such dissolution can be promoted, according to Hanna and Somasundaran, by the minerals interacting with each other.

Considering Figure 5, it is of interest to also note log concentration diagrams for the Ce (III) system. Such diagrams are to be found in Smith and Steiner, and in Fuerstenau and Pradip. From the diagrams it can be seen that as pH increases from 5 to about 8 the concentrations of charged aqueous cerium hydroxy species increase. Fuerstenau and Palmer have shown that such species are particularly surface-active and readily adsorb onto mineral surfaces, making them more positively charged.

As pH is raised to about 7.8, Ce(OH)$_3$ starts precipitating from solution and as pH is further raised to about 8.5, most of the cerium has precipitated out of solution. According to Parekh (1979), when a mineral is present in a solution containing metal ions, such as the cerous charged species, and pH is raised, as soon as the metal hydroxide starts precipitating from solution it condenses onto the mineral surfaces. The condensation increases as pH is further raised until the surface becomes, in essence, a metal hydroxide surface of the metal in solution. When the surface becomes, in this case, a cerous hydroxide surface, the electrokinetic behavior of the mineral becomes identical to that of cerous hydroxide. It can be seen in Figure 5, as compared to Figure 1, that the pH of zero mobility for all the minerals has moved to more basic values, presumably near that of cerous hydroxide. Such coatings should make it difficult to separate the minerals from one another.

Figure 6 shows the effect of both sodium carbonate and oleate on the zeta potential of the minerals. The Na$_2$CO$_3$ concentration was 1 × 10^{-4} kmol/m^3 and the oleate concentration 1 × 10^{-4} kmol/m^3. It is of interest to compare Figure 6 with Figure 3: the change in zeta potential at pH 9 of the minerals upon addition of the oleate to the system containing sodium carbonate was about −13 mV for bastnaesite, −28 mV for barite, and nil for calcite.

Thus, at pH 9 the greatest change in zeta potential is for barite and the least for calcite. It appears, then, that with sodium carbonate and oleate present it should be possible to float bastnaesite and barite from calcite using an anionic collector, and that barite probably would float better than bastnaesite. However, comparison of Figure 6 with Figure 2, which is quite similar, makes this statement somewhat equivocal.

Figure 7 illustrates the effect of the presence of both cerium chloride and oleate on the zeta potential of the minerals. Cerium chloride and oleate concentrations were both 1 × 10^{-4} kmol/m^3. This figure should be compared to Figures 2 and 5. It can be seen that the cerium salt added to the system has a major effect on the zeta potential and the position of the curves for the three different minerals. Note that all the curves are close together and that any flotation separation of the minerals would be unlikely under such conditions (compare the displacement of the barite curve in Figure 2 from the other two curves).

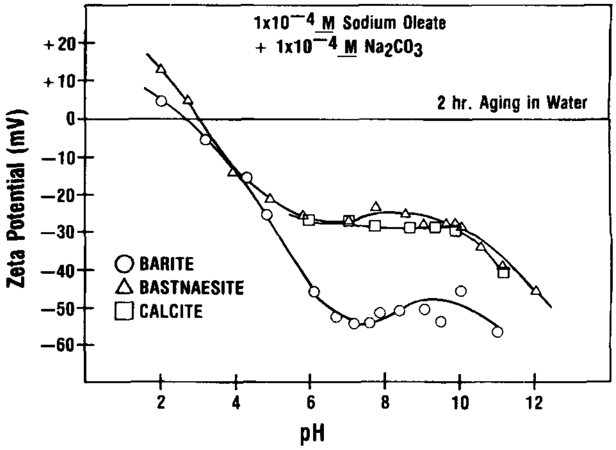

Figure 6. Effect of 1 × 10^{-4} kmol/m^3 sodium carbonate addition on zeta potential of barite, bastnaesite, and calcite in 1 × 10^{-4} kmol/m^3 sodium oleate solution as a function of pH.

Figure 8 shows the effect of the presence of 1 × 10^{-4} kmol/m^3 sodium lignin sulfonate and 1 × 10^{-4} kmol/m^3 of sodium oleate on the zeta potential of the minerals. These figures are only of moderate interest since both lignin sulfonate and oleate lower the zeta potential of the minerals. However, it is interesting to compare Figures 8, 2, and 4, noting that the curves of Figure 8 are more like those of Figure 4 than like those of Figure 2. In particular, in the basic pH region the measured zeta potentials of barite are quite similar in Figures 8 and 2. Overall, this indicates that lignin sulfonate is apparently adsorbing onto all the minerals in preference to oleate, particularly in the case of barite. Here, then, is very indirect evidence of the greater depression of barite by the lignin sulfonate than of the other two minerals.

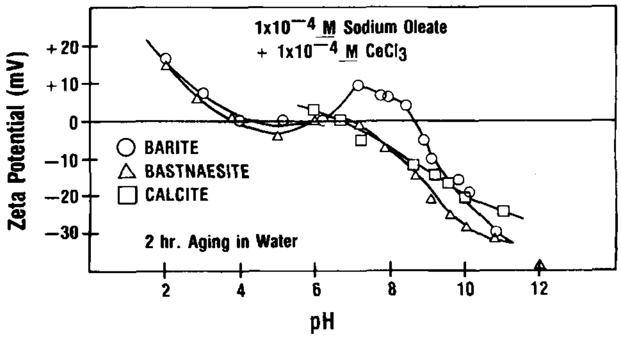

Figure 7. Effect of 1 × 10^{-4} kmol/m^3 cerous chloride addition on zeta potential of barite, bastnaesite, and calcite in 1 × 10^{-4} kmol/m^3 sodium oleate solution as a function of pH.

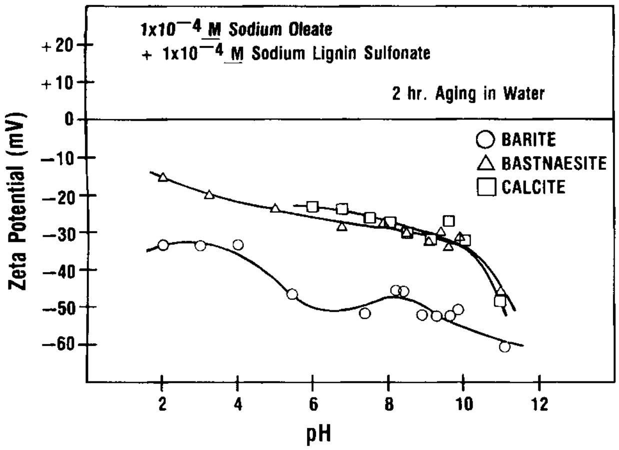

Figure 8. Effect of 1×10^{-4} kmol/m^3 lignin sulfonate addition on zeta potential of barite, bastnaesite, and calcite in 1×10^{-4} kmol/m^3 sodium oleate solution as a function of pH.

Conclusions

From the electrophoresis study undertaken on bastnaesite, barite, and calcite the following have been deduced:

1. Barite is the most positively charged of the minerals and calcite the least positively charged. Thus, flotation of bastnaesite from both of the other minerals should be difficult unless there are modifiers in the system.

2. Electrokinetic studies in systems containing sodium oleate in the absence of modifiers indicates most adsorption of oleate onto barite and least onto calcite, at least at basic pH values.

3. Addition of sodium carbonate to pure mineral systems in the absence of other modifiers or a collector produces little change in the electrokinetic behavior of bastnaesite, but produces more negative surfaces on calcite and barite. Thus, sodium carbonate appears to be a crucial modifier in these systems.

4. Although sodium lignin sulfonate functions as a depressant for all three minerals as suggested by the electrokinetic experimentation, it has greatest effect on barite; therefore, its main function must be to depress barite in bastnaesite flotation from barite and calcite.

5. Cerous chloride markedly affects the electrokinetic behavior of all three minerals. It must so function by adsorbing and/or condensing on all minerals in hydroxy complex form, giving rise at pH values between neutrality and about pH 8.5 to a partly cerous, and above about pH 8.5 to a wholly cerous hydroxide surface. Thus, in bastnaesite flotation if significant amounts of Ce (III) go into solution, means should be taken to either reduce the amount of Ce (III) going into solution or to tie it up in some complex.

Acknowledgment

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