SOLUTION CHEMISTRY OF
SALT-TYPE MINERAL FLOTATION①

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ABSTRACT

Solution chemical equilibria involving flotation agents (hereafter flotagents), minerals and solution play a crucial role in determining the behavior of complex flotation systems. Salt-type minerals such as calcite, apatite etc are sparingly soluble in aqueous solution and form dissolved mineral species in bulk solution. It has been found that such dissolved species interact with the minerals, and often lead to surface conversion of the minerals. In addition, they can interact with various flotagents and lead to surface or bulk precipitation and loss of selectivity in the flotation. Relevant solution equilibria of these salt-type minerals and their interactions with conventional and structurally modified reagents are discussed. Better selectivity in their flotation can be achieved by controlling such interactions and manipulating the solution chemical equilibria.

Key words: Salt-type mineral　oleate　sulfonate　solution chemistry

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1　INTRODUCTION

A considerable amount of work has been done in the past on flotation chemistry of salt-type minerals such as calcite, apatite, dolomite, scheelite and wolframite[1~6]. The flotation process in these cases is complicated due to similarities in the chemical composition and the semi-soluble nature of the constituent minerals. Poor selectivity is often obtained in many of these flotation schemes. Our previous work has shown that surface conversion and dissolved mineral species-flotagent interactions are two major reasons for the poor selectivity in phosphate flotation separation [7~9]. It is, therefore, helpful to understand various solu-
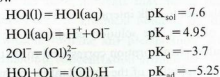
tion chemical equilibria in these systems in order to improve the selectivity in flotation. In this paper, three types of solution equilibria of flotagents, mineral-solution and mineral flotagents and their implications to flotation are examined.

2　SOLUTION EQUILIBRIA of FLOTAGENTS

Most minerals, with the exception of sulfides, require long chain surfactants for their flotation. The behavior of long chain surfactants in solution is determined by the properties of the polar heads and hydrophobic tails and the resultant tendency of the solvent to accommodate them under various conditions.

Hydrolyzable flotagents can undergo special association interactions that can influence their adsorption and flotation properties. For example, oleic acid undergoes dissociation to form ions (R^-) at high pH values and exist as neutral molecules (RH) at low pH values [10,11]. In the intermediate region, the ions and neutral molecules can associate to form ion-molecule complexes. As the collector concentration is increased, micellarization or precipitation of the collector can occur in the solution. In addition, surfactant species can associate to form other aggregates such as dimers (R_2^{2-}) in premicellar solutions. Since the surface activities of these species can be marketedly different from those of each other, flotation of minerals in their presence can be expected to be dependent upon solution conditions such as pH. The solution equilibria of oleic acid are shown as below [12]

$$HOl(l) = HOl(aq) \qquad pK_{sol} = 7.6$$
$$HOl(aq) = H^+ + Ol^- \qquad pK_a = 4.95$$
$$2Ol^- = (Ol)_2^{2-} \qquad pK_d = -3.7$$
$$HOl + Ol^- = (Ol)_2H^- \qquad pK_{ad} = -5.25$$

It can be seen from ref. [13] that (1) pH of precipitation of oleic acid at the given concentration is 7.45; (2) activities of oleate monomer and dimer remain almost constant above the pH of precipitation and decreases sharply below it; (3) the activity of the acid-soap (R_2H^-) exhibits a maximum in the neutral pH range. On the other hand, solution equilibria of cationic flotagents such as dodecylamine are similar to that of oleate [14]. In this case the neutral molecule (RNH_2) precipitates in the high pH value range and ionic species RNH_3^+ and $(RNH_3)_2^{2+}$ dominate in the acidic pH range. Again, the ion-molecule complex exhibits a maximum as the pH value of the solution is changed.

Strongly ionizable surfactants such as dodecylsulfonate may not form acid-soap in significant amounts, but can be expected to form dimers (R_2^{2-}). The calulated distribution of various sulfonate species [13] indicates the presence of R_2^{2-} throughout the pH region, but acid-soap and neutral acid are present in comparable proportions only at very low pH.

3 MINERAL-SOLUTION EQUILIBRIA

When salt-type mineral particles are contacted with water, they will undergo dissolution, of which the extent is dependent upon the type and concentration of chemicals in solution. The dissolved mineral species can undergo further reactions such as hydrolysis, complexation, adsorption and even surface or bulk precipitation. The complex equilibria involving all such reactions can be expected to determine the interfacial properties of the particles and their flotation behavior. For example, in the case of phosphate minerals such as apatite, calcite and dolomite under atmospheric condition, the dissolution of these minerals in water will be followed by pH-dependent hydrolysis and complexation of the dissolved species [7]. For both calcite and apatite, Ca^{2+} is the most predominant species in the acidic pH range while carbonate species of CO_3^{2-} and HCO^{3-} predominate in the basic pH range. The major phosphate species from apatite are $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} depending on pH. For dolomite, Ca^{2+} and Mg^{2+} species are the dominant species below pH10 while carbonate and hydroxyl species of Ca and Mg become predominant above pH10. The solubility of dolomite in water decreases with increase in pH.

For the above sparingly soluble minerals, the effect of dissolved species on interfacial

properties can be marked, for zeta-potential data obtained for calcite-apatite in water and in the supernatants of each other[15]. When apatite is contacted with calcite supernatant, its zeta-potential is seen to shift to that of calcite in water and vice versa, suggesting surface conversion of apatite to calcite and calcite to apatite respectively. Implications of such conversion on selective flotation is to be noted.

　　Surface conversion due to reactions of the dissolved species with the mineral surface can be predicted using thermodynamic stability diagrams for heterogeneous mineral systems based on relevant mineral dissociation equilibria.

　　The activity of Ca^{2+} species 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 surface to that of calcite can be expected in calcite-apatite system. Similarly, the calcite-dolomite and apatite-dolomite singular points occur at pH 8.2 and 8.8, respectively.

　　Solution conditions for the conversion of apatite to calcite by dissolved species can be more readily identified by considering the chemical reaction responsible for the process

$$Ca_{10}(PO_4)_6(OH)_{2(s)} + 10CO_3^{2-} =$$
$$10CaCO_{3(s)} + 6PO_4^{3-} + 2OH^-$$
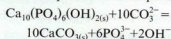
　　It can be seen that, depending on the pH of the solution, apatite can be converted to calcite if the total carbonate in solution is above a certain critical level. In fact, the amount of dissolved carbonate from atmospheric CO_2 does exceed that required to convert apatite to calcite under high pH conditions. Although the kinetics of such transformations is unknow, such reactions can be important in determining the surface characteristics of minerals. Simlar chemical equilibria have been de-

veloped also for other heterogeneous systems made up of calcite, magnesite, dolomite, gypsum, wolframite, etc[6,7,15].

　　It is evident from this discussion that dissolution equilibria of salt-type minerals can play a major role in determining the surface properties of mineral particles. Selective hydrophobization of such particles using surfactants is a key to flotation separation.

4　MINERAL-FLOTAGENT EQUILIBRIA

　　Chemical equilibria in aqueous solutions containing both minerals and flotagents can be expected to be much more complex than in either of the individual systems. In addition to flotagent adsorption at the solid-liquid interface, interactions of the dissolved mineral species with various flotagent species in solution can be expected. It may be noted that the process of adsorption in many cases shows several similarities to bulk interactions. Also in a number of cases, the solution conditions for the so-called chemisorption correspond to that for the precipitation of the surfactant in the interfacial region, suggesting that chemisorption may be in fact a surface precipitation phenomenon.

　　Both francolite and dolomite show two-region linear isotherms with a change in the slope at a concentration of about 10^{-4} kmol / m^3. At a concentration higher than 1.7×10^{-4} kmol / m^3, slopes of both curves are higher indicating that more oleate species is depleted from the mineral slurries[16,17]. Simultaneous analysis of dissolved mineral species in the supernatants of samples used in adsorption experiments (Fig. 1) shows that there is a sharp decrease in the concentration of both Ca and Mg species in solution when oleate concentration exceeds 1.0×10^{-5} kmol / m^3 in the case
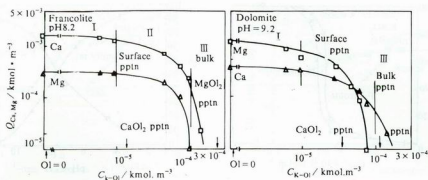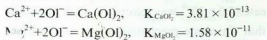
Fig. 1   Dissolved Ca and Mg levels from francolite / dolonite Suspensions as a function of oleate concentration

of francolite and 3.0×10^{-5} kmol / m³ in the case of dolomite. This suggests that bulk precipitation of calcium and magnesium species with oleate can occur under such conditions. As seen from these results, in the low concentration range ($< 10^{-4}$ kmol / m³), the linear rise in the isotherm suggests that oleate adsorption on both minerals may occur predominantly due to chemical bonding on surfaces without forming any precipitation. At an intermediate concentration around 10^{-4} kmol / m³, the solubility limit of Ca and Mg oleates can be reached in the interfacial region but not in the bulk solution, suggesting the occurrence of surface precipitation on both the minerals. In the high concentration range ($> 5 \times 10^{-4}$ kmol / m³), oleate depletion in the case of both the minerals may be predominated by the precipitation of Ca and Mg species with oleate, both on the mineral surface and in the bulk solution[17,18].

Major chemical equilibria for the precipitation of Ca and Mg species and oleate can be described as follows [19,20]

$$Ca^{2+} + 2Ol^- = Ca(Ol)_2, \quad K_{CsOl_2} = 3.81 \times 10^{-13}$$
$$Mg^{2+} + 2Ol^- = Mg(Ol)_2, \quad K_{MgOl_2} = 1.58 \times 10^{-11}$$

The formation of Ca and Mg oleates on the mineral surfaces as well as in the bulk solu-

tion can lead to surface and bulk precipitation. The onsets of the precipitation of $CaOl_2$ and $MgOl_2$ are calculated from their solubility products in dolomite / oleate and francolite / oleate systems and are marked in Fig. 1 The oleate concentration at the onset of precipitation calculated from the solubility data for $CaOl_2$ ang $MgOl_2$ and that obtained by dissolved species analyses are in good agreement with each other. The role of surface and bulk precipitates in mineral flotation can be elucidated by correlating onsets of flotation and surface precipitation in dolomite / francolite systems. Preferential partitioning of the surfactant in the bulk precipitate as opposed to surface precipitate appears to deleteriously affect the flotation of dolomite and francolite. Flotation behavior of francolite and dolomite was studied as a function of oleate concentrations and pH (Fig. 2). It appears from Fig. 2 that the floatability of both dolomite and francolite is quite similar and very sensitive to the oleate concentration. It can be also observed from Fig. 2 that selective flotation of francolite is possible above pH 9.0 or dolomite below pH 5.0. However, selective flotation was absent in the case of flotation of a binary mixture of dolomite and francolite (Table 1).
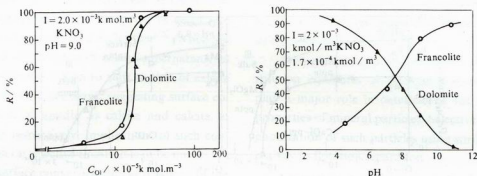
Fig. 2   Flotation of francolite and dolomite as a function of oleate concentration at pH 9.0 (left)

and Flotation of francolite and dolomite as a function of pH with 1.7×10^{-4} mol / L oleate (right)

Table 1   Separation of binary mixture of

francolite and dolomite

Conditions		Grade / %	Recovery / %
K—OLEATE	1.7×10^{-4} mol / L		
	pH = 5.2	58.0	85.0 (dol.)
	pH = 9.0	58.7	86.1 (fran.)
K—OLEATE	7.0×10^{-6} mol / L		
Ethoxylated	7.0×10^{-5}	77.0	92.0 (dol.)
Sulfonate	5.0×10^{-5}		

A major problem in oleate flotation is the low solubility of oleic acid and its poor tolerance for multivalent cations. It has been found that such precipitation can be avoided by using ethoxylated sulfonates as collectors in the case of flotation of dolomite and francolite[9]. Adsorption isotherms of octylbenzenesulfonate (as a reference) and ethoxylated sulfonate on dolomite and francolite are shown in Fig. 3. The isotherms of octylbenzenesulfonate on both minerals are S shaped with four regions and those of ethoxylated sulfonate are typical Langmuir type with only rising part and plateau region. The comparison of the adsorption isotherms of the two surfactans shows that ethoxylated sulfonate adsorbs more than octylbenzenesulfonate on the minerals before the plateau is reached , but there is a significant reduction of its adsorption in the plateau re-

gion of the isotherm. The reduced plateau adsorption may be due to specific interaction of ethoxyl groups with the surface, or steric effects (interference of bulky hydrated ethoxyl groups with close packing of the alkyl chains). Analysis of dissolved Ca and Mg species in the supernatant (Fig. 4 and 5) shows that there is precipitation of Ca disulfonate above a concentration of 1.0×10^{-3} mol / L octylbenzenesulfonate and not that of Mg disulfonate (Fig. 4). Redissolution of Ca disulfonate precipitates occurs around $3 \sim 4 \times 10^{-3}$ mol / L octylbenzenesulfonate. Redissolution is attributed to solubilization of Ca disulfonate by micelles[21]. However, the levels of Ca and Mg species in dolomite and francolite / ethoxylated sulfonate systems remain constant over the tested concentration range, indicating the absence of any precipitation (Fig. 5). This is attributed to the increased salt tolerance of the surfactant due to the addition of ethoxyl groups into the alkyl chain of the sulfonate.

With a mixture of oleic acid and ethoxylated sulfonate as collector, the level of oleate (7.0×10^{-6}) was selected in such a manner that Ca oleate precipitation was avoided (see Fig. 1). Dolomite (77% grade and 92% recovery) can be floated selectively but only in the
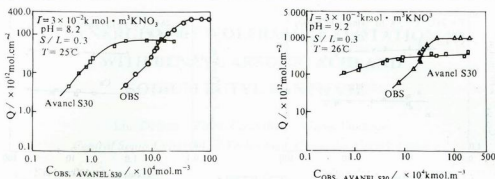
Fig. 3 Absorption isotherms of ethoxylated sulfonate (Avenal S30) and

octylbenzenesulfonate (OBS) on francolite (left) and dolomite (right)

acidic range from a binary mixture of dolomite and francolite (1 : 1) (Table 1). The reagent consumption is found to be reduced by half when oleate and ethoxylated sulfonate mixtures are used (total concentration of 8.0×10^{-5} mol / L).

Factors which can be manipulated to further enhance selectivity include pH, flotagent concentration, ionic strength, temperature and conditioning. The role of chemicals may be different in different systems and it may include alterations of surface properties of solids and complexation of ions / species which causes unintentional activation of the surfactant.

5 CONCLUSIONS

Solution chemistry of sparingly soluble minerals and flotagents in flotation systems is complex, and governs the flotation behavior of minerals in mixed systems. Dissolution of salt-type minerals such as dolomite, apatite and francolite mainly depends upon the solution conditions such as pH and ionic strength, forming dissolved mineral species. The resultant dissolved species can interact with mineral particles leading to surface conversion of the minerals and can also interact with oleate species leading to surface or bulk precipitation. An examination of adsorption and flotation in a number of systems such as oleate / dolomite
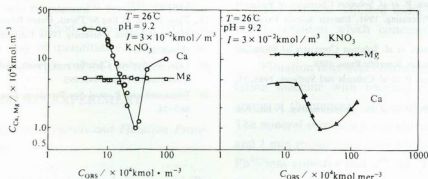

Fig. 4 Dissolved Ca and Mg levels in francolite (left) and dolomite (right)

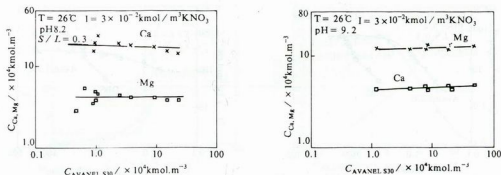**suspensions as a function of OBS concentration.**

Fig. 5 Dissolved Ca and Mg levels in (left) francolite, (right) dolomite

suspensions as a function of ethoxylated sulfonate concentration

and sulfonate / francolite / dolomite shows that such precipitation can be controlled by selecting appropriate flotagents and solution conditions to achieve better selectivity in flotation.

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