Flotation Chemistry and Technology of Nonsulfide Minerals


The dimensions of nonsulfide flotation technology extend in many directions, as might be expected from the diversity of the mineral classes, which include soluble salt minerals (potash, borax, and trona), semisoluble salt minerals (phosphate minerals, fluorite, calcite, and barite), and insoluble oxides/silicate minerals (iron oxide minerals, rutile, mica, quartz, and feldspar). Consequently, some flotation separations are accomplished from saturated brine, though other separations are achieved in solutions of rather low ionic strength. Also, certain nonsulfide minerals are naturally hydrophobic, such as talc, graphite, and coal. However, in general, the nonsulfide minerals are hydrophilic and require relatively high levels of collector addition on the order of 1 lb/ton to establish a hydrophobic surface state. In addition, the nonsulfide collectors generally are anionic or cationic surfactants, having hydrocarbon chains of 10 carbon atoms or greater. In many instances, the collector is sufficiently insoluble so that a distinct collector phase is present in the system, existing as a liquid dispersion or as a collector colloid. This situation further complicates the analysis of nonsulfide flotation chemistry. Thus, in some cases, the hydrophobic surface state is created by the adsorption of water-soluble collector species, though in others, the hydrophobic surface state is created by the wetting/spreading of insoluble collector oils or by the attachment of insoluble collector colloids. In view of the foregoing, it is evident that the flotation chemistry of nonsulfide minerals is distinctly different from the flotation chemistry/electrochemistry of sulfide minerals.

Nonsulfide flotation also differs technically from sulfide flotation technology with respect to particle size. In many, though not all, nonsulfide systems, flotation is accomplished with deslimed feed and a particle size that extends up to several millimeters in diameter (coal, phosphate, and potash). On the other hand, some nonsulfide flotation systems involve flotation of micron-size particles (taconite and kaolin).

With respect to flotation rate, the variation is great, with long retention times (even 1 hour) required for the flotation of impurities (anatase, etc.) from kaolin, whereas rather rapid flotation (a few minutes of retention time) is required for phosphate flotation.

In this chapter, fundamental flotation chemistry issues are discussed for nonsulfide mineral systems, and important examples of industrial significance have been selected from each system. In the case of the oxide–silicate system, fundamental issues of flotation chemistry are discussed in general for aluminosilicates, and specifically for kaolin and iron ore, in industrial practice. In the case of the semisoluble salts system, the fundamental flotation chemistry is discussed in general, and technology associated with the processing of phosphate rock is presented. Finally, for the soluble salt system, a general review of fundamentals is followed with discussion of current flotation practice in the potash industry.
Insoluble Oxides and Silicates
M.C. Fuerstenau

FUNDAMENTALS
Many minerals fall into this category, and whether a particular mineral can be floated with a particular collector depends on the electrical properties of the mineral surface, the electrical charge of the collector, the molecular weight of the collector, the solubility of the mineral, and the stability of the metal-collector salt. Depending on these phenomena, adsorption of collector may occur by electrostatic interaction with the surface (physical adsorption), specific chemical interaction with surface species (chemisorption), or by surface reaction/precipitation.

Flotation by Physical Adsorption
Many collectors achieve adsorption by electrostatic interaction with oxide and silicate surfaces. Such collectors can be used only with knowledge of the point-of-zero charge (PZC) values for the minerals in question. Figure 1 clearly shows the dependence of goethite flotation on electrostatic phenomena when either amines or certain anionic collectors are used. These anionic collectors do not form insoluble metal-collector salts in this system. Below the PZC, the surface is positively charged; negatively-charged sulfonate ions are adsorbed in this region, and complete flotation is effected. Above the PZC, the surface is negatively charged, aminium ions that are positively charged are adsorbed, and flotation results. Sulfonate ions are repelled from the surface under these conditions.

Extensive hydrogen bonding of water molecules occurs on oxide and silicate surfaces. As a result, the presence of hemimicelles of collector or precipitates of collector appear to be necessary to render these surfaces sufficiently hydrophobic for effective flotation to occur. As shown in Figure 2, the concentration associated with a rapid rise in flotation recovery of quartz in the presence of various amines provides evidence of these phenomena. Verification

![Figure 1](image-url)
of this premise has been provided by D.W. Fuerstenau, Healy, and Somasundaran (1964). These authors showed that a plot of the logarithm of collector concentration required for a rapid rise in flotation recovery as a function of the number of carbon atoms in the hydrocarbon chain yields a straight line with a slope corresponding to a specific adsorption potential of $-0.62$ kcal/mol CH$_2$ group. This is the free-energy decrease associated with the removal of hydrocarbon chains from solution by either hemimicelle formation or precipitate formation. The association of hydrocarbon chains (hemimicelles) at the solid–liquid interface is shown in Figure 3.

These phenomena are shown very clearly with the adsorption isotherm of dodecyl sulfonate on alumina at neutral pH, as shown in Figure 4. Three distinct changes in slope of the isotherm can be noted. At low concentration of collector, physical adsorption of individual ions occurs, and the zeta potential remains constant (Region I). With increasing additions of dodecyl sulfonate, adsorption density increases markedly, hemimicelles form, and zeta potential decreases drastically with concentration (Region II). At even higher concentration, a

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**FIGURE 2** The effect of hydrocarbon chain length on relative flotation response of quartz in the presence of various ammonium acetates at neutral pH

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**FIGURE 3** Schematic representation of the electrical double layer in the presence of surface-active organic compounds: (a) adsorption as single ions at low collector concentration, (b) hemimicelle formation at higher concentrations, and (c) co-adsorption of collector ions and neutral molecules

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Source: Aplan and Fuerstenau 1962.
**FIGURE 4** Adsorption density and zeta potential of alumina as a function of dodecyl sulfonate concentration at pH 7.2 and $2 \times 10^{-3}$ mol/L ionic strength


**FIGURE 5** Correlation of adsorption density, contact angle, and zeta potential with flotation of quartz with $4 \times 10^{-5}$ M dodecyl ammonium acetate additions

third change in slope occurs, which probably marks the formation of a bilayer of sulfonate ions at the interface (Region III).

Optimal adsorption of dodecyl amine and flotation of quartz are shown in Figure 5. D.W. Fuerstenau (1957) has explained the optimum flotation response to be due to hemimicelle formation, with hemimicelle formation being facilitated by the coadsorption of neutral amine molecules and amonium ions. Laskowski, Vurdela, and Liu (1988) have suggested that the colloids of precipitated amine formed in alkaline solution may be responsible for quartz flotation under these conditions (see Figure 6). The amine colloids are charged in solution, and they have a PZC at relatively high pH; for example, dodecyl amine has a PZC at pH 11.

The association of hydrocarbon chains, whether as hemimicelles or as a precipitate of collector salt on the mineral surface, is desirable for flotation. Interactions in the interfacial region depend essentially on the relative concentrations of surfactant required to form hemimicelles and to precipitate the surfactant salt. If the concentration of hemimicelle formation is the lower of the two, the formation of hemimicelles would be preferred over collector salt precipitation.
Flotation by Chemisorption
In flotation systems in which covalent bonding occurs, interaction of the collector with the mineral surface, with and without movement of metal atoms from their lattice sites, can occur. With no movement of surface atoms, this is termed “chemisorption,” and adsorption is limited to monolayer coverage only. An example of this system is huebnerite/hydroxamate in which Bogdonov et al. (1973) achieved flotation with 20%–25% of monolayer coverage.

Flotation by Surface Reaction/Precipitation
Surface reaction/precipitation involves interaction of collector with the mineral surface and with metal atoms that have moved from their lattice sites. In many cases, surface reaction of high-molecular-weight collectors on oxides and silicates appears to involve hydrolysis of cations comprising these minerals. Minerals that illustrate these phenomena well are pyrolusite, chromite, and chrysocolla. With minerals that exhibit much greater solubility, such as calcite and fluorite, hydroxy complex formation is not needed for surface reaction, and flotation is not so pH specific.

Pyrolusite/Oleate. A speciation diagram for Mn$^{2+}$ is presented in Figure 7. MnOH$^+$ is present maximally about pH 9 and Mn(OH)$_{2(5)}$ precipitates at about the same pH with $1 \times 10^{-4}$ M Mn$^{2+}$ addition. The flotation response of pyrolusite with oleate as collector is given in Figure 8. Two maxima are present; that at pH 4 is attributed to physical adsorption of oleate on the positively-charged surface. The PZC of this mineral is 7.4. The flotation observed at pH 9 is due to surface reaction involving hydrolysis of Mn$^{2+}$. Additional support for hydroxy complex/metal hydroxide involvement in these systems is provided in Figure 9. The zeta potential of rhodonite (MnSiO$_3$) changes sign in the pH range in which MnOH$^+$/Mn(OH)$_{2(5)}$ are formed with an addition of $1 \times 10^{-4}$ M Mn$^{2+}$.

![Speciation diagram for $1 \times 10^{-4}$ mol/L Mn$^{2+}$](image-url)
**FIGURE 8** Flotation recovery of pyrolusite as a function of pH with $1 \times 10^{-7}$ mol/L oleate

**FIGURE 9** Zeta potential of rhodonite as a function of pH in the absence and presence of Mn$^{2+}$

**Chromite/Oleate.** A second example is chromite, FeO-Cr$_2$O$_3$ flotated with oleate. In nature, Mg$^{2+}$ is frequently substituted for Fe$^{2+}$, whereas Al$^{3+}$ is frequently substituted for Cr$^{3+}$ in chromite. Flotation response with oleate is given in Figure 10. The PZC of this mineral is pH 7, and similarly to pyrolusite, the flotation response at pH 4 is attributed to physical adsorption of oleate. The responses at pH 8 and 11 are attributed to surface reaction involving FeOH$^+$/Fe(OH)$_2$ in part, and to MgOH$^+$/Mg(OH)$_2$ (see Figures 11 and 12). In view of the mechanisms involved in these systems, one would assume that the hydroxy complexes of Cr$^{3+}$ and Al$^{3+}$ would control the flotation characteristics of chromite. In fact, the system is depressed in the pH range in which Cr(OH)$_2^{2+}$ is maximum (Palmer, Fuerstenau, and Aplan 1975). In chromite, aluminum and chromium are coordinated octahedrally with
oxygen, whereas the divalent cations are coordinated tetrahedrally with oxygen. As a result, the divalent cations will dissolve more readily than the trivalent cations. Interestingly, then, the divalent ions comprising this and similar minerals control flotation response.

Chrysocolla/Hydroxamate. The chrysocolla/hydroxamate system provides dramatic evidence of these phenomena. Flotation of chrysocolla occurs around pH 6.3 (Figure 13). This is the pH of maximum concentration of CuOH⁺ (Peterson et al. 1965). Further, when
FIGURE 12 Logarithmic concentration diagram for $1 \times 10^{-4}$ M Mg$^{2+}$

FIGURE 13 Flotation of chrysocolla as a function of pH with various concentrations of octyl hydroxamate

A cupric salt is added, the zeta potential of chrysocolla changes sign from negative to positive in this same pH region (Palmer, Gutierrez, and Fuerstenau 1975; Figure 14). Multilayers of cupric hydroxamate are visibly apparent on chrysocolla after contact with octyl hydroxamate. Chrysocolla changes from its characteristic blue-green color to apple green, the color of cupric hydroxamate.

In this system, movement of copper atoms from lattice sites occurs. As the copper atoms emerge into solution at the solid–liquid interface, formation and adsorption of
FIGURE 14  Zeta potential of chrysocolla as a function of pH in the absence and presence of Cu^{2+}

Chemisorption

\[ \text{Me}^{3+} + Xm^- \rightarrow \text{Me}^{2+} + Xm^- \]
\[ \text{Me}^{3+} + HXm \rightarrow \text{Me}^{2+} + Xm^- + H^+ \]
\[ \text{Me}^{3+} + \text{OH}^- \rightarrow \text{Me}^{2+} + \text{OH}^- \]

Adsorption with Surface Reaction

\[ \text{Me}^{3+} + HXm \rightarrow \text{(MeXm)}^+ + H^+ \]
\[ \text{Me}^{3+} + Xm^- \rightarrow \text{(MeXm)}^+ \]
\[ \text{Me}^{3+} + \text{OH}^- \rightarrow \text{(MeOH)}^+ \]
\[ \text{Me}^{3+} + \text{HCO}_3^- \rightarrow \text{(MeHCO}_3 \text{)}^+ \]

Surface Reaction

\[ \text{(MeOH)}^+ + Xm^- \rightarrow \text{(MeXm)}^+ + \text{OH}^- \]
\[ \text{(MeOH)}^+ + HXm \rightarrow \text{(MeXm)}^+ + \text{H}_2\text{O} \]
\[ \text{(MeOH)}^+ + \text{OH}^- \rightarrow \text{Me} \text{(OH)}_2 \]
\[ \text{(MeOH)}^+ + 2HXm \rightarrow \text{Me} \text{(Xm)}_2 + H^+ + \text{H}_2\text{O} \]


FIGURE 15  Representation of surface reaction/precipitation between insoluble oxides/silicates and hydroxamate as collector

hydroxy complexes occur in the pH range of hydrolysis. Because of the stability of the hydroxy complexes, dissolution of the surface metal atoms is facilitated by hydroxyl ion at these pH values. Collector species or hydroxyl can react with the hydroxy complexes, depending on the pH.

A schematic representation of surface metal atom dissolution, hydroxy complex formation and adsorption, and collector adsorption (hydroxamate) is shown in Figure 15.
Aluminosilicates
J.D. Miller, K. Fa, and X. Wang

**FUNDAMENTAL CONSIDERATIONS**

In the case of aluminosilicate minerals, the fundamental flotation chemistry review by D.W. Fuerstenau and Raghavan (1978) is especially noteworthy. Basically, the aluminosilicate minerals or their magnesia equivalent consist of silica tetrahedra (silica layer) and alumina octahedra (gibbsite layer) or their equivalent such as magnesia octahedra (brucite layer), organized in different structures that distinguish one aluminosilicate mineral from another. Because of the similarity in size between aluminum, $\text{Al}^{3+}$, and silicon, $\text{Si}^{4+}$, the substitution of $\text{Si}^{4+}$ by $\text{Al}^{3+}$, or the substitution of $\text{Al}^{3+}$ by $\text{Fe}^{2+}/\text{Mg}^{2+}$ also influences the aluminosilicate mineral structure. Because the aluminosilicate minerals are composed of a mixture of $\text{Al}–\text{O}$ and $\text{Si}–\text{O}$ bonds, the surface properties of cleaved aluminosilicate mineral particles are determined by the exposure of $\text{Si}–\text{O}$ and $\text{Al}–\text{O}$ sites and their physicochemical properties. The $\text{Si}–\text{O}$ and $\text{Al}–\text{O}$ chemical bonds in aluminosilicate minerals have both covalent and ionic bonding characteristics.

The composition of aluminosilicate minerals varies widely from an alumina to silica weight ratio of 3.0 in the case of kyanite to a ratio of 0.86 in the case of kaolinite. In similar fashion, the structure of aluminosilicate minerals varies considerably from orthosilicate in the case of kyanite minerals to the framework aluminosilicates, such as feldspars and quartz. A classification of aluminosilicate minerals and examples of each class are presented in Table 1, together with reported PZC values.

The PZC of well-hydrated alumina (gibbsite) generally occurs at about pH 9.0, whereas that of silica occurs between pH 2.0 and 3.0. Because the surface properties of aluminosilicate minerals are determined by the combination of $\text{Si}–\text{O}$ and $\text{Al}–\text{O}$ bonds, it is expected that the PZCs of aluminosilicate minerals will lie between pH 2.0 and 9.0. The presence of Li, Ca, K, and Na ions in some aluminosilicate minerals may introduce deviation from the previously mentioned statement, as shown in Table 1 for the case of orthoclase.

Since the review by D.W. Fuerstenau and Raghavan in 1978, some research progress has been made regarding aluminosilicate mineral surface chemistry and flotation technology. Several industrially important aluminosilicate minerals such as kaolin, illite, kyanite, talc, mica, and pyrophyllite are considered.

<table>
<thead>
<tr>
<th>Mineral Class</th>
<th>Structure</th>
<th>Example Mineral</th>
<th>Chemical Formula</th>
<th>PZC, pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthosilicate</td>
<td>Independent tetrahedra</td>
<td>Sillimanite</td>
<td>$\text{Al}_2\text{SiO}_5$</td>
<td>6.8</td>
</tr>
<tr>
<td>Metasilicate</td>
<td>Closed independent rings of tetrahedra</td>
<td>Beryl</td>
<td>$\text{Al}_3\text{Be}_3\text{B}<em>6\text{O}</em>{18}$</td>
<td>3.2</td>
</tr>
<tr>
<td>Metasilicate chains</td>
<td>Continuous chains of tetrahedra</td>
<td>Spodumene</td>
<td>$\text{LiAl(SiO}_3\text{)}_2$</td>
<td>2.6</td>
</tr>
<tr>
<td>Layer silicate</td>
<td>Continuous sheets of tetrahedra</td>
<td>Kaolinite</td>
<td>$\text{Al}_4(\text{Si}_2\text{O}_7)(\text{OH})_2$</td>
<td>3.4</td>
</tr>
<tr>
<td>Framework silicate</td>
<td>Three-dimensional network of tetrahedra</td>
<td>Orthoclase</td>
<td>$\text{K}((\text{AlSi}_3\text{O}_8))$</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quartz</td>
<td>$\text{SiO}_2$</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Kaolin

**Surface Structure and Properties.** Kaolin clay consists largely of the mineral kaolinite, which is a two-layer silicate consisting of alternating layers of silica tetrahedra and aluminum hydroxide octahedra, as shown in Figure 16. The hydrogen bonding between the hydroxyl ions of one sheet with tetrahedral oxygens of the next layer holds the structure together. The hydrogen bonds are weak and, consequently, kaolinite clay is a soft material.

For a kaolinite particle, two different surfaces, the basal planes (001) and (00 1) and the edge planes (110) and (010), are created during fracture or particle breakage. Kaolinite is known to have a heterogeneous surface charge. The basal surfaces of the kaolinite are believed to carry a constant structural charge due to the isomorphous substitute of Si$^{4+}$ by Al$^{3+}$, whereas the charge on the edges is due to the protonation/deprotonation of exposed hydroxyl groups and thus depends on the solution pH. In acidic solution, the edge carries a positive charge, whereas in alkaline solution, the edge is negatively charged, as shown in Figure 17 (Hu et al. 2005). Johnson et al. (2000) reported that the PZC for the kaolinite edge is about pH 7.3 (see Figure 18).

Electrophoretic mobility measurements for kaolinite particles show that the effective PZC value of kaolinite is about pH 3.6 (Hu, Liu, and Xu 2003). They further examined the relationship of PZC with material properties and found that the PZC of kaolinite is closely related to the ratio of alumina (Al$_2$O$_3$) to silica (SiO$_2$) for samples used in these electrophoresis
measurements (Hu and Liu 2003). The greater the $\text{Al}_2\text{O}_3$ content, the greater the PZC, as shown in Table 2.

**Surfactant Adsorption and Flotation.** Researchers in Hu’s group at Central South University, P.R. China (Hu 2003; Qin, Qiu, and Hu 2003; Hu et al. 2003; Luo et al. 2001; Hu and Liu 2003; Hu, Jiang, and Wang 2003; Hu, Liu, and Xu 2003) have made significant contributions toward the understanding of surfactant adsorption of aluminosilicate minerals such as kaolinite, pyrophyllite, and illite, and the development of new, efficient collectors for the separation of aluminosilicate minerals from diasporic bauxite resources. This research group has used froth flotation to improve the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio so that flotation can provide satisfactory products for the Bayer process. Reverse flotation was applied to remove aluminosilicates from bauxite, as the Bayer process requires a mass ratio of alumina to silica of greater than 10.

Because the PZC of kaolinite is about pH 3.6, cationic surfactants have been considered and developed for the removal of silica from bauxite by reverse flotation (Zhao et al. 2003a, b; Wang et al. 2004; Hu, Jiang, and Wang 2003). It was found that the cetyltrimethylammonium
bromide (CTAB) adsorption density increased with an increase in solution pH (Hu, Jiang, and Wang 2003), whereas the flotation recovery of kaolinite, pyrophyllite, and illite decreased with an increase in solution pH. This anomalous behavior of kaolinite flotation was explained by consideration of the crystal structure.

**New Flotation Chemistry.** A new type of cationic collector, DN$_{12}$ (N-decyl-1,3-diaminopropanes), was synthesized and used as collector in the reverse flotation of aluminosilicates from bauxite (Hu 2003; Hu et al. 2003). Because it carries two amine groups, DN$_{12}$ exhibited much stronger bonding with aluminosilicates than dodecyl ammonium acetate (DAA). The flotation response of kaolinite and illite using DN$_{12}$ as collector was improved greatly compared to that using DAA as collector. It has been reported that Fourier transform infrared (FTIR) spectra show that the possible adsorption of cationic surfactants at the negatively charged surface of kaolinite particles is through electrostatic and/or hydrogen bonding (Hu 2003; Hu, Liu, and Xu 2003; Hu et al. 2005).

Improvement in the alumina-to-silica ratio of bauxite resources can be achieved by reverse flotation to remove the aluminosilicate minerals. The flotation tailings are taken as the useful product for the Bayer process. Flotation results show that in a wide pH region, diaspore exhibits a better floatability than kaolinite (Hu, Liu, and Xu 2003). During the reverse flotation, depression of diaspore is required to improve the separation efficiency. In this regard, starch derivatives have been considered for diaspore depression. Starch is an important natural polysaccharide. Because of the presence of OH groups in their basic structural unit, D-glucose, starch molecules are hydrophilic and are broadly applied in mineral processing as either flocculant and/or depressant. However, ordinary starch shows poor selectivity and depressing effect in the reverse flotation of aluminosilicates such as kaolin from bauxite. Hu and colleagues introduced a hydroxamic acid group into the starch molecule to improve the depressing effect on diaspore. The hydroxamic acid starch (HAS) demonstrates a good depressing effect on diaspore flotation while facilitating kaolinite flotation below pH 6.0 (Hu, Liu, and Xu 2003). HAS molecules adsorb at diaspore particle surfaces probably by chemical or hydrogen bonding.

Bittencourt, Lin, and Miller (1990) have studied the separation of gibbsite [Al(OH)$_3$] and kaolinite from quartz. Anionic surfactants, such as sodium dodecyl sulfate (SDS), were used as collector at about pH 2.0. A recovery of about 80% was achieved. The flotation of gibbsite and kaolinite using amine collectors was not applied in the separation because of a significant amount of quartz. The flotation results indicate that gibbsite has a rather strong adsorption potential for alkyl sulfates under acidic conditions, which is in agreement with FTIR spectroscopic analysis. Kaolinite in the flotation concentrate was further separated from the gibbsite using amines as collector below pH 6.0. A final gibbsite concentrate was obtained containing 64.7% Al$_2$O$_3$ with a final alumina recovery of 71.6%.

**Illite**

**Surface Structure and Properties.** Illite is a three-layer aluminosilicate. The isomorphous substitution of Si$^{4+}$ in tetrahedral silicates by Al$^{3+}$ occurs along with varying degrees of substitution of water for lattice hydroxides. Therefore, illite with a chemical formula such as (KAl$_2$[(OH)$_2$][AlSi$_3$O$_10$]) is a potassium aluminum silicate hydroxide hydrate mineral of the clay group. The compensating ions are potassium, which bridge two neighboring sandwiches. In the tetrahedral layers, one-quarter of the Si is replaced by Al. The negatively-charged layers, Al$_2$(OH)$_2$[AlSi$_3$O$_10$], are held together by K$^+$ ions. The isoelectric point (IEP) of illite is about pH 2.8 (Figure 19).
Surfactant Adsorption and Flotation. N-(3-aminopropyl)-dodecanamide (APDA), DN12, and DAA have been studied as cationic collectors for illite flotation. Recent results (Hu, Liu, and Xu 2003) show that in the acid region, the interaction between the collector cation and negatively-charged mineral surface is mainly by electrostatic forces, but in the alkaline region, the interaction is mainly due to hydrogen bonding.

All the cationic surfactants, such as APDA, DN12, and DAA, were studied in the flotation separation of illite from diaspore bauxite (Zhao et al. 2003b). The flotation of illite basically follows a behavior similar to that observed for kaolinite. Flotation recovery of illite drops from acidic solution to alkaline solution as explained in the case of kaolinite, whereas flotation recovery rises with an increase of cationic collector concentration in acidic solution. Generally, a recovery of 80% can be achieved with these cationic collectors.

Kyanite Minerals

Surface Structure and Properties. The kyanite aluminosilicate minerals include sillimanite, kyanite, and andalusite [Al₂SiO₅]. They belong to the orthosilicate class, the structural unit that consists of isolated or independent SiO₄²⁻ tetrahedra linked by aluminum ions. Lateral linkage between the octahedral chains is through the remaining silicon, with aluminum and oxygen atoms being tetrahedrally coordinated with four oxygen atoms alternating with Al between four, five, and six oxygen atoms for sillimanite, andalusite, and kyanite, respectively. The silicon lying between four oxygen atoms thus gives a structure of independent SiO₄ tetrahedra.

Different polymorphs of these aluminosilicates having the same Si/O ratio can exhibit PZCs that depend on the Si/Al ratio in the surface region of the polymorphs (D.W. Fuerstenau and Raghavan 1978). If the PZCs are determined by the Si/Al ratio of the cleavage planes, the PZC of sillimanite might be expected to be the lowest of the three minerals and the PZC of andalusite and kyanite to be about the same. However, electrokinetic measurements indicate that the PZC is about pH 8.0 for sillimanite (Kumar, Prabhakar, and Raju 2002) and pH 6.0 for kyanite (Bulut and Yurtsever 2004), as shown in Figure 20. The PZC
for andalusite is about pH 5.2 (Choi and Oh 1965). As indicated by Smolik (Smolik, Harman, and Fuerstenau 1966) during the electrophoretic mobility measurements, the particles have a more random surface arrangement (sample particles had to be prepared by extended comminution) and, hence, exhibited hysteresis in their electrokinetic behavior.

**Surfactant Adsorption and Flotation.** Oleic acid is usually used as a collector for sillimanite flotation. Adsorption studies indicate that the PZC point shifts to acid side because of oleic acid adsorption. The maximum adsorption of oleic acid by sillimanite was observed at pH 7.5 to 8.0 (Kumar, Prabhakar, and Raju 2002). This pH region is close to the PZC value where the surface is neutral and highly hydroxylated. A density plateau at 5.0 mmol/m² was observed in the adsorption isotherm (Kumar, Prabhakar, and Raju 2002). This adsorption density corresponds to monolayer coverage of oleate molecules (effective parking area for oleate of 33.0 Å²). This may indicate that oleic acid molecules initially form a monolayer, and the precipitation of aluminum oleate multilayers occurs after monolayer adsorption. Kumar, Prabhakar, and Raju (2002) suggested that the hydroxyl sites are essential for oleic acid to react with aluminum ion at the mineral surface. The hydroxyl groups from AlOH and protons from –COOH groups combine to form H₂O molecules and the chemisorption of aluminum oleate at the surface.

Kyanite can be floated with an amine type of collector above its PZC point where the surface is negatively charged. In the acidic pH range, kyanite can be floated using a sulfate type of collector (such as SDS). The adsorption study suggested that when these two collectors were used, the electrostatic interaction accounts for collector adsorption at the mineral surface (Bulut and Yurtsever 2004).

In addition, oleate is used as a collector for kyanite flotation at a neutral and mildly basic pH range. In this case, the adsorption mechanism seems to involve chemisorption as in the oleate–sillimanite system. During the oleate flotation of kyanite, metal ions (such as aluminum, ferric ions) were recognized as activators (Dong and Chen 1996). On the other hand, calcium and magnesium were found to depress kyanite flotation.
A collector has been developed by the Chemical Mineral Institute in China and is successfully being used by industry for the flotation of sillimanite (Wang 1993). The main component of the collector is a fatty acid sodium salt.

Also, a fatty acid and hydrocarbon sulfonic acid blend was studied for sillimanite flotation (Fang and Luo 1994). By using this collector blend, a concentrate ($\text{Al}_2\text{O}_3$, 56.31%; $\text{Fe}_2\text{O}_3$ [hematite], 1.07%; $\text{TiO}_2$ [rutile], 1.0%; alkalis, 0.2%) was obtained with 70% recovery.

**Mica, Quartz, and Feldspar**

**Surface Structure and Properties.** The common mica-type aluminosilicate minerals include biotite [$\text{K(Mg,Fe,Mn)}_3(\text{OH,F})_2\text{AlSi}_3\text{O}_{10}$], margarite [$\text{CaAl}_2(\text{AlSi}_2\text{O}_{10})(\text{OH})_2$], muscovite [$\text{KAl}_2(\text{Si}_3\text{O}_{10})(\text{OH,F})_2$], and lepidolite [$\text{K}_2\text{(Li,Al)}_6(\text{Si}_6\text{Al}_2\text{O}_{20})(\text{OH,F})_4$]. Mica-type aluminosilicate minerals have marked similarities in properties. Mica is an aluminosilicate mineral of layered structure as shown for muscovite in Figure 21. The bases of the tetrahedra are symmetrically opposed so that two opposite hexagonal rings outline a large cavity into which a potassium atom is situated with 12-fold coordination. The potassium ions are used to neutralize the negatively-charged sheets because of the substitution for some of the $\text{Si}^{4+}$ within the silica tetrahedra.

When muscovite is cleaved, the surface of the sheet carries a fixed or constant negative charge that essentially depends only on the degree of Al/Si substitution in the tetrahedra. The zeta potential at a muscovite surface as a function of pH is shown in Figure 22. A constant zeta potential is observed in the pH range examined. The PZC of muscovite mica is about pH 1.0, which indicates that in the common flotation pH range, the muscovite mica surface should be negatively charged.

Mica minerals often occur with quartz and feldspar in a mineral deposit. Quartz and feldspar belong to the framework silicate class and consist of silica tetrahedra linked by the
sharing of oxygen in three dimensions. The quartz crystal is constructed by the sharing of
each oxygen atom between two silicon atoms. The replacement of approximately 25% of
the silicon atoms by aluminum and the introduction of alkali metal ions such as K⁺, Na⁺, and
Ca²⁺ to neutralize the charges gives rise to the feldspar minerals such as orthoclase
[KAlSi₃O₈], albite [NaAlSi₃O₈], anorthite [CaAl₂Si₂O₈], and so forth. The PZC of quartz
is between pH 2.0 and 3.0. The PZCs of orthoclase, albite, and anorthite are reported to be
at pH 1.4, 1.9, and 2.0, respectively (D.W. Fuerstenau and Raghavan 1978).

**Surfactant Adsorption and Surface Micelle Formation.** Mica is easily floated in both
acid and alkaline solutions: an acid system using a cationic collector and a basic system using
an anionic collector (Sekulic et al. 2004; Miller, Tippin, and Pruett 2002). The unique sheet
structure enables mica to be easily peeled layer by layer, and an atomically smooth surface
can be obtained with satisfactory dimensions for scientific research. In the past decade, sub­
stantial progress regarding adsorbed surfactant structure at atomically smooth mica has
been made using modern diagnostic tools such as atomic force microscopy (AFM). Cationic
surfactant adsorption on muscovite mica and the interaction force between mica surfaces
has been studied extensively, as reported in the literature.

The zeta potential of mica as a function of surfactant concentration in the presence
of 1 mM KCl as background electrolyte at neutral pH is shown in Figure 23. A point of zeta
reversal, or PZR, is observed for both dodecyltrimethylammonium bromide (DTAB) and
CTAB. This type of behavior was first observed in 1955 for the adsorption of dodecyl
amine by quartz (Gaudin and Fuerstenau 1955b). The reversal in the zeta potential indi­
cates the substantial adsorption of cationic surfactant molecules at the negatively-charged
mica surface. The PZR for CTAB is shifted to a smaller concentration than that for DTAB.
This is consistent with the common knowledge about the surfactant behavior in bulk solu­
tion and at surfaces. Longer-chain surfactants have greater adsorption potential and cause
reduced surface tension at an equivalent molar concentration. Also, smaller critical micelle
concentration (CMC) values are observed when compared to shorter-chain surfactants.
FIGURE 23  Zeta potential at muscovite surface in the presence of surfactants (CTAB and DTAB). The background electrolyte solution is 1 mM KCl at neutral pH.

Nishimura et al. (2000) reported that the PZR shifts to higher concentration for amines in the order of quaternary > tertiary > secondary > primary, corresponding with the order of head-group radius from quaternary to primary amine (Nishimura et al. 2000).

Only in the last decade, with the development of the AFM soft-contact imaging technique, has direct observation of "wormlike" micelle structures been made at atomically smooth mica surfaces. Before that, most reported research discussed the cationic ammonium surfactant adsorption at mica surfaces as being in a monolayer or multilayer conformation (Rutland, Waltermo, and Claesson 1992). Since 1995, a number of AFM soft-contact images in the literature have provided direct evidence that meandering micelles are formed at mica surfaces at concentrations below the solution CMC values of cationic amine molecules. Figure 24 shows the micellar structure for CTAB at mica surfaces. For CTAB at 0.1-mM concentration, the meandering linear structures are believed to be cylindrical surface micelles, whereas for DTAB, the CMC value is about 15 mM; at a concentration of 20 mM, a micellar structure similar to that shown in Figure 25 was observed by Ducker and Wanless (1996).

The meandering micellar structures of CTAB and DTAB at mica surfaces are different from the micellar structures of CTAB and DTAB at the atomically smooth graphite surface, where linear and parallel hemicylindrical micellar structures were observed. This difference indicates that the topographic structure of the substrate template has a significant influence on the formation of surface micelles. Also, these AFM image analyses are supported by measurement of the diameter of these micelle structures, about 5 nm, which corresponds to the total length of two surfactant molecules.

SDS bears a negatively-charged head group. SDS is not expected to adsorb at the negatively-charged surface of mica, and no surfactant surface structures were observed in the case of SDS. It is thus concluded that electrostatic interaction plays an important role for the adsorption of cationic surfactants at muscovite mica surfaces.

In contrast, at a smooth SiO₂ surface, spherical micelle structures are observed for CTAB below the solution CMC (0.1 mM) as shown in Figure 25.
New Flotation Chemistry. In addition to studies of adsorption and molecular conformations of cationic amines at mica surfaces, the separation of mica from galena using dextrin as a depressant was investigated by Rath and Subramanian (1998). From pH 6.4 to 11.3, the adsorption density of dextrin for galena was observed to be quite high compared to that for mica. Both adsorption isotherms exhibited Langmuir behavior. Flotation results showed that dextrin is a depressant for galena but not for mica. In alkaline solution at about pH 11.0, maximum adsorption of dextrin at the galena surfaces occurs. Separation of mica from galena is achieved above pH 8.5.

Because the adsorption of amine by quartz is a well-established physical adsorption process, the zeta potential of quartz particles is known to play a critical role in adsorption (Gaudin and Fuerstenau 1955b). Figure 26 shows the correlation of flotation recovery of quartz with DAA as collector with the corresponding zeta potentials at pH 5.0 and 9.8 (Takeda and Usui 1987). Complete recovery of quartz particles corresponds well with the PZR values at two different pH values. Takeda and Usui found that at pH 5.0, complete recovery of quartz is achieved at an adsorption density of DAA of only a few percentages of monolayer, whereas at pH 9.8, complete flotation requires a surface coverage of DAA of more than a complete monolayer.

Quartz cannot be easily recovered using anionic collector without activation in neutral and basic solution because quartz particles are negatively charged. Multivalent metal cations have been found to serve as activators in the flotation of quartz using anionic surfactants such as carboxylates, sulfates, and sulfonates. M.C. Fuerstenau and Palmer (1976) have systematically studied the adsorption of cations, such as Fe$^{3+}$, Al$^{3+}$, Pb$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, and Ca$^{2+}$, at quartz surfaces and their influence on quartz flotation response with anionic surfactants such as sulfonate and lauric acid as collector. As shown in Figure 27, activation of quartz occurs in the pH range in which metal ions hydrolyze to hydroxyl complexes. The pH at which the first hydroxy complex becomes significant in concentration is shown, together with the edges outlining minimum values in pH for flotation for each of the cations. Flotation occurs, then, in a similar fashion to that with which insoluble oxides and silicates are floated by surface reaction with anionic collectors (Figures 8 and 9). The complete range of pH in which flotation is obtained is shown in Figure 28. The absence of flotation above the
FIGURE 26  Flotation recovery and zeta potential of quartz at pH 5.0 and 9.8 as a function of the equilibrium concentration of DAA in the presence of $1 \times 10^{-3}$ M KCl

FIGURE 27  Minimum flotation edges of quartz as a function of pH (Conditions: $1 \times 10^{-4}$ M sulfonate, $1 \times 10^{-3}$ M metal ion)

Source: M.C. Fuerstenau and Palmer 1976.
maximum flotation edge is due to the stability of the metal hydroxide relative to the metal collector salt and below the minimum flotation edge to an insufficient amount of hydroxyl complex required for flotation.

Precipitation of the metal collector has been involved in some of these systems. As shown in Figure 29, flotation of quartz occurred only after precipitation of calcium laurate occurred in solution. Arrows indicate the activity of laurate at which calcium laurate precipitated in each system. The critical effect of collector addition relative to that of activator has been shown by Gaudin and Rizo-Patron (1942) and Cooke and Digre (1949). In systems where
precipitation of the metal collector has occurred, at constant collector addition, increasing
the metal ion addition by an order of magnitude reduced the minimum pH at which flota­
tion occurred by one unit.

James and Healy (1972) provided an excellent analysis of these systems in terms of
competing energy changes as an ion approaches an interface. The attractive energy is the
electrostatic free energy, possibly supplemented by short-range forces. The opposing energy
involves the secondary solvation energy changes as parts of the solvation sheath are rearranged
or replaced. Their analysis shows that solvating energy change is much more favorable for a
hydroxy complex than for a hydrated divalent ion with a solid of low dielectric, such as
quartz. Hence, the overall free energy of adsorption will be much more favorable.

Flotation separation of Na-feldspar from K-feldspar has been studied by Demir, Abra­
mov, and Celik (2001). Because of the similarities in the physical and physicochemical prop­
erties of Na- and K-feldspars, their flotation separation was considered very challenging.
However, it was found that with addition of monovalent salt, such as NaCl or KCl, and
bivalent salts, such as CaCl$_2$ or BaCl$_2$, satisfactory separation using froth flotation technique
can be achieved (Demir, Abramov, and Celik 2001; Demir et al. 2003). The fundamental
nature of this separation was considered to be the result of ion exchange between the added
cations and those in the crystal lattice.

**Talc and Pyrophyllite**

**Surface Structure and Properties.** Both talc and pyrophyllite have three-layer sheet
structures. In the case of talc [Mg$_3$(Si$_4$O$_{10}$)(OH)$_2$], no replacement of silicon by aluminum
occurs. The brucite layer has the positive charges to neutralize the two hexagonal networks
of silica tetrahedra to give the crystal the sandwich construction shown in Figure 30. There
is no net charge on the three-layer sheets. The three-layer sheets are held together only by
van der Waals forces so that the layers are capable of slipping easily over one another. There­
fore, talc is a very soft and smooth material. As shown in Figure 31, pyrophyllite has a three-
layer sheet structure similar to talc, in which the magnesium atoms are replaced by aluminum
atoms to neutralize the sheet by forming a gibbsite layer sandwiched between two tetrahe­
dral sheets. In the case of pyrophyllite [Al$_2$(Si$_4$O$_{10}$)(OH)$_2$], each three-layer sheet is also
electrically neutral, and the bases of these sheets are held together only by weak van der Waals forces. The lack of surface polarization provides talc and pyrophyllite with natural floatability.

**Surfactant Adsorption.** The faces of talc and pyrophyllite are naturally hydrophobic, as expected, based on their crystalline structure. However, the edges of the talc and pyrophyllite particles are created by the breakage of the Si–O or Al–O bonds, and, consequently, the edges are hydrophilic. The ratio of hydrophilic/hydrophobic surface sites is expected to affect the electrokinetic properties and the flotation behavior of these minerals. The PZC for pyrophyllite is reported as pH 2.4 (Hu, Liu, and Xu 2003), whereas for talc the PZC is reported to be pH 3.0 (M.C. Fuerstenau, Lopez-Valdivieso, and Fuerstenau 1988).

Because talc has natural floatability, collectorless flotation of talc is expected to be achieved. Yehia and Al-Wakeel (1999) achieved about 60% recovery of talc using only frother in laboratory flotation experiments at neutral pH. By column flotation using methyl isobutyl carbinol (MIBC), an 83% recovery of talc was reported by Kho and Sohn (1989). Erdemoglu and Sarikaya (2002) reported that 60% to 70% of pyrophyllite can be recovered using diethylhexanol as frother.

**New Flotation Chemistry.** The effect of the hydrolyzed Al$^{3+}$, Cr$^{3+}$, and Fe$^{3+}$ on hydrophobic talc particles was examined by Fuerstenau and colleagues with electrokinetic and microflotation studies (M.C. Fuerstenau, Lopez-Valdivieso, and Fuerstenau 1988). At a concentration of $1 \times 10^{-4}$ M, all the cations were found to reverse the zeta potential of talc from negative to positive. Because talc is comprised of polar and nonpolar surfaces, the change in zeta potential is believed to be due to the adsorption of metal hydroxy complex species at the polar edges. Microflotation results showed that talc flotation is depressed in a specific pH range, where the polyvalent cations precipitate as metal hydroxides. From the analysis of species distribution diagrams, it was concluded that uptake of metal hydroxide precipitate occurs on both the polar and nonpolar surfaces at pH values below the PZC of the hydroxides, resulting in the loss of natural hydrophobicity.

**Depression with Organic Colloids.** Talc depression is important because in many cases talc is considered as a gangue mineral in the flotation separation. This is particularly important in the case of sulfide flotation. For example, talc is a common component of the gangue minerals associated with the platinum-group-metal sulfide ores in South Africa. Because of its natural hydrophobicity, significant amounts of talc minerals are entrained in the froth phase, resulting in a decrease in the concentrate grade. Parolis, Groenmeyer, and Harris (2004) investigated the effect of metal cations on the adsorption of carboxymethylcellulose. They found that the presence of Ca$^{2+}$ or Mg$^{2+}$ reduces the electrostatic repulsion between the carboxymethylcellulose and the talc edge, resulting in a higher adsorption density of carboxymethylcellulose at talc surfaces. The high ionic strength also has the effect of allowing the polymer to form in a more tightly coiled conformation so that a higher adsorption density is achieved. These researchers also found that an increase in the polymer molecular weight did not significantly affect adsorption at the talc surfaces. Poly(oxyethylene)alkyl ethers ($\text{C}_{12}(\text{EO})_n$, $n = 8, 5, 3$) and polysaccharides such as guar gum and carboxymethylcellulose have been studied as depressants for talc by other research groups (Pugh and Tjus 1990; Pugh 1991; Shortridge et al. 2000). Three poly(oxyethylene)dodecyl ether derivatives with a definite number of oxyethylene units ($n = 8, 5, 3$) were found to have an increasing depression effect on talc in the order of $\text{C}_{12}(\text{EO})_8 > \text{C}_{12}(\text{EO})_5 > \text{C}_{12}(\text{EO})_3$, which can be related to size of the ethoxy unit. The flotation recovery minimum was reached at a critical concentration for all three derivatives. By careful control of the depressant concentration, a
satisfactory separation of galena from talc could be achieved, as revealed from the flotation experiments (Pugh and Tjus 1990). The predominant interaction forces between poly(oxyethylene)alkyl ether and talc were proposed as hydrophobic interactions and/or hydrogen bonding occurring at faces and edges. Recent research has shown the significance of hydrophobic bonding for dextrin adsorption at the nonpolar talc surface. Figure 32 shows the dextrin molecular structure optimized using PM3. The OH group and oxygen atoms are intended to align at one side of the dextrin molecule. This side of the molecule is expected to have strong polar properties though the other side of the molecule reveals a nonpolar region. The adsorption of dextrin molecules at talc surfaces may be explained as a result of hydrophobic attraction between dextrin molecules and talc surfaces.

Shortridge et al. (2000) reported about the study of polysaccharide depressants on the flotation of talc. They found that guar was a much more effective depressant than carboxymethylcellulose. Also, as the molecular weight of the guars increased, their depressing ability on talc increased accordingly.

**SUMMARY AND CONCLUSIONS**

Some substantial research progress has been made during the last two decades. First, reverse flotation of aluminosilicate minerals from bauxite ores has been used to remove aluminosilicates such as kaolinite, pyrophyllite, and illite. The surface characteristics and flotation behavior of kaolinite, pyrophyllite, and illite have been studied and analyzed by Hu's group. New collectors and depressants were developed with success. A satisfactory product can be obtained for the further Bayer process for recovery of diasporic bauxite resources.

Second, the surface micelle structure at the surface of mica has been extensively studied using the AFM soft-imaging technique and interaction force measurements. These studies provide straightforward information about how the surfactant molecules adsorb and pack at the mineral surfaces and what the driving forces are for adsorption. Visualization of micellar structure at atomically smooth mica surfaces and at the surface of silicon wafers verified the long-held assumption that surfactant molecules are intended to form a micelle structure at the mineral surfaces and a good flotation response could be achieved at the concentration of surface CMCs, which are usually smaller than the solution CMCs.

Third, progress in the depression of naturally hydrophobic talc has been made. Many types of long-chain organic molecules or polymers and the influence of some cations on the adsorption of these large molecules at talc surfaces have been investigated. However, because of the complexity of the depression process, new discoveries and techniques are required to efficiently depress talc particles. This review shows the relationship between surface properties of aluminosilicates and their flotation behavior. The hydrophobic or hydrophilic nature
FLOTATION CHEMISTRY

of an aluminosilicate is determined by its intrinsic crystal chemistry properties of the cleavage surface in water. Because a wide range of crystal structures are present in aluminosilicate minerals, studies of their surface chemistry and crystal structure provide the basis for understanding their flotation chemistry. Traditionally, aluminosilicates were considered as the flotation gangue materials. With the developments and requirements of economy and technology, several aluminosilicate minerals have been recovered worldwide during the last two decades. The further study of surface chemistry and new flotation technology will be expected and required for better utilization of aluminosilicate resources.

Kaolin Flotation Practice
C. Basilio and S. Mathur

BACKGROUND
Kaolin is a naturally occurring, relatively white clay material composed predominantly of kaolinite, a hydrous aluminum silicate mineral. Kaolinite can be formed via residual weathering, hydrothermal alteration, or sedimentation. Kaolins are generally classified as primary or secondary deposits (Prasad, Reid, and Murray 1991). Primary kaolin is formed in situ, usually by alteration of crystalline rocks like granite or gneiss. The alteration can be by surface weathering or action of hydrothermal fluids. A good example of primary kaolin is the deposit in Cornwall, England. On the other hand, secondary kaolin is a sedimentary mineral that has been eroded, transported, and deposited as beds or lenses associated with other sedimentary rocks. Most of the secondary deposits, such as those found in Georgia (United States) and Brazil, were formed by the deposition of kaolinite that had been formed elsewhere.

The whiteness, brightness, and platy shape of kaolin makes it useful as coatings and fillers for paper. Kaolin gives opacity, gloss, and good printability to coated paper and board. Other properties of kaolin, such as chemical inertness, ultrafiness, platy shape, and so forth, make it an excellent filler, carrier, opacifier, or diluent in a variety of industrial products such as paints, fiberglass, plastics, cement, rubber, fertilizers, textiles, pharmaceuticals, cosmetics, and detergents.

In 2003, about 25 Mt of kaolin were produced in the world with the United States being the largest producer. Production in the United States was about 7.9 Mt and valued at $960 million (Virta 2004). The average value of U.S. kaolin produced was estimated to be $212 per ton. About 50% of the world’s kaolin production was for the paper industry. In the United States, 55% of total domestic sales for kaolin was for paper applications, 16% for refractory products, 5% for fiberglass, 4% for catalyst, 3% for rubber, and 17% for other applications.

Generally, kaolin clay, as mined, contains a variety of mineral impurities such as iron oxides, titaniferous minerals, silica, feldspar, mica, sulfides, and sometimes organic matter such as lignite, graphite, and so forth. Crude clays require purification from associated impurities in order to make them acceptable for the uses mentioned previously. The colored impurities, primarily the titaniferous minerals (iron-anatase), must be reduced to acceptable levels to produce high-brightness clay products. Several process applications are currently used on an industrial scale. The first stage of processing includes washing and degritting to remove the coarse impurities, such as silica and mica. Next, the discoloring impurities are
removed by several beneficiation processes, such as froth flotation, high-gradient magnetic separation, selective flocculation, and leaching.

High-gradient magnetic separation (HGMS) has been widely used in the kaolin industry to remove colored impurities, mainly titaniferous minerals (iron-anatase). HGMS involves the use of a magnetic field to remove the impurities with magnetic susceptibility, such as anatase, rutile, hematite, mica, and pyrite. However, this method is not very effective for submicron particles and is limited in its capability to produce high-brightness kaolin products. A major breakthrough in HGMS technology is the development of the superconducting HGMS (Clark 1985). Using superconducting technology, extremely high magnetic fields (up to 50 kilogauss) can be achieved with very minimal power consumption.

Selective flocculation is an effective process for recovering fine to ultrafine kaolin minerals that respond poorly to conventional beneficiation processes, such as flotation and magnetic separation. This process has been successful in beneficiating fine-grained kaolins and involves activating impurities with polyvalent cations (Maynard, Skipper, and Millman 1968; Mercade 1972, 1975; Sheridan 1974), conditioning with ammonium salt (Shi 1986), or fatty acid and polyvalent cations (Behl, Willis, and Young 1996), and then selectively flocculating the impurities with anionic polymers. The drawback is the relatively low recoveries obtained in this process.

The leaching of kaolin clay involves the use of iron-reducing reagents, such as zinc or sodium hydrosulphite. This leaching method is limited to removing iron contaminants only. Typically, this process is carried out at very acidic conditions. Other known leaching reagents and/or processes are not economical for removing titanium impurities.

Froth flotation is regarded as one of the most effective methods in the kaolin industry for removing titaniferous discoloring impurities from kaolin clays. Typically, kaolin clay to be beneficiated by froth flotation is first blunged in the presence of a dispersant and pH modifier to prepare a stable slurry. Next, the slurry is conditioned with a collector to render the impurity minerals hydrophobic. The conditioned impurities are then removed by flotation via the attachment of hydrophobic impurities to air bubbles. There are a number of kaolin flotation technologies using a variety of process strategies to make the impurities hydrophobic.

The discoloring impurities found in kaolin clays are mainly titaniferous minerals, specifically iron-anatase and iron oxides. Although commercial anatase is pure white with brightness close to 100, the iron-anatase naturally occurring in kaolin is beige to dark reddish brown in color. This is due to the substitution of iron within the lattice of the anatase at levels typically less than 5%. Therefore, removal of the iron-anatase from kaolin results in an increase in the brightness of kaolin clays. The iron oxides are typically removed by acid leaching in reducing environments. Brightness is a measure of the blue reflectance of pigments. The brightness scale is calibrated with respect to pure magnesium carbonate (MgCO₃), which has been arbitrarily assigned a value of 100. Brightness is measured at an effective wavelength of 457 nm and is distributed throughout the spectral range of 400 to 500 nm.

Kaolin clays, unlike most minerals beneficiated by flotation, are very fine with particle sizes of about 50% to 90% passing 2 microns. It is known from the literature that flotation of most minerals is optimum in the particle size range of 100 to 10 microns (Wills 1992). Below 10 microns, flotation is considered very difficult, although there has been no evidence of a critical size below which particles will not respond to flotation. In the case of kaolin flotation, the gangue minerals (i.e., iron-anatase) are actually the ones floated, so the
majority of the fine particles (i.e., kaolinite) are hydrophilic and remain in suspension. The reverse flotation of kaolin may partly help explain the success found in the flotation of such fine particles.

**Flotation Strategies**

All kaolin deposits do not respond to flotation in the same way. The presence of various trace impurities, particle size distribution of kaolin and iron-anatase, and the extent of liberation of the coloring impurities are key factors that govern the selectivity and yield in the flotation of kaolin clays. Coarse soft clays found in the Middle Georgia area of the United States respond better to flotation than the East Georgia kaolin deposits. The East Georgia kaolin deposits have a finer particle size, higher surface area, and higher TiO₂ content than those of the Middle Georgia kaolin clays. Flotation of kaolin clays from other major secondary deposits, such as Brazil, is currently not practiced.

The various surface chemical interactions involved between collector molecules and the minerals—specifically, iron-anatase in providing selectivity in the flotation processes—are provided in the following sections.

**Carrier Flotation.** Carrier flotation, also known as ultraflotation or piggyback flotation, was the first successful commercial flotation process in the kaolin industry (Greene, Duke, and Hunter 1961). In this process, the kaolin clay is slurried using sodium silicate as a dispersant and degritted using 325-mesh screens. The slurry is then conditioned with tall oil in the presence of calcium carbonate. The dissolved calcium ions from the calcium carbonate act as an activator for the iron-anatase surface to absorb the tall oil. The fine coloring impurity (i.e., iron-anatase) "piggybacks" to the calcium carbonate, which acts as the carrier mineral (see Figure 33). Because of the relatively coarser particle size of the carrier mineral, flotation is enabled at reasonable rates. The carrier used is calcite (typically ~325 mesh), which is also conditioned with tall oil to make its surface hydrophobic. Calcite is a satisfactory carrier mineral because of its low cost, excellent flotation response, availability, and ease of removal from the froth. Frother is not needed because the tall oil provides sufficient froth.

Wang and Somasundaran (1980) studied the mechanism of carrier flotation by measuring the zeta potential of anatase, kaolinite, and calcite as a function of sodium oleate concentration. Their results showed both anatase and calcite to be negatively charged in the
presence of oleate collectors. This suggests that the “piggyback phenomenon” of attachment of anatase onto calcite is due to hydrophobic interaction between the oleate layers adsorbed on the mineral surfaces, not electrostatic attraction.

In addition, Wang and Somasundaran (1980) provided an explanation for the beneficial effect of high-speed agitation during the conditioning process in ultraflotation. Dissolved calcium ions adsorb on both kaolinite and anatase surfaces, facilitating the adsorption of tall oil. However, their data showed that the zeta potential of kaolinite decreases with increasing high-shear agitation but that of anatase does not change. The authors concluded that collector adsorption by kaolinite is relatively weak as compared to its adsorption by calcite and anatase. Therefore, upon high-shear agitation, the collector coating on kaolinite is readily removed though it remains on iron-anatase, allowing for selectivity to be achieved in the flotation process.

Carrier flotation has been practiced successfully to overcome the fine particle size problems associated with the coloring impurity and to be able to produce high-brightness kaolin clays. However, this process has certain inherent disadvantages: (1) high reagent consumption is required because of the need to condition the carrier mineral; (2) low pulp density is required for greater efficiency; and (3) carrier mineral in the kaolin clay product needs to be removed completely and needs to be recovered in the froth phase for recirculation.

The recovery by carrier flotation may be improved by centrifuging the froth to separate the coarse calcium carbonate–titania aggregates from the entrained kaolin (Gantt et al. 1994). A mechanical separation process, such as a centrifuge or a hydrocyclone, will not accomplish the separation if all of the particles are dispersed. The presence of a flotation collector to agglomerate the impurities is essential for mechanical separation and to enhance the overall recovery of kaolin.

**Fatty Acid Flotation.** Cundy (1969) developed the first carrierless flotation process for the removal of titaniferous impurities from kaolin. The two essential features of this process are high-energy scrubbing of the kaolin slurry at 40% to 60% solids and the presence of activator ions, such as calcium. According to Cundy, the scrubbing action resulting from the high-shear agitation at high-solids content cleans the mineral surfaces from contamination, resulting in an improved difference between the different mineral particles. It is, however, more likely that this process facilitates liberation of the colored impurities from kaolin and thus prepares the slurry for conditioning with the oleic acid in presence of calcium ions. As discussed for the carrier flotation process, the high-speed agitation probably also leads to the collector coating the iron-anatase particles only, which results in flotation selectivity. In addition, the collector-coated iron-anatase particles may be selectively coagulated under high-speed agitation, which effectively increases the particle size and allows flotation.

In the Cundy process, the high-energy scrubbing is conducted at relatively high solids content in two stages. Initially, the kaolin crude is scrubbed in the presence of a dispersant (e.g., sodium silicate) and a pH modifier (e.g., ammonium hydroxide). The second stage of scrubbing involves conditioning with calcium salts and fatty-acid-type collector (e.g., oleic acid). After conditioning, the pulp density is reduced to about 15% to 20%, and conventional mechanical flotation cells are then used to remove the colored impurities. Again, similar to carrier flotation, the fatty acid collector provides the frothing action required for flotation.

The fatty acid flotation by Cundy was modified by Young, Morris, and Brooks (1985) to what is called the titanium removal and extraction process (TREP). This carrierless flotation uses oleic acid as a conditioning reagent in the presence of a calcium activator but under
acidic conditions. A major difference between the TREP and the previous kaolin flotation processes is that in the TREP, flotation is accomplished at the same high solids as during conditioning, that is, in excess of 25%, the benefit of which is higher throughput and lower dewatering costs. Other unique features of TREP compared to previous flotation methods are the novel high-intensity conditioner (Bacon and Brooks 1984) and column-like flotation cell (Bacon 1984). In the TREP conditioner, the temperature of the conditioned slurry reaches in excess of 93°C (200°F). The conditioned product is then treated with a dispersant (i.e., sodium polyacrylate) prior to being floated in the column flotation cell described in the patent by Bacon (Bacon 1984).

The high conditioning temperature facilitates higher solubility of oleic acid and also decreases the $pK_a$ of the oleic acid. As a consequence, even though the pH of the conditioner feed is in the range of 6.1 to 6.3, interaction between the oleic acid and the iron-anatase particles occurs through a bridging mechanism with calcium ions. The conditioning under acidic pH distinguishes the TREP from the Cundy process. A typical result of TREP flotation is given in Table 3.

The separation efficiency is sensitive to the dispersant added prior to conditioning and flotation. Young, Morris, and Brooks (1985) showed that organic dispersants, such as polyacrylates or inorganic dispersants such as sodium polyphosphates, added prior to conditioning inhibit flotation (see Table 3). The results show dramatically that the addition of a polyacrylate dispersant prior to conditioning is very detrimental to TiO$_2$ removal. The polyacrylate salt added before conditioning provides only one-fourth of the TiO$_2$ removal obtained otherwise. However, the conditioned product could be best dispersed for flotation with polyacrylate rather than an inorganic dispersant, as illustrated in Table 4. These results show that the polyacrylate dispersant added to the conditioned product results in an almost twofold TiO$_2$ removal during flotation compared to no dispersant. Further, the inorganic dispersants offer only a marginal improvement as compared to no dispersant addition prior to flotation. The effects of dispersant added after conditioning are shown in Table 5.

A major drawback to TREP is that the high-intensity conditioning is time intensive, which significantly increases the processing cost. In addition, equipment wear is more pronounced, resulting in higher maintenance costs. Efforts to reduce the conditioning time have resulted in inadequate flotation separation and/or low kaolin recovery.

### TABLE 3 Effect of TREP on beneficiation of kaolin

<table>
<thead>
<tr>
<th>Sample</th>
<th>% TiO$_2$</th>
<th>GE Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>1.76</td>
<td>84.7</td>
</tr>
<tr>
<td>TREP product</td>
<td>0.53</td>
<td>89.1</td>
</tr>
</tbody>
</table>

Source: Young, Morris, and Brooks 1985.

### TABLE 4 Effects of dispersant addition prior to conditioning

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersant Added Before Conditioning</th>
<th>Dosage, kg/ton</th>
<th>Product, % TiO$_2$</th>
<th>GE Brightness</th>
<th>% TiO$_2$ Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>—</td>
<td>—</td>
<td>1.83</td>
<td>85.6</td>
<td>—</td>
</tr>
<tr>
<td>TREP product</td>
<td>Sodium silicate</td>
<td>1.15</td>
<td>0.53</td>
<td>90.9</td>
<td>71.0</td>
</tr>
<tr>
<td>TREP product</td>
<td>Sodium silicate</td>
<td>1.15</td>
<td>1.50</td>
<td>87.0</td>
<td>18.0</td>
</tr>
<tr>
<td>TREP product</td>
<td>Sodium polyacrylate</td>
<td>0.85</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Source: Young, Morris, and Brooks 1985.
**Hydroxamate Flotation.** Carrier flotation and the fatty acid flotation technologies are based on the use of fatty acid– or tall oil–type collectors and require the use of divalent or trivalent cations for activation. The presence of activator ions makes the process sometimes difficult to control because of the necessity to maintain a proper balance between the amounts of collector and activator added. For instance, an excessive use of activator can induce coagulation of the clay particles and makes the separation difficult. Further, activators may also cause the flotation of the clay particles themselves rather than the colored impurities, resulting in poor selectivity and a decrease in clay recovery. It is therefore desirable to have a collector for colored impurities that does not require activators.

The use of alkyl, aryl, or alkylaryl hydroxamates in the flotation of minerals that chelate with hydroxamate is also known in the industry (Nagaraj 1988). Hydroxamates are powerful collectors in flotation due to their ability to selectively chelate at the surfaces of minerals that contain titanium, yttrium, lanthanum, cerium, niobium, tantalum, tin, iron, manganese, and copper. Mixtures of minerals containing copper and iron have been successfully beneficiated by flotation using hydroxamates as the collector (Peterson et al. 1965; M.C. Fuerstenau, Miller, and Gutierrez 1967; M.C. Fuerstenau, Harper, and Miller 1970).

Yoon and Hilderbrand (1986) first patented a successful kaolin flotation process based on hydroxamate collectors. The hydroxamate collectors can be used effectively at pH values above 6, under which conditions clay dispersion is readily achieved. The amounts of these reagents required for flotation are considerably less than those typically used in the conventional tall oil flotation process. Also, the hydroxamate collectors possess frothing properties so that frother addition is not required for flotation. An improved manufacturing process for hydroxamates was patented by Wang and Nagaraj (1989). This process is used for the commercial production of the alkyl hydroxamate (Aero 6493 Promoter) currently used in the kaolin industry.

Flotation with hydroxamate collectors consists of similar basic steps as those described in the other processes, such as dispersing the clay slurry and conditioning with the collector. Conditioning solids can be as high as 70%, and the flotation solids can be between 15% and 45% with the use of hydroxamate collector. Activators such as calcium ions are not required for hydroxamate flotation. The distinguishing features with the hydroxamate collectors are relative insensitivity to the dispersant type and high solids during conditioning and flotation (Yoon et al. 1992). The conditioning pH is generally maintained between pH 8 and 10, because the process is not as efficient at lower pH values and more alkaline pH results in excessive frothing that inhibits effective separation. In many flotation systems that use hydroxamate as collectors, the optimum pH has been between pH 9 and 9.5, which is similar

### TABLE 5  Effects of dispersant addition after conditioning

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersant Added After Conditioning</th>
<th>Dosage, kg/ton</th>
<th>Product, % TiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>GE Brightness</th>
<th>% TiO&lt;sub&gt;2&lt;/sub&gt; Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>None</td>
<td>1.76</td>
<td>84.7</td>
<td>36.4</td>
<td></td>
</tr>
<tr>
<td>TREP product</td>
<td>None</td>
<td>1.12</td>
<td>86.0</td>
<td>39.8</td>
<td></td>
</tr>
<tr>
<td>TREP product</td>
<td>Trisodium polyphosphate/sodium carbonate (Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>1.0</td>
<td>86.8</td>
<td>39.8</td>
<td></td>
</tr>
<tr>
<td>TREP product</td>
<td>Sodium silicate</td>
<td>0.95</td>
<td>87.3</td>
<td>46.0</td>
<td></td>
</tr>
<tr>
<td>TREP product</td>
<td>Sodium polyacrylate</td>
<td>0.53</td>
<td>89.1</td>
<td>69.9</td>
<td></td>
</tr>
</tbody>
</table>

Source: Young, Morris, and Brooks 1985.

Table 6 shows the results of two laboratory flotation tests comparing tall oil flotation to potassium octyl hydroxamate flotation (Yoon et al. 1992). The tall oil flotation used 1.28 kg/t of calcium acetate as an activator while the hydroxamate flotation did not use any activator. As shown, the use of hydroxamate gave significantly better TiO₂ removal than the tall oil. The hydroxamate kaolin clay product also has much higher brightness than the product obtained from tall oil flotation. The hydroxamate collector renders the iron-anatase more hydrophobic, resulting in a faster flotation rate, better selectivity, and improved recovery. The chelation of the hydroxamate with either the titanium or iron on the surface of iron-anatase is responsible for the strong collecting action of this reagent.

New, modified hydroxamate collectors were developed (Basilio et al. 2000) to overcome some of the shortcomings of the commercially available alkyl hydroxamate (Cytec Aero 6493 promoter). The alkyl hydroxamate activities of the modified reagents are higher than that of Aero 6493 Promoter (i.e., >30% active). These reagents also have different carrier solvents that allow the alkyl hydroxamate to remain soluble at ambient temperatures. In addition, some of the reagents use a carrier solvent that has some frothing properties; thus reducing the frother requirement for flotation. These modified hydroxamates can be tailored via the use of different carriers and methods of synthesizing the reagent. Flotation tests conducted on a kaolin crude sample from Georgia in the United States show that reagent S-8706 promoters give better flotation performance than Aero 6493 promoter and tall oil at a lower collector dosage (see Table 7).

Another recent development in hydroxamate flotation is the use of hydroxamate for TREP flotation, described previously. Mathur, Brooks, and Finch (2002) used hydroxamate instead of tall oil/calcium chemistry in the TREP conditioner, which resulted in a decrease in the conditioning time by at least 50% and a lower temperature. Because of these benefits, lower processing and maintenance costs were obtained. Table 8 provides the flotation test results comparing the use of oleic acid and hydroxamate collector in the TREP flotation system. As shown, about 75% reduction in conditioning time is obtained without significant change in flotation performance.

Co-collector Flotation. The very high selectivity of hydroxamate flotation without the need of an activator has made this technology a good alternative for kaolin flotation. The main disadvantage of hydroxamate as a collector is its relatively poor frothability (as compared to fatty acids), which makes its application in column cell flotation difficult because of the deep stable froth required. Consequently, the use of a frother is required, which results in a more complicated reagent-addition system. Excessive foaming of the flotation product has detrimental downstream processing effects and must be avoided. In addition, the reagent cost of hydroxamate is higher than that of tall oil.

### Table 6 Tall oil flotation vs. hydroxamate flotation

<table>
<thead>
<tr>
<th>Collector</th>
<th>Dosage, kg/ton</th>
<th>Product, % TiO₂</th>
<th>GE Brightness</th>
<th>% TiO₂ Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>—</td>
<td>1.42</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tall oil</td>
<td>1.5</td>
<td>0.48</td>
<td>88.7</td>
<td>66.2</td>
</tr>
<tr>
<td>Octyl hydroxamate</td>
<td>0.75</td>
<td>0.16</td>
<td>92.4</td>
<td>88.7</td>
</tr>
</tbody>
</table>

Source: Yoon et al. 1992

---

*Note: Some text has been abbreviated for brevity.*
The use of a combination of fatty acid–type collector (i.e., tall oil) and hydroxamate was more effective in removing ritaniferous impurities from kaolin clays than using either collector alone (Shi and Yordan 1996). Lower amounts of collectors are needed to obtain improved or equivalent flotation performance than when either reagent is used alone. In addition, a more stable froth is obtained with this “co-collector flotation chemistry” than that with hydroxamate alone.

The process is essentially similar to that used for hydroxamate flotation. The only difference is the addition of the two collectors, hydroxamate and tall oil, during conditioning. This has resulted in the effective application of hydroxamate flotation to column cells. Table 9 shows the improved flotation performance obtained with the use of the co-collector system compared to either the hydroxamate- or tall-oil-only flotation chemistries. In addition, the hydroxamate dosage has been significantly reduced for the co-collector chemistry. Interestingly, the co-collector chemistry circumvents the need for an activator that is typically required for tall oil flotation.

SUMMARY
For more than 40 years, flotation has been used in the kaolin industry to improve the brightness and color of kaolin clays for pigment applications. Kaolin flotation, unlike most flotation systems, involves minerals with very fine particle sizes ranging from about 50% to 90% passing 2 microns. Flotation of such very fine particles has been difficult with most minerals, but with the adoption of various technologies, successful separation has been obtained.

### TABLE 7 Modified hydroxamate vs. Aero 6493 promoter and tall oil

<table>
<thead>
<tr>
<th>Collector</th>
<th>Dosage, kg/ton</th>
<th>Product, % TiO₂</th>
<th>% Clay Recovery</th>
<th>% TiO₂ Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tall oil</td>
<td>1.0</td>
<td>0.79</td>
<td>67</td>
<td>43.6</td>
</tr>
<tr>
<td>Aero 6493 promoter</td>
<td>1.0</td>
<td>0.27</td>
<td>80</td>
<td>80.7</td>
</tr>
<tr>
<td>Reagent S-8706 promoter</td>
<td>0.625</td>
<td>0.33</td>
<td>96</td>
<td>76.4</td>
</tr>
</tbody>
</table>

*0.25 kg/ton CaCl₂ is added as an activator.
†0.2 kg/ton of propylene glycol–based frother is added.

### TABLE 8 Hydroxamate vs. oleic acid in TREP flotation

<table>
<thead>
<tr>
<th>Collector</th>
<th>Conditioning Time, min</th>
<th>Conditioning Temperature, °C</th>
<th>Product, % TiO₂</th>
<th>% Clay Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid</td>
<td>80</td>
<td>93</td>
<td>0.51</td>
<td>86</td>
</tr>
<tr>
<td>Aero 6493 promoter</td>
<td>20</td>
<td>54</td>
<td>0.47</td>
<td>84</td>
</tr>
</tbody>
</table>


### TABLE 9 Co-collector flotation vs. tall oil and hydroxamate-only flotation

<table>
<thead>
<tr>
<th>Collector</th>
<th>Dosage, kg/ton</th>
<th>Product, % TiO₂</th>
<th>% Clay Recovery</th>
<th>% TiO₂ Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tall oil</td>
<td>1.5</td>
<td>0.40</td>
<td>81.6</td>
<td>74.2</td>
</tr>
<tr>
<td>Alkyl hydroxamate</td>
<td>1.0</td>
<td>0.41</td>
<td>96.4</td>
<td>73.5</td>
</tr>
<tr>
<td>Tall oil/alkyl hydroxamate</td>
<td>0.5/0.25</td>
<td>0.27</td>
<td>84.8</td>
<td>82.6</td>
</tr>
</tbody>
</table>

Source: Shi and Yordan 1996.
*0.25 kg/ton CaCl₂ is added as an activator.
†0.2 kg/ton of propylene glycol–based frother is added.
in the kaolin industry. Contributing to this success is the fact that kaolin flotation utilizes reverse flotation which only requires the flotation of a very small fraction of the feed material. Currently, flotation is the most efficient method for removal of discoloring impurities from kaolin and production of high-brightness kaolin clay pigments.

A review of the current flotation technologies used in the kaolin industry reveals a variety of innovative processes, from carrier flotation to the use of hydroxamate collectors. Interestingly, carrier flotation, which was developed more than 40 years ago, is still being used in the kaolin industry. In terms of flotation machines, the kaolin industry has adapted well with the use of both conventional mechanical flotation cells and column cells.

Despite the kaolin industry's ability to adapt the various flotation technologies to fine particle processing, many technological challenges need to be addressed, including

- Variable flotation response of kaolin clays from different sources,
- High conditioning-energy requirements,
- Low flotation pulp densities that entail a large amount of water removal downstream, and
- Removal of the iron oxide impurities.

A fundamental understanding of the industrial practice is certainly needed to refine the existing processes and to develop new flotation technologies. The move to specific collector chemistry such as hydroxamates has shown a lot of promise in designing robust flotation processes. The hydroxamate collector gives more flexibility, because it can be used for different kaolin crude sources and for more varied process conditions. However, the current downside is the higher cost associated with the use of this reagent.

**Chemistry of Iron Oxide Flotation**

K.H. Rao and K.S.E. Forssberg

**INTRODUCTION**

World iron ore production totaled 1,045 Mt in 2001 and is forecast to reach 1,119 Mt by 2007 based on current mine capacities, planned expansions, and the development of new iron ore mines. The largest production increases will come from traditional sources in Australia and Brazil, and from the growth regions of India and South Africa. The bulk use of iron ore is for the production of pig iron to make steel and other alloys. Demand for iron ore, therefore, depends on the necessity for a vital construction material—steel and its alloys. Steel is still the core of the building industry regarding transportation by rail, ship, and road vehicles (including roads and bridges). The importance of iron and steel, and therefore the need to process iron ore, continues to be a major factor for the medium-grade iron ores as well as for improving high-grade iron ores in the overall economic development of all nations. Direct reduction steelmaking uses <5% of mined ore, and traditional blast furnace operations use most of the iron ore produced. This underlines the importance of iron ore processing for the traditional blast furnace—basic oxygen steelmaking will continue to be the technological workhorse of the iron and steel industry for many years to come. The blast furnace takes most of the iron ore produced as lumps in the form of graded ore in close size range and, to a lesser extent, agglomerates—sinters and pellets. For slag control in the blast furnace for the purpose of reduction in solid wastes and increased productivity, and for
coke rate reduction intended for energy economy, no impurities are preferred in the iron ore burden except the bound oxygen. The dictum for iron ore production is to increase the iron content in ores that are gradually being depleted in quality.

The most important iron ores are the oxides. Magnetite (Fe₃O₄), hematite (Fe₂O₃), goethite (Fe₂O₃·H₂O), siderite (FeCO₃), and pyrite (FeS₂) are the primary source of iron minerals, although more than 300 minerals contain iron. The first three are of major importance because of their large occurrence; a deposit must contain at least 25% iron to be considered economically viable. The gangue minerals or the impurities in iron ores are of three types: siliceous, calcareous-siliceous, and siliceous and/or calcareous clay. From the blast furnace standpoint, the slag-forming acidic impurities are silica (SiO₂) and alumina (Al₂O₃), and the basic impurities are lime (CaO) and magnesia (MgO), though the deleterious impurities are sulfur, phosphorous, and other metallic oxides. The process steps applied to iron ore beneficiation to meet the blast furnace requirements are milling (crushing and grinding), washing, filtration, sizing, gravity concentration, magnetic separation, flotation, and agglomeration (pelletizing, sintering, briquetting). Flotation is primarily used to upgrade concentrates from magnetic separation by reducing the silica and phosphorous content of the concentrate and can be applied in the production of super concentrates for direct reduction. Importantly, flotation is being applied to meet the increasing demand of high-grade feed materials for the steel industry.

The principles and industrial practice of iron ore flotation have been reviewed from time to time (Houot 1983; Iwasaki 1983, 1989, 1999; Nummela and Iwasaki 1986; Uwadiale 1992), and the reagents used in iron ore processing were presented by Yang (1988). In this section, a brief overview of the chemistry of iron ore flotation is presented.

SURFACE CHEMISTRY OF IRON MINERALS

When iron particles are ground to flotation size range, the particles have a high surface-to-volume ratio and, hence, a significant proportion of the atoms is located at the particle surface on breakage. The surface Fe atoms are unsatisfied, and in the presence of water, they coordinate with hydroxyl ions or water molecules. The particles acquire an electric charge in aqueous media through the ionization of surface hydroxyl groups. The charge on the surface influences the distribution of nearby ions in aqueous phase where the counterions are attracted toward the surface and co-ions are repelled from the surface, ensuring that the interfacial region is electrically neutral. The charged surface, together with a layer of counterions in the solution phase, constitute the electrical double layer. Because the charge on iron oxides stems from the preferential adsorption of protons and hydroxyl ions, these ions are called "potential determining ions." The earliest Helmholtz model, besides the Gouy–Chapman diffuse layer model and the Stern model describing the distribution of charges, is widely used to explain the electrochemical properties of iron oxides, the adsorption phenomena of surfactants (collectors), and flotation behavior (Figure 34). The significance of electrical double-layer models in flotation research was first recognized by Gaudin and Fuertenau (1955b).

The pH of the solution determines the iron oxide net surface charge according to the following dissociation (ionization) reactions (Cornell and Schwertmann 1996):

\[
\text{FeOH}_2^+ \leftrightarrow \text{FeOH}^+ + \text{H}^+
\]
The pH at which the charge on the surface is zero is referred to as the point of zero charge (PZC) which is the same as isoelectric point (IEP) when there is no specific adsorption. The IEP is the pH at which the net surface charge is zero and is measured by electrophoresis. The PZC is the pH at which the net adsorption of potential determining ions on the oxide is zero and is obtained by potentiometric titration of the oxide in an indifferent electrolyte.

The above acid/base equilibria reactions are represented by a two-constants (pK_a values) model with the following equilibrium constants (conditional acidity or stability constants, K_a^s):

\[
K_{a1}^s = \frac{[FeOH][H^+]}{[FeO^2+]}, \quad K_{a2}^s = \frac{[FeO^2+][H^+]}{[FeOH^2+]}.
\]

The free energy of proton adsorption, \( \Delta G_{ads} \), can be written as

\[
\Delta G_{ads} = \exp(-\Delta G_{ads}/RT).
\]

The chemical and electrostatic components contribute to the free energy of protons adsorption on a charged surface, therefore,

\[
\Delta G_{ads} = \Delta G_{chemical} + \Delta G_{coulombic}.
\]

The acidity constant is thus represented by

\[
-K_{\text{a} \text{cond}} = -RT \ln K_{\text{a} \text{cond}} = -RT \ln K_{\text{a} \text{int}} + zF \psi^o
\]

which rearranges to

\[
K_{a \text{int}}^s = K_{a \text{cond}} \exp(-zF \psi^o/RT),
\]

where \( K_{a \text{int}}^s \) is the intrinsic acidity constant, \( z \) is the charge of the adsorbed species, \( F \) is the Faraday constant, and \( \psi^o \) is the surface potential. Thus, the acidity constants for surface hydrolysis reactions incorporate both a mass balance and an electrostatic term.

The acid/base titration data, together with site density data of oxides, are used to determine the conditional acidity constant, \( K_{a \text{cond}}^s \). The charge on the oxide surface affects the acidity of the surface hydroxyl groups and, therefore, the acidity constants are not constant but depend on the degree of ionization of OH groups and ionic strength. The dissociation reactions...
of surface hydroxyl groups at zero surface charge is defined as the intrinsic acidity constants \( K_{a1}^{int} \) and cannot be measured directly but can be obtained from the conditional constants either by extrapolation to a situation of zero charge or by fitting the experimental data by an appropriate double-layer model to compute the electrostatic term. The equilibrium constants for the surface protolysis reactions provide a measure of surface charge as a function of pH, and the pK_a values for iron oxides fall between 5 and 10 (Table 10). The variation in the values is largely related to the chosen site density and the double-layer model when modeling the proton adsorption.

The distribution of positive, negative, and neutral surface groups on an iron oxide surface where \( K_{a1}^{*} = 7.09 \) and \( K_{a2}^{*} = 11.11 \) is presented in Figure 35. The positive, negative, and neutral groups coexist on the oxide surface. The \( \text{FeOH}_2^+ \) groups predominate over \( \text{FeO}^- \) groups below the PZC; at the PZC, the numbers of positive and negative groups are equal, and as the pH increases, the \( \text{FeO}^- \) groups increase. The PZC of iron oxides by potentiometric titration was in the pH range 6–10 with goethite close to the upper end of the range and magnetite and maghemite at the lower end. The IEP of iron oxides as determined

<table>
<thead>
<tr>
<th>Oxide</th>
<th>pK_a1(int)</th>
<th>pK_a2(int)</th>
<th>PZC</th>
<th>IEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>7.47</td>
<td>9.51</td>
<td>7.5</td>
<td>6.1, 6.7, 5.9–7.2</td>
</tr>
<tr>
<td></td>
<td>6.70</td>
<td>9.00</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.09</td>
<td>11.11</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>8.86</td>
<td>10.10</td>
<td>7.8</td>
<td>5.0, 6.0, 6.7, 8.2,</td>
</tr>
<tr>
<td></td>
<td>6.70</td>
<td>10.10</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.80</td>
<td>11.10</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td>5.6</td>
<td>—</td>
<td>7.1</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>5.6</td>
<td>—</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>8.30</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>Maghemite</td>
<td>3.8</td>
<td>9.40</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>Quartz</td>
<td>—</td>
<td>6.80</td>
<td>—</td>
<td>1.4, 4.8, 2.2</td>
</tr>
</tbody>
</table>

Source: Cornell and Schwertmann 1996; Parks and De Brnyn 1962; Parks 1965; M.C. Fuerstenau and Palmer 1976.

**FIGURE 35** Schematic representation of the distribution of positive, negative, and neutral surface hydroxyl groups on an iron oxide surface
by electrophoresis are, in general, the same. However, there are slight variations influenced by several factors such as origin/mineralogy, sample preparation, aging in water, and also the methods for determining the zeta potentials (Table 10). The surface charge is important for understanding both anionic and cationic flotation of iron oxide minerals.

**Solution Chemistry of Reagents**

Mostly the anionic fatty acids (mainly oleic acid), alkyl sulfates, sulfonates, or hydroxamate collectors have been used for flotation of iron oxides. In anionic flotation, the iron oxides are floated from siliceous gangue material. When the calcareous phosphate gangue minerals are floated from the iron oxides, modified fatty acids are employed. The silica and silicate minerals are floated from iron oxides by cationic flotation using alkyl amines or their salts. The ether amines or diamines (1,3-propenediamine) are also commonly used in cationic flotation.

The alkyl sulfates or sulfonate collectors are strong electrolytes, and they are mostly in ionized form in the entire flotation pH region. The alkyl carboxylic or hydroxamic acids and alkyl amines or diamines are weakly acidic and basic surfactants, respectively, and in aqueous solution depending on the pH, ionic or molecular species predominate. Thus, the dissociation constants of these weak acid and base surfactants are important because they determine the proportion of ionic molecules to neutral molecules in the system. When the solubility limit of the surfactants is exceeded in a pH range where the molecular form predominates, the fatty acid and amine solutions comprise a typical colloidal solution. Besides hydrolysis reactions, the neutral molecules and ions associate together, resulting in dimers and ionomolecular species. Using the reported thermodynamic equilibrium constants of these reactions, the species distribution diagrams as a function of pH have been composed to explain the interactions of fatty acid and amine collectors on iron oxides and silicate minerals, and their electrokinetic and flotation behavior (Somasundaran and Ananthapadmanabhan 1979; Smith and Akhtar 1976; Laskowski 1989).

The distribution of oleate species at a total concentration of 0.02 mM is presented in Figure 36a. The oleic acid exists as ions, RCOO⁻ and R(COO)₂⁻, at high pH values and as neutral molecules at low pH values. The ionomolecular complex, (RCOO)₂H⁺, forms in the mid-pH region, but this species contributes only 0.2% of the total concentration of collector species. However, the surface activity of this complex has been reported to be seven orders of magnitude higher than that of the oleate ion and five orders of magnitude higher than that of the neutral oleic acid molecule (Ananthapadmanabhan and Somasundaran 1988). Similarly, the pH changes the form of dodecyl amine in solution (pKₐ = 10.6; pKsol = 8.41), the ionic RNH₃⁺ being predominant in the pH range neutral to acidic, though the molecular form predominates in very alkaline solutions; at pH 10.65, the concentrations of NH₃⁺ and NH₂(aq) are equal. The species distribution diagram for C₁₆-diamine is presented in Figure 36a at a total concentration of 0.01 mM. The pK₁ and pK₂ values of 6.8 and 9.3, and pKsol value of 8.69 for C₁₆-diamine reported by Scott and Smith (1991) are used. The doubly charged amine species are predominant below pH 6.5, and above which pH the diamine precipitates. The singly charged species increases with increasing concentration, and at pH 6.5, both the singly and doubly charged species are in equal proportion. The pKₐ value for alkyl hydroxamic acids is 9.0 (D.W. Fuerstenau and Pradip 1984), and, accordingly, the proportion of molecular and ionized species of these acids becomes equal at pH 9.

Sodium silicate is widely employed to disperse the particles in flotation pulp and/or depress the iron oxides when the calcareous gangue is floated from iron ores. The solution chemistry of silica is complex, because the hydrolysis of sodium silicate produces a number
FIGURE 36  (a) Species distribution diagram of oleic acid and C16-diamine vs. pH at total concentrations of 0.02 and 0.01 mM. (b) Distribution of silicate species as a function of pH at a total concentration of 1 mM.

of monomeric, polymeric, and colloidal species (Sjoeberg and Ohman 1985). The species distribution diagram as a function of pH at 1 mM total concentration is shown in Figure 36b. Monosilicic acid is the predominant species below pH 9.8, and above which are the monosilicate ions. At high concentrations of sodium silicate, several polymeric silica species appear with high negative charge. Thus, the function of sodium silicate depends on the concentration and flotation pH.

Different starch and starch derivatives are effectively employed in the depression of iron minerals in the reverse cationic flotation of silica and silicates, and also as selective flocculants for fine iron oxides (Cooke, Schulz, and Lindroos 1952; Chang, Cooke, and Huch 1953; Chang 1954; Iwasaki and Lai 1965; Lien and Morrow 1978; Sresty, Raja, and Somasundaran 1978). Starch is a natural nonionic polymer consisting of a linear polymer amylose, which is made up of D-glucose monomers joined by C1–C4 bonds and a branched amyllopectin polymer with the same monomers also linked by C1–C6 bonds. The amylose and amyllopectin components in starches vary depending on their source; they are derived from starch-containing vegetables. Most starches contain 20% to 30% amylose, 70% to 80% amyllopectin, and minor components of lipids and proteins (<1%). The hydroxyl groups surrounding the glucose monomers participate in the interaction of starches on iron oxides and impart hydrophilic character because of large numbers of hydroxyl groups, while the polymer chain bridges between mineral particles and causes flocculation. The synthetic polyacrylic acid and anionic polyacrylamide polymers are also used in selective flocculation of nonmagnetic iron oxides from quartz (Sresty and Somasundaran 1980; Drzymala and Fuerstenau 1981; Weissenborn, Warren, and Dunn 1994).

The long-chain carboxylates, sulfonates or sulfates, and amines produce adequate froth and serve the dual purpose of collector and frother in iron ore flotation. However, pine oil, aliphatic alcohols, polyglycol, and cresol are used in flotation practice (Yang 1988). The neutral oils, such as fuel oil, kerosene, diesel, and so forth, are also employed to control the properties of froth.
Flotation of Iron Oxides from Silicates

Several authors investigated the iron oxide–quartz flotation system using anionic collectors with different functional groups of sulfate, sulfonate, hydroxamate, and carboxylates (lauryl and oleic acids) and also with the cationic amine collectors. In general, the flotation responses as a function of pH are in good agreement with the electrical nature of the surfaces (Figure 37) where the anionic and cationic collectors float the oxides at a pH region below and above the PZC of the minerals, respectively. Because the PZCs of hematite, goethite, and magnetite are very close, their flotation responses were similar with anionic and cationic collectors. The classical results illustrating the electrostatic interactions between collectors and iron oxides are presented in Figure 1 (Iwasaki, Cooke, and Colombo 1960; Iwasaki, Cooke, and Choi 1960, 1961; Iwasaki 1983).

The results in Figure 37a show complete flotation of hematite with sodium dodecyl sulfate (SDS) for pH values less than the PZC and no flotation for pH greater than the PZC. Dodecyl amine flotation of hematite only occurred above the PZC of hematite (pH 6.7) where it exhibits negative surface charge. The results obtained by Smith (1979) on hematite flotation behavior using the same two reagents were also similar. The PZC of magnetite is pH 6.5, and its flotation response with these two collectors is comparable with hematite (Figure 37c). The PZC of goethite is pH 6.7, and with dodecyl sulfate and dodecyl sulfonate collectors, flotation occurs below pH 6.7 and takes place above this pH with dodecyl amine (Figure 37b). The PZC of quartz is about pH 2, and its flotation characteristics, once again, illustrate the electrostatic interaction of collectors. The flotation, adsorption, and electrokinetic results of anionic SDS on positive hematite surface reported by other workers (Shergold and Mellgren 1969; Shergold and Kitchener 1975; Rajala and Smith 1983; Wei and Smith 1984; D.W. Fuerstenau, Li, and Hanson 1991; Kallay et al. 1994) are consistent with the hemimicelle theory of collector adsorption of coulombic attraction and hydrophobic association (Gaudin and Fuerstenau 1955b). The flotation responses of hematite with sodium dodecyl benzene sulfonate (SDBS) collector are almost similar to SDS collector (Boulos, Messawarti, and Hilal 1979; Smith, Haddenham, and Schroeder 1973; Bibawy and

![Figure 37](image-url)

*Dodecyl ammonium chloride

FIGURE 37 (a) Electrophoretic mobility and flotation of hematite (H) and quartz (Q); (b) the dependence of flotation properties of goethite on surface charge; and (c) electrophoretic mobility and flotation of magnetite (M), cummingtonite (C), and quartz (Q)
The selective flotation of iron oxides from silicates is, thus, related to the differences in the PZC of the constituent minerals in ores. The PZCs of oxide and silicate minerals are extensively reported (Parks 1965; M.C. Fuerstenau and Palmer 1976; D.W. Fuerstenau and Raghavan 1978) as well the selectivity of flotation reagents (Aplan and Fuerstenau 1962; D.W. Fuerstenau 1970; D.W. Fuerstenau and Fuerstenau 1982; Smith and Akhtar 1976). The difficulty in achieving high selectivity in an iron ore containing quartz, magnetite, and cummingtonite is linked with the intermediate PZC of cummingtonite (Figure 37c), and, in this case, insufficient removal of siliceous gangue or excessive loss of iron units occurs in cationic silica flotation (Iwasaki 1989).

The flotation of iron oxides with various fatty acids showed identical collecting abilities where the C18-aliphatic acids (stearic, linolenic, linoleic, elaidic, and oleic acids) are equally effective on positively-charged surfaces but with a difference in stearic acid behavior compared to four other acids because of its extremely low solubility (Cooke, Iwasaki, and Choi 1959; Iwasaki, Cooke, and Colombo 1960). In subsequent years, considerable research was directed toward oleic acid–iron oxide flotation systems because of distinct results observed by various workers induced by the complex solution chemistry of oleic acid. The studies showed no correlation between oleate adsorption and flotation responses. Maximum flotation of hematite occurs in the neutral pH region, whereas the adsorption of oleate on hematite increases with decrease in pH (Pope and Sutton 1973; Kulkarni and Somasundaran 1975). There is also no absolute agreement among workers on the mechanism of oleate adsorption onto hematite. The reasons for discrepancies underlying the experimental techniques used in adsorption experiments are elaborated by Yap et al. (1981) and Morgan (1986). Of course, the precipitation of the acid or salts must be considered.

The typical lack of correlation between oleate adsorption on hematite and floatability of hematite by oleate is shown in Figure 38 (Morgan 1986). The floatability of hematite exhibits a sharp maximum in the neutral pH region, whereas the adsorption density decreases continuously with increase in pH. Careful experimentation devoid of artifacts of oleate depletion (adsorption obscured by precipitation) and subtraction of the amount of oleic acid precipitated as judged by the chemical equilibria (Figure 37a) revealed that the
adsorption curve depicts a maximum in the neutral pH region correlating with the flotation curve. The maximum flotation of hematite with oleate in the neutral pH region is observed to be a general feature, and several other oxide minerals of significantly different surface chemical and electrochemical properties also exhibit maximum flotation in the pH range of 7–8 (Somasundaran and Ananthapadmanabhan 1979). This is attributed to the acid–soap complex formation in this pH region and its high surface activity (Kulkarni and Somasundaran 1975; Ananthapadmanabhan and Somasundaran 1988). Jung, James, and Healy (1988) also reported that the acid–soap complex species has remarkable concentration at the goethite–water interface. The acid–soap complex occurs at high ionic strength, but the amount is insignificant at low oleate concentrations and low ionic strength (Yap et al. 1981). The neutral pH region of maximum flotation also corresponds to the pKₐ value of oleic acid and, in this region, both the molecular and ionic species exist in equal proportion. The hematite flotation with hydroxamate collectors is also maximum at a pH region corresponding to their pKₐ values (M.C. Fuerstenau and Cummins 1967; M.C. Fuerstenau, Miller, and Gutierrez 1967; M.C. Fuerstenau, Harper, and Miller 1970; Raghavan and Fuerstenau 1975; D.W. Fuerstenau and Pradip 1984).

The zeta potential studies of hematite in the presence of fatty acids at acidic pH values (less than the PZC of hematite) showed that the particles are coated with the molecular form of collector precipitates corresponding to the precipitation domain of fatty acids (Laskowski, Vurdela, and Liu 1988). The IEP data for various oxide mineral–oleate systems are remarkably constant at pH 3.2 (Jung, James, and Healy 1987), which is the same as the IEP of molecular oleic acid precipitates. When the adsorption studies are performed at concentrations free from insoluble oleic acid or metal oleates, the results demonstrate a coulombic control on adsorption, hydrophobic interactions (hemimicelle formation), and coadsorption of soluble neutral oleic acid and oleate ion (Jung, James, and Healy 1987). The maximum flotation of iron oxides in the pH region corresponding to pKₐ of oleic acid and pKₐ of hydroxamic acids may suggest that the adsorbed layer is composed of both neutral and ionic species where the neutral molecule fitting between the two charged ions screen the repulsion from each other at the interface. Being a single-surfactant system but existing in neutral and ionic form with the same alkyl chain length, the adsorbed layer could be very packed, thereby increasing the surface hydrophobic character and flotation. The adsorption of oleate on hematite at pH values and concentration range precluding the formation of liquid oleic acid and acid–soap complexes showed chemisorption and physical adsorption at higher coverages (Yap et al. 1981). Chemisorption of oleate (Peck, Raby, and Wadsworth 1966) and hydroxamate (M.C. Fuerstenau, Harper, and Miller 1970; Han, Healy, and Fuerstenau 1973; Raghavan and Fuerstenau 1975) collectors on hematite was observed by infrared spectroscopic studies.

Several authors studied the iron oxide flotation using primary alkyl amine salts besides the studies of Iwasaki referred to previously. The earlier adsorption and contact angle studies of DAA on hematite by Gaudin and Marrow (1954) showed a steady increase in these parameters with increasing pH up to a value of about 8. Thereafter, even a slight increase in pH resulted in a large increase in adsorption density and contact angles. The maximum flotation of hematite with DAA occurred between pH 9 and 11 (Mukai, Kano, and Wakamatsu 1962). The adsorption of amine was compared with the adsorption of H⁺ and OH⁻ ions on hematite (Joy and Watson 1964; Joy, Watson, and Cropton 1964) and showed that the adsorption of RNH₃⁺ ions corresponds to the negative sites on the surface. The total amount of amine adsorbed was much larger than the RNH₃⁺ ion adsorption, presumably
caused by the adsorption of neutral amine molecules. These authors also showed hematite flotation at pH 1.5 with dodecyl amine, provided that certain other ions are present as activators. Flotation occurred in the presence of chloride (or fluoride or sulfate) ions together with ferric ions (supplied by the dissolution of hematite) by dodecyl amine at pH 1.5 (Shergold, Prosser, and Mellgren 1968). The negative sites on hematite for RNH$_3^+$ adsorption are supposedly formed by the ferric and chloride ions (or F$^-$ or SO$_4^{2-}$) in the form of surface complexes. Their batch flotation tests on a synthetic hematite-quartz mixture showed that the hematite selectively floated with more than 90% recovery and almost 100% grade at pH 0.8–2.0.

The pH region of hematite flotation depends on the concentration of dodecyl amine extending to a wide pH region of 2–12 at higher concentrations (Partridge and Smith 1971). Shergold and Mellgren (1971) also reported a wide pH range of 3–10, but a maximum flotation of hematite occurred in the pH range of 5–7. Using amine acetate (Armac C) collector, the hematite flotation recovery was maximum at pH 8 and steadily decreased on either side of this pH value (Quast 2000). Thus, some of the flotation results reported in the hematite–dodecyl amine system cannot be explained with electrostatic interaction mechanism alone.

Smith and Akhtar (1976) illustrated a close relationship between the pH of molecular amine precipitation of primary, secondary, and tertiary amines and the pH of maximum flotation. Castro and Laskowski (1988) observed that the adsorption of dodecyl amine on hematite was low for pH <9 and increased markedly for pH >9.5 where dodecyl aminedodecyl amine precipitates. Several workers measured the electrokinetic behavior of hematite in the presence of amines. Akhtar and Lai (1975) observed that the IEP of hematite shifted to a low pH value as the concentration of dodecyl amine was increased. Thus, chemisorption of neutral amine molecules on negative surface sites is proposed. The IEP of dodecyl amine precipitate was determined to be at pH 11 (Castro, Vurdela, and Laskowski 1986). Laskowski, Vurdela, and Liu (1988) measured the electrophoretic mobility versus pH for hematite particles in the presence of 0.1 and 1.0 mM of dodecyl amine, and these results are presented in Figure 39. The mobility curve in 1 mM dodecyl amine coincides with the curve of dodecyl amine precipitate alone. This was also the case in 0.1 mM dodecyl amine but in the pH range of 10.5 to 11.5, coinciding exactly the pH range of dodecyl amine precipitation. Thus, electrostatic adsorption between RNH$_3^+$ species and hematite takes place only in the pH region above the PZC of hematite but below the pH of amine precipitation. When amine is in molecular form, the hematite is covered with precipitated amine.

Flotation of Silicates from Iron Oxides
The primary long-chain alkylammonium salts are most commonly used for silicate flotation. In particular, the ether amines and diamines are used to remove siliceous material from iron ores where the diamines are reported to be more effective than monoamines. However, little research work has been done with diamines compared to monoamines. The quartz–amine system was studied extensively by flotation recovery, electrokinetic, contact angle, and surface force measurements during the years, and the interaction mechanism has been summarized in several review articles (D.W. Fuerstenau and Raghavan 1978; Smith and Scott 1990; M.C. Fuerstenau 1995).

There is a general consensus that the mechanism of amine adsorption on silicates depends on pH. When the silicate is negatively charged (pH 2–7), the adsorption of the
amines has been explained mainly by the hemimicelle model (Gaudin and Fuerstenau 1955a). This model postulates that amine cations are adsorbed in the outer Stern layer because of electrostatic attraction by the negatively-charged surface. At some threshold concentration, the actual concentration of amine near the quartz surface becomes higher than the CMC, and a two-dimensional (2D) process similar to ordinary bulk (3D) micellization takes place. The 2D aggregates are called "hemimicelles" and the critical concentration is referred to as the "critical hemimicelle concentration," or CHC. Recent FTIR and X-ray photoelectron spectroscopy (XPS) studies of amine adsorption on silicates at pH 6–7 showed the presence of molecular amine above the CHC in addition to the protonated form at the interface, and, accordingly, a model of successive 2D and 3D precipitation of long-chain amines on the silicate surface was suggested (Chernyshova et al. 2000, 2001; Rao et al. 2001). In alkaline pH, correlation between the oxide floatability and the precipitation of neutral amine molecules seems to be well established (Laskowski 1989; Smith and Scott 1990). Silicates are also floated using anionic collectors with metal ion activation. The extensive works of Fuerstenau and co-workers (M.C. Fuerstenau, Martin, and Bhappu 1963; M.C. Fuerstenau et al. 1966; M.C. Fuerstenau, Harper, and Miller 1970; M.C. Fuerstenau and Cummins 1967; M.C. Fuerstenau and Elgillani 1966; Palmer, Gutierrez, and Fuerstenau 1975; Palmer, Fuerstenau, and Aplan 1975) explain that the activating species is the first hydroxyl complex, and flotation occurs only in the pH region corresponding to the formation of primary hydroxyl species. The flotation responses of quartz correlate to the concentration of anionic collector on the precipitation edge of metal soap, implying that the hydroxyl complex interacts with oleate or sulfonate to form the collecting species.

Takeda and Usui (1988) attempted the cationic flotation of quartz from a synthetic mixture of fine-grained quartz and hematite using hexylamine acetate (HAA) and DAA as collectors. The adsorption and flotation results showed that selective flotation of quartz from hematite with HAA was possible in the pH range 9–10, whereas concurrent flotation of hematite occurred with DAA (Figure 40). The quartz and hematite floated completely
with DAA at 100% surface coverage of collectors but complete flotation of quartz took place at 10% surface coverage of HAA. The adsorption of neutral dodecyl amine is reasoned for zero zeta potentials of quartz and hematite at pH 9.8 and for high surface coverage with DAA.

The flotation of quartz using 1,3 diaminopropanes of 8C, 12C, and 16C alkyl chain lengths showed that the effect of chain length was comparable to that observed with monoamines (Scott and Smith 1991). The stronger effect of diamine in quartz flotation, due to the doubly charged diamine species (Figure 37a), is demonstrated. However, quartz flotation from an artificial mixture with hematite of fine particles using mono-, di- and tri-amine acetates as collectors by Gan, Takeda, and Usui (1986) showed that it is impossible to float quartz in acidic pH because of heterocoagulation. The flotation results were little better in alkaline media near pH 10 using diamine and triamine in comparison with monoamine. However, selective flotation of quartz from hematite is observed with di-hexylamine acetate (di-HAA), among the three amines of mono-, di-, and tri-HAA studied (Takeda and Matsuoka 1990).

Because of the narrow pH region where the quartz and hematite are oppositely charged favorable to amine flotation of silicates, the amine collectors tend to adsorb on both the minerals, resulting in poor selectivity. However, the iron oxides are depressed successfully with the addition of depressants when silica is floated with amine collectors. Starches or dextrins have been used effectively. The chemical nature of starches and their selectivity toward iron oxides were investigated by several researchers. The role of various starches and their substituted derivatives in the depression of iron oxides showed higher depressing ability of cornstarch than other starch products (Cooke, Schulz, and Lindroos 1952; Chang, Cooke, and Huch 1953; Chang 1954).
Iwasaki and co-workers (Iwasaki 1965; Iwasaki and Lai 1965; Iwasaki, Carlson, and Parmeter 1969; Balajac and Iwasaki 1969a, b) observed that starches containing higher amylopectin components adsorb on hematite more than the starch with amylose. They also showed that the cationic starch was superior to unmodified starch for hematite depression, but it is equally or more effective on quartz. The treatment of starch with sodium hydroxide was observed to be superior for solubilization, but a special procedure adapted by Lien and Marrow (1978) showed very selective adsorption of degraded starch on iron oxides.

Studies by Subramanian and Natarajan (1988) showed partial irreversible adsorption of starch on hematite, and, accordingly, adsorption through hydrogen bonding and chemical interaction via ferric ions has been suggested. Their FTIR and XPS results corroborated the chemical interaction mechanism between hematite and starch. Recent infrared (IR) studies by Pavlovic and Brandao (2003) showed the formation of a chemical complex (chemisorption) between starch and the iron atoms on the hematite surface. The specific adsorption of starch on hematite is also distinguished by the shift in the IEP of hematite (Montes-Soto-mayor, Houot, and Kongolo 1998). Starch was found to adsorb on both hematite and quartz, but in alkaline media and in the presence of amine collector, starch desorbed on quartz and not on hematite. The efficiency of cornstarches in the depression of iron oxides showed that zein, the most abundant corn protein, is a hematite depressant and is as efficient as amylopectin and conventional cornstarch (Peres and Correa 1996). Several other studies also showed that amylopectin had a stronger depression effect than starch or amylose in flotation, and a combination of amylopectin (75%) and amylose (25%) found in cornstarches gave the best selective flocculation results of iron oxides compared to using either component separately (Pinto, De Araujo, and Peres 1992; Weissenborn 1996).

The effective selective flocculation process of iron oxides using starches prior to desliming followed by cationic flotation of silicates applied to finely grained iron ores (Villar and Davc 1965; Colombo 1980) illustrates the remarkable preferential adsorption of starch materials on hematite. This exceptional selectivity has not been examined thoroughly except for the mechanism of structure specificity involving the binuclear complexation between the Fe surface sites and the end OH groups of starch proposed by Pradip (1994). Because the O–O distance in starch end groups of 2.85 Å and the Fe–Fe distance at the cleavage plane of hematite of 2.852 Å are the same, the exceptional selectivity of starches toward iron oxides is linked to structural compatibility.

**FLOTATION OF CALCAREOUS MATERIALS FROM IRON OXIDES**

Phosphorus in iron ores is detrimental to blast furnace technology, and its content as low as 0.01% affects the mechanical properties of high-quality steel products. Phosphorus is removed by fatty acid flotation. Early investigations of fatty acid apatite flotation from iron oxides (Gaudin 1957; Sundelin 1962) and anionic silica and phosphorous flotation in the presence of ammonium fluoride (NH₄F) (Hanna and Anastia 1983) were reviewed and discussed by Nummela and Iwasaki (1986). These studies showed that a phosphorus content of 1% in iron ore is reduced to about 0.12% at pH 10 in the presence of starch or sodium silicate depressant and at elevated temperatures. When the ore contained apatite and calcite, best results were obtained in a two-stage flotation process of anionic silica flotation at alkaline pH, which also recovered calcite and apatite, followed by anionic flotation of iron oxides.
The beneficiation of apatite from a low-grade magnetite-apatite ore was studied by Dasgupta and Taluja (1988) using sodium oleate collector and sodium silicate depressant. A concentrate suitable to the phosphate industry was received, but no details of magnetite grade and recovery were presented. Qi and colleagues used sodium silicate as iron oxide depressant in the selective flotation of apatite (Qi et al. 1992; Qi, Klauber, and Warren 1993). They observed that the pH, sodium oxide (Na₂O)/SiO₂ ratio, aging, and the presence of polyvalent metal ions in the sodium silicate solution all influenced the selectivity. The polymeric silicate species at higher concentrations (1–10 mM) were found to have a strong depression effect, but at moderate concentrations, oleate adsorption on hematite reduces and oleate displaces the adsorbed silicate on apatite. The strong depression effect of sodium silicate on apatite at concentrations of 2 mM and above was also observed in other studies (Rao, Antti, and Forssberg 1990).

When OS 130 (a fatty acid–based collector) was used at the LKAB plant in Sweden to float apatite from magnetite, the fatty acid was found to contaminate magnetite surfaces, which had an adverse effect in the followup pelletization step caused by the loss of strength of the green balls. Nearly 20% of the total collector addition of 90 g/t was adsorbed on magnetite surfaces (Rajala and Smith 1983). The process water contained about 140 ppm of calcium ions, and fatty acid is adsorbed on magnetite via bridging calcium ions. Subsequently, a more efficient selective collector (Atrac-1562, a modified fatty acid) for apatite flotation was developed, and several investigations using this collector showed efficient flotation of apatite at very low additions of collector and sodium silicate, meeting the requirement of below 0.025 wt % phosphorus in magnetite concentrate (Rao, Su, and Forssberg 1999; Su et al. 1998a, b, c). The results obtained as a function of collector and sodium silicate concentrations at an optimum pH of 8–9 are shown in Figure 41.

![Figure 41](image-url)

SUMMARY
The methods for separating iron oxides from siliceous, calcareous-siliceous, and siliceous and/or calcareous clay are (1) anionic flotation using sodium oleate or petroleum sulfonate, (2) fatty acid flotation with alkaline earth cation activation of siliceous material, and (3) cationic flotation using primary amines and diamines to ether amines and diamines, respectively. In the first case, iron oxides are floated, and in the latter methods, silicates are floated, which is usually a process called reverse flotation.

The strong electrolyte surfactants (alkyl sulfate and sulfonates) interact with iron oxides mainly through coulombic forces and cause effective flotation below the PZC of iron oxides (pH ≈ 6.7). The weak hydrolyzable (fatty acids, alkyl amines, alkyl hydroxamic acids) surfactants interact electrostatically to oppositely charged iron oxide surfaces, and flotation occurs with anionic and cationic collectors below and above the PZC of iron oxides (pH 6.7), respectively; the mechanism of their interaction depends on their solution chemistry and the form of different species present in the solution. The chemical interaction of oleate and hydroxamate collectors on iron oxides is evidenced by IR studies. The maximum flotation of iron oxides occurs at a pH corresponding to the pKₐ of these surfactants where the distribution of ionized and molecular species is equal. In the case of oleate, the maximum flotation at the neutral pH region, which is also its pKₐ value, is explained because of the formation of acid-soap complex and its high surface activity. At acidic pH values where neutral oleic acid molecule precipitation occurs, the particles are coated with oleic acid precipitates. Similarly, the cationic amine flotation of iron oxides is effective above the PZC of iron oxides, but several studies showed their flotation in a wider pH region, depending on the concentration of amine. The pH of maximum flotation of iron oxides with amines also varied but seems to occur close to the pKₐ value of amine. In the pH range 10.5–11.5 where the amine precipitation takes place, the particles are coated with amine precipitates. The maximum flotation of silicates also occurred at the pKₐ value of amines, and the flotation responses with diamines are similar to monoamines.

The adsorption, flotation, and electrokinetic results of alkyl sulfate or sulfonate collectors on iron oxides and amines on silicates are consistent with the hemimicelle hypothesis of electrostatic interaction and hydrophobic association. Recent IR and x-ray photoelectron spectroscopic studies of amine adsorption on silicates at pH 6–7, however, reveal that the ammonium ions are hydrogen bonded to the silanol groups at concentrations less than CHC and show the presence of molecular amine and ammonium ions at concentrations greater than CHC. Accordingly, the adsorption of amine on silanol groups is realized with the amino group H-bonded to surface silanol in the case of molecular amine, whereas the ammonium group formed owing to a charge transfer in strong H-bond between nitrogen of the amino and silanol groups:

\[ = \text{SiOH} \cdots \text{H}_2\text{N}^+\text{R} \leftrightarrow = \text{SiO} \cdots \text{H}_3\text{N}^+\text{R} \]

This equilibrium exists at the interface when the molecular amine appears at the surface corresponding to the CHC. Before the region of increased adsorption ammonium head groups are H-bonded to the negatively charged silanols and when the local surfactant concentration at the interface approaches a critical value, the adsorbed layer transforms into a crystalline state because of precipitation of neutral amine. As a first step, this process is 2D and the adsorbed amine establishes the above equilibrium. Screening the electrostatic repulsion between the head groups, the neutral molecules change the structure of the adsorbed
layer substantially and enhance the adsorption and increase the density of the monolayer. The second-phase transition (3D precipitation) occurs when the bulk solubility limit is reached at the interface. Based on these experimentally observed phenomena, a modified adsorption model involving 2D (hemimicelles are in crystalline state but in 2D space) and 3D precipitation is proposed.

The common behavior of maximum flotation response of oxides at the pKₐ values of anionic (or cationic) collectors suggests the potential adsorption of neutral molecular species when they appear in solution. In the presence of neutral molecule, the hemimicelle phenomenon takes place at a smaller concentration of collector. The intrusion of nonionics either between the oleate (or hydroxamate) anions or between the amine cations shields the adjacent ionic head–head repulsion and lowers the CMC of the hemimicelles. Therefore, the coadsorption of neutral molecules results in a closer-packed layer, improving the hydrophobic character and flotation. The extensive literature explaining that the acid–soap complex for hematite flotation, and, to a lesser extent, the amine–ammonium complex for silicate flotation, is mostly based on data for indirect thermodynamic solution chemistry, surface tension, and so forth, and perhaps requires more direct spectroscopic evidence.

Semisoluble Salts
J.D. Miller and J. Nalaskowski

FUNDAMENTAL CONSIDERATIONS
Numerous semisoluble salt minerals are recovered by flotation (phosphate minerals, fluoro-
rite, calcite, scheelite, barite, and celestite). In many cases, the hydrophobic surface state is
created by adsorption of water-soluble collector species. Most frequently, anionic collectors
such as carboxylates and sulfonates are used. The hydrophobic surface state is generally
established by chemisorption and/or surface precipitation reactions. Probably the most
studied and best understood system is the fluorite–oleate system. Rather detailed quantita-
tive information regarding adsorption phenomena has been obtained by various experimen-
tal techniques. Most recently, the in-situ FTIR/internal reflection spectroscopy (IRS)
technique has further extended understanding of adsorption phenomena and the state of the
adsorbed collector.

Adsorption Phenomena of Soluble Collectors. In general, the oleate adsorption iso-
therms presented in Figure 42 are characterized by at least two regions. At low-equilibrium oleate concentra-
tions (<1 × 10⁻⁵ M) in the absence of calcium dioleate precipitation, the
density of the calcium surface sites shown in Table 11 dictates the adsorption density in this
plateau region for the endothermic chemisorption reaction (Lu, Drelich, and Miller 1998).
In the case of fluorite, the adsorption density plateau for adsorbed oleate is 6.5 to 6.8 μmol/m²,
such as would be expected for a close-packed monolayer. Taking into consideration the den-
sity of calcium sites, this corresponds to a calcium-to-carboxylate ratio of about 2:1 and sug-
gests that bridging occurs between the carboxylate group and two calcium ions at the
fluorite surface (see Figure 43). Such coordination appears to explain the spectral features of
the chemisorbed carboxylate group (Lu and Miller 2002). On the other hand, the chemi-
sorption “plateau” for calcite and apatite as determined from Figure 42 at low-equilibrium oleate concentra-
tions is significantly less, approximately 1 to 2 μmol/m². Clearly, a close-packed
monolayer is not achieved for calcite and apatite at low concentrations, which accounts for a diminished state of hydrophobicity under these circumstances when compared to fluorite. For example, it has been found that for a $1 \times 10^{-5}$ M equilibrium oleate concentration, fluorite exhibits a contact angle of close to 90°, whereas bubble attachment at a calcite surface does not occur (Young and Miller 2000).
In Region II at higher equilibrium oleate concentrations (>1 \times 10^{-4} \text{ M}) , where adsorption exceeds an effective close-packed monolayer, the maximum adsorption densities are found to be about 300 \text{ \mu mol/m}^2 at a calcite surface, 100 \text{ \mu mol/m}^2 at a fluorite surface, and only 11 \text{ \mu mol/m}^2 at an apatite surface. In this region, it appears that the adsorption is mainly due to surface precipitation of calcium dioleate or heterocoagulation (attachment) of calcium dioleate collector colloids. Therefore, it is reasonable to relate adsorption density to the extent and kinetics of calcium ion release to solution as has been discussed in the literature (Young and Miller 2000; Free and Miller 1997). In this regard, the adsorption isotherm is quite sensitive to the level of dissolved calcium, particularly in Region I, the chemisorbed layer. If even a modest amount of calcium is present in solution prior to oleate addition, the precipitation event can overwhelm chemisorption, and the plateau, so characteristic of the chemisorbed monolayer, can be eliminated as demonstrated for the fluorite system by Free and Miller (1997).

The significance of mineral composition is revealed in oleate adsorption studies for different apatites, as shown in Table 12 (Yehia, Miller, and Ateya 1993). Sensitivity of the adsorption reaction and the hydrophobic surface state to apatite composition is clearly revealed from the data. Greater hydrophobicity is obtained for the fluorapatite, which may account, in part, for the activation of francolite phosphate minerals that can be achieved with the addition of sodium fluoride (Miller et al. 1987).

The two regions of oleate adsorption (chemisorption and surface precipitation) are also revealed from thermochemistry studies of the fluorite–oleate system (Miller, Hu, and Jin 1989) and for the calcite–oleate system (Young and Miller 2000). As shown in Table 13, adsorption at low-equilibrium oleate concentrations reveals an endothermic reaction of oleate at the fluorite surface, whereas at high-equilibrium oleate concentrations, an exothermic reaction associated with multilayer adsorption by surface precipitation of calcium dioleate is observed.

The organization of carboxylates at the fluorite surface has been studied by in-situ FTIR/IRS technique (Jang, Drelich, and Miller 1995), and the results show that spontaneous
adsorption of oleate or stearate from solution results in a self-assembled chemisorbed mono­layer almost identical to the structure of transferred Langmuir–Blodgett films as shown in Table 14. These results again support bridging of the chemisorbed oleate, as shown in Figure 43.

In summary, based on these adsorption densities, thermochemistry, and spectroscopic considerations, chemisorption predominates at low equilibrium concentrations (low adsorption densities), and a precipitated calcium dioleate predominates at higher equilibrium concentrations. In the case of fluorite, a close-packed monolayer of oleate forms during the chemisorption reaction, creating a strong hydrophobic state at the fluorite surface. On the other hand, in the case of calcite and apatite, monolayer formation is incomplete during chemisorption in region one, and, at best, a weak hydrophobic state is created at these surfaces.

WETTING/ATTACHMENT OF INSOLUBLE COLLECTORS

It is evident from the foregoing that the solubility limit of long-chain carboxylate collectors can be exceeded, and under these circumstances another phase appears in the system, either a collector oil (oleic acid) or a collector colloid (calcium dioleate). Under such conditions the hydrophobic surface state may be created by the attachment of this new collector phase at the surface (Laskowski 1999). For example, such phenomena have been discussed in the literature for semisoluble salt minerals including fluorite (Giesekke and Harris 1985). These results suggest that the interaction of calcium dioleate collector colloids at the fluorite surface can be quite strong, leading to a very hydrophobic surface.

This expectation is revealed by flotation recovery curves for fluorite and calcite with calcium dioleate as collector (Fa et al. 2003). As shown in Figure 44, flotation of fluorite is

<table>
<thead>
<tr>
<th>Monolayer Type</th>
<th>Adsorption Density, $10^{-10}$ mol/cm²</th>
<th>Molecular Orientation Angle, degrees</th>
<th>Advancing Contact Angle, degrees</th>
<th>Receding Contact Angle, degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-assembled</td>
<td>7.6</td>
<td>21</td>
<td>110–115</td>
<td>75–85</td>
</tr>
</tbody>
</table>

Source: Jang, Drelich, and Miller 1995.

![Figure 44](image_url)
quite strong with the calcium dioleate collector colloid; such is not the case for calcite. The tendency for attachment of the calcium dioleate collector colloid at fluorite and calcite surfaces is revealed from AFM force–distance diagrams using a 14-micron calcium dioleate sphere as the colloidal probe (see Figure 45). Significant attraction in the case of fluorite is evident. Furthermore, if the fluorite has a chemisorbed monolayer of oleate, the attractive force between calcium dioleate and the surface is so strong that measurement is difficult with standard cantilevers.

Probably of greater commercial significance is the flotation chemistry associated with phosphate rock. The chemistry fundamentals of fatty acid flotation of phosphate minerals have been studied extensively, and this research provides a basis for the understanding of industrial practice. However, there is still much unknown regarding the collector adsorption and oil wetting phenomena that occur in the actual flotation of phosphate rock at plant operations. Important issues include water quality as well as structure and composition of phosphate minerals.

However, it is generally recognized in Florida plant operations that flotation of the francolite phosphate mineral is not effective without the use of an insoluble collector oil, a mixture of fatty acid, and fuel oil, which selectively wets the phosphate mineral surface during high-solids conditioning. At a critical coverage of the oil, aggregation of the wetted phosphate mineral particles occurs with the formation of dense aeroflocs that are separated into the multiphase froth. As shown from the 3D X-ray micro-CT (computed tomography) image in Figure 46, the structure of the froth is rather complex, with not only mineral particles, water, and air bubbles, but also the oil phase.

Of particular importance in the case of coarse particle flotation with insoluble collector oils is the distribution of the oily collector to facilitate selective wetting/spreading at the mineral surface, a phenomenon that is of importance not only to the phosphate industry but also to the coal and potash industries. In this regard, dispersion of the oily collector (high-solids conditioning with a fatty acid–fuel oil mixture for phosphate rock) is an important factor, which has been discussed and demonstrated in several studies (Lu et al. 1999; Yu, Ye, and Miller 1990). In the case of phosphate flotation, the use of certain nonionic surfactants
facilitates the flotation of coarse phosphate, which is due in part to the improved dispersion of the fatty acid–fuel oil mixture (see Figure 47).

Recent research relates the improved flotation with high-solids conditioning to the selective wetting of phosphate minerals by the fatty acid–fuel oil mixture (Lu, Drellich, and Miller 1997). Results from an experimental study with a high-speed video system clearly show the preferential transfer of oil to a francolite surface (carbonate fluorapatite) and helps to explain the high-solids conditioning mechanism. When a quartz particle with an attached oil drop interacts with a francolite particle, the oil drop will spread at the francolite interface. When these two particles are forced apart, a major portion of the oil drop is transferred to the francolite surface (see Figure 48). A small portion of the oil drop may remain at the quartz surface. This process happens again and again during high-solids conditioning, and the fatty acid–fuel oil collector which initially may be randomly distributed will ultimately
be transferred to the surfaces of francolite particles. In this way, flotation selectivity is improved. Therefore, both recovery and selectivity in phosphate flotation with fatty acid–fuel oil are improved by high-solids conditioning.

Phosphate Flotation Practice
H. El-Shall, P. Zhang, N. Abdel Khalek, and P. Somasundaran

FLOATATION TECHNOLOGY FOR SILICEOUS PHOSPHATES
Practically, each ore deposit has its own characteristics and, thus, its own processing flowsheet. For instance, the phosphatic mineral in igneous deposits is well-crystallized apatite (with small specific surface because it is nonporous). It has a much greater floatability than the phosphatic mineral components constituting sedimentary deposits. The flowsheets are generally simple, direct flotation of apatite with anionic reagents being the general rule (Houot 1982). Recently, El-Shall and Zhang (2004) summarized information about the flotation of these igneous phosphate ores, such as those found in Kola in Russia, Phalaborwa in South Africa, the Brazilian apatites in Jacupiranga and Araxa, and the Finnish phosphates.

Sedimentary phosphates, on the other hand, show a wide variety of textures that reflect complex geologic origins and histories. The central Florida land–pebble phosphate deposit of the United States is a typical example of the siliceous francolite type (Smith 1976). Florida plants divide the beneficiation process into three general segments: washing, sizing, and flotation. The function of the washer is to remove most of the –150 mesh slimes, and to separate the deslimed matrix into two fractions, including a coarse feed of –16+35 mesh and a fine feed of –35+150 mesh. In some of the old plants, the coarse feed is subjected to agglomeration or skin flotation using shaking tables, or spiral or belt flotation, and the –35+150 mesh fraction is subjected to froth flotation (Moudgil and Barnett 1977). Currently, only one plant is still using spiral flotation, and the skin flotation units have been replaced by froth flotation.

The francolite-quartz flotation circuits are quite simple. The material, in general, follows a simple Crago process flowsheet consisting of anionic flotation of phosphate using fatty acid collectors and deoiling of the rougher concentrate with sulfuric acid ($H_2SO_4$) to remove reagents, followed by cationic flotation of the entrained silica from the rougher concentrate to produce a final concentrate assay of low silica content (Lawver, Raulerson, and
Another example of siliceous sedimentary phosphate is that present in Jordan. The fatty acid flotation circuit comprises a multistage flotation system, which produces a well-balanced final product in terms of $P_2O_5$ and silica content (Hummadi, Oweis, and Mubaideeu 1994).

Sedimentary carbonaceous phosphates are, by far, the most common deposits in the world and constitute more than two-thirds of present-day reserves. The biggest difficulty facing flotation separation of carbonate impurities from such resources arises from the fact that the physicochemical properties of phosphatic minerals and carbonates are very similar. In the last three decades, numerous studies have been carried out to separate carbonaceous gangue from sedimentary phosphate ores. Such research and development activities as well as fundamental aspects of phosphate flotation are discussed in the following sections.

**FLOTATION TECHNOLOGY FOR CARBONACEOUS PHOSPHATES**

Separation of carbonate minerals from sedimentary phosphate minerals by flotation is extremely complex. The poor selectivity encountered with flotation of carbonaceous phosphates 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 (Somasundaran and Zhang 1999).

During flotation 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 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

$$
Ca_{10}(PO_4)_6(OH)_2(s) + 10CO_3^{2-} \leftrightarrow 10CaCO_3(s) + 6PO_4^{3-} + 2OH^{-}
$$

This equation shows 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 carbon dioxide does exceed that required for converting apatite to calcite under high-pH conditions. A similar carbonation reaction occurs at the surface of fluorite and other semisoluble salt minerals.

Somasundaran and co-workers (Ananthapadmanabhan and Somasundaran 1984; Amankonah and Somasundaran 1985; Somasundaran, Amankonah, and Ananthapadmanabhan 1985) have suggested the use of stability diagrams for heterogeneous mineral systems to predict surface conversion of minerals in contact with dissolved species. They have demonstrated that the activity of $Ca^{2+}$ in equilibrium with various solid phases shows that the singular point for calcite and apatite is pH 9.3. Above this pH, apatite is less stable than calcite and, hence, conversion of apatite to 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. Such surface conversions in a calcite–apatite system have been confirmed experimentally. When apatite is contacted with 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 apa­
tite, respectively (Amankonah and Somasundaran 1985).

On the other hand, the solution chemistry of fatty acids is another important element
in the anionic flotation of phosphate minerals where Ca^{2+}, present in solution, affects the
grade of concentrates by activating quartz 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. Because calcium silicate and quartz are
negatively charged, detachment of calcium silicate from quartz can occur and, thus, quartz
can be depressed (Dho and Iwasaki 1990). In addition, for anionic fatty acid collectors, such
as oleate, precipitation of calcium dioleate and/or oleic acid may occur, and this significantly
influences the flotation response of the system.

In carbonate-phosphate systems with fatty acids as collectors, apatite is depressed in
the acid media (pH 5.5 to 6.0) whereas carbonate is floated. The depression of phosphate at
this pH range is possibly due to the adsorption (or formation) of aqueous calcium hydrogen
phosphate (CaHPO_{4}^{-}) on its surface, preventing surfactant ions from approaching the sur­
face of the phosphate particles. Free Ca^{2+} in solution can affect the formation of aqueous
CaHPO_{4} (Somasundaran and Zhang 1999). From thermodynamic considerations, it can be
predicted that selective flotation of carbonates from phosphates in acid media can be
enhanced by minimizing free Ca^{2+} in solution and by increasing hydrogen phosphate
(HPO_{4}^{2-}) in the system. This can be done by decreasing free Ca^{2+} concentration in the sys­
tem to low values by adding suitable chemical reagents such as sulfuric acid or chelating
agents such as oxalic acid, and by adding soluble salts to enhance the depression of phos­
phate minerals (Elgillani and Abouzeid 1993). In addition, collector adsorption is much
stronger at the carbonate surface than at the apatite surface, and this, in itself, may facilitate
the preferential flotation of the carbonate minerals.

Thus, the attention of researchers has been directed mainly toward improving the selec­
tivity of separation processes between carbonates and phosphates in two areas: (1) applica­
tion of different depressants and/or pH modifiers to control the wettability of either
phosphates or carbonates, and (2) development of new collectors to be more selective in the
flotation of sedimentary phosphates. It is clear that attention in both cases must be given to
flotation chemistry considerations for efficient separation and recovery of sedimentary
phosphates.

Reverse flotation of carbonate gangue, using fatty acid, with depression of the phos­
phate mineral is one of the more promising selective separation techniques that have been
tried by several investigators (El-Shall, Zhang, and Snow 1996; Elgillani and Abouzeid
1993; Anazia and Hanna 1987). They have shown that selective flotation of dolomite from
sedimentary phosphate (francolite) can be achieved under slightly acidic conditions, pro­
vided an apatite depressant is added to the system. In this regard, the action of different
depressing agents (such as hydrofluosilicic acid, phosphoric acid, sulfuric acid, sodium tri­
polyphosphate, alizarin red S, and starch) as well as a mixture of acids (e.g., sulfuric and
phosphoric acids) have been investigated by various authors (Zhang and Snow 1995;
have discussed several examples of technologies that have been developed both at bench and
pilot scale. However, recently, a new process called the CLDRI process has been developed,
and the results are promising. The process was developed by the Chinese Lianyungang
Design and Research Institute (CLDRI) through a project funded by the Florida Institute
of Phosphate Research (FIPR). A typical flowsheet of the CLDRI process involves grinding,
TABLE 15  Summary of pilot testing results on two dolomitic pebble samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO, %</th>
<th>P2O5, %</th>
<th>MgO, %</th>
<th>Phosphate Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLA-6</td>
<td>3.54</td>
<td>29.7</td>
<td>1.14</td>
<td>76.5</td>
</tr>
<tr>
<td>FLA-7</td>
<td>2.81</td>
<td>29.0</td>
<td>0.81</td>
<td>81.8</td>
</tr>
</tbody>
</table>

dolomite flotation, and silica flotation. Unlike most previous processes, the CLDRI process does not require the desliming step after grinding, thus reducing phosphate loss (Zhang and Yu 2000). Results obtained from pilot-plant testing of this process on samples from two different mines are given in Table 15. The final concentrates contained more than 29.0% P2O5 and less than 1% MgO with an overall P2O5 recovery of more than 80%.

Research and Development
Current flotation technology has limitations such as low recovery of coarse phosphates and high reagent costs, especially for the Crago process, and so forth. Therefore, research efforts have been conducted in many laboratories to improve flotation separation. These efforts are directed toward understanding flotation fundamentals, developing new flowsheets and/or reagent schemes, and developing new flotation devices. Some of these research activities are reviewed in the following sections.

Understanding High-Solids Conditioning. A high-solids conditioning (>70% by weight) with fatty acid–fuel oil mixtures is used extensively in the Florida phosphate industry to improve phosphate recovery and reduce reagent consumption. Some research has been carried out to investigate the phenomena involved and to optimize the conditioning parameters (Davis and Hood 1993, 1994; Damodaran, Fahey, and Moudgil 1996; Maltesh, Somasundaran, and Gruber 1996). Phosphate recovery increases as the energy input for conditioning increases up to a critical value, and then decreases as the energy is increased further. This response appears to be due to an improved dispersion and utilization of the insoluble fatty acid–fuel oil collector. At a higher level of energy input, recovery decreases because of the generation of slimes under extremely strong agitation (Davis and Hood 1993; Damodaran, Fahey, and Moudgil 1996; Maltesh, Somasundaran, and Gruber 1996). In view of the mechanisms of anionic collector adsorption, reducing the water content of the conditioner slurry has the dual effect of increasing the concentration of collector in the aqueous phase and reducing the quantity of activating ions. Thus, high-solids conditioning promotes chemisorption of collector on phosphate minerals and reduces the potential for physisorption on quartz.

Further research (Lu, Drelich, and Miller 1997) at the University of Utah relates the improved flotation with high-solids conditioning to the selective wetting of phosphate minerals by the fatty acid–fuel oil mixture. The results from an experimental study with a high-speed video system clearly show the preferential transfer of oil to a francolite surface and help to explain the importance of high-solids conditioning. When a quartz particle with an attached oil drop interacts with a francolite particle, the oil drop will be forced mechanically and thermodynamically to spread at the francolite-quartz interface (Lu, Drelich, and Miller 1997). When these two particles are forced apart, a major portion of the oil drop is transferred to the francolite surface. A small portion of the oil drop may remain at the quartz surface. This procedure happens again and again during high-solids conditioning, and the fatty acid–fuel oil collector, which initially may be attached at the quartz surfaces, will ultimately
be transferred to the surface of francolite particles. Therefore, high-solids conditioning improves both recovery and selectivity. The results from high-speed video experiments provide strong evidence for this oil-transfer mechanism (Lu, Drelich, and Miller 1997).

**Enhanced Recovery of Coarse Phosphate Feed.** Low recovery (about 60% to 70%) of coarse phosphate particles (16 × 35 mesh, i.e., above 0.5 mm) is generally obtained in industrial flotation operations. Efforts have been made to improve phosphate recovery from the coarse particle size fraction. One study conducted to enhance the recovery of coarse phosphate particles (Moudgil 1992) indicated that using emulsified collector and frothers would increase the recovery of coarse phosphate particles. Additionally, an increase in flotation recovery was observed when a certain portion of fine particles was added to stabilize the froth.

Recently, it has been indicated that the use of nonionic polymers as auxiliary flotation reagents, together with the traditional fatty acid–fuel oil collector, significantly improves the recovery of coarse phosphate (Lu et al. 1999). It was found that polyethylene oxide (PEO) polymer surfactants having a molecular weight from 1,200 to 8,000 are effective. At about the same collector level, phosphate recovery can be improved by 10% to 30% with PEO addition. The study suggests that there is an interaction between PEO and fatty acid. The improved phosphate recovery with PEO addition has been attributed to the improved froth stability and improved dispersion/adsorption of the fatty acid collector (Lu et al. 1999).

**Development of an Alternative to the Crago Process.** In the Crago process, sized flotation feed is dewatered and conditioned at about 70% or higher solids with fatty acid–fuel oil at about pH 9 for 3 minutes. The phosphate is then floated to produce a rougher concentrate and a sand tailing. It must be emphasized that a significant amount (30%-40%) of silica is also floated in this step. The rougher concentrate goes through a dewatering cyclone, an acid scrubber, and a wash box to remove the reagents from the phosphate surfaces. After rinsing, the deoiled rougher concentrate is transported into flotation cells where amine is added. The silica is finally floated from the rougher phosphate concentrate at neutral pH.

In this conventional process, about 30% to 40% by weight of the sands in the feed are floated twice, first by fatty acid and then by amine. The Crago process is, therefore, inefficient in terms of collector utilization, and one of the major drawbacks is the deoiling process. Deoiling consumes a significant amount of sulfuric acid, which calls for special safety precautions and equipment maintenance. Insufficient deoiling, which is not an infrequent phenomenon, often causes loss of phosphate and poor concentrate grade. Deoiling also causes loss of fine phosphate particles, amounting to more than 1% phosphate recovery in most operations. Another problem with the Crago process involves the amine flotation step. Not only are amines more expensive than fatty acids, but they are also very sensitive to water quality, particularly the slime content of the water.

**Single-Reagent Flotation**

Direct flotation using anionic reagents was practiced on high-grade flotation feeds in some U.S. plants and is still being used in a plant in Mexico. Some research efforts have also been directed at developing an anionic flotation process for phosphate, but the interest faded because of the stringent requirement in the past for acid-insoluble (AI at 4%-5%) content in the phosphate rock product. Such requirement has been relaxed, however, in recent years, with companies now accepting concentrate analyzing as high as 10% AI, which an anionic rougher-cleaner process could achieve without sacrificing much flotation recovery.

One major problem with most of the previously developed anionic flotation processes for phosphate is the conflict between recovery and concentrate grade. Although this conflict
TABLE 16  Anionic rougher-cleaner flotation results of various feeds

<table>
<thead>
<tr>
<th>Feed</th>
<th>Concentrate</th>
<th>% P$_2$O$_5$</th>
<th>% Al</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsized feed</td>
<td>Rougher</td>
<td>28.98</td>
<td>11.23</td>
<td>92.1</td>
</tr>
<tr>
<td></td>
<td>Bulk cleaner</td>
<td>30.37</td>
<td>7.28</td>
<td>85.7</td>
</tr>
<tr>
<td></td>
<td>Size (at 65 mesh)/cleaner</td>
<td>29.60</td>
<td>9.82</td>
<td>91.4</td>
</tr>
<tr>
<td>Fine feed</td>
<td>Rougher 1</td>
<td>29.47</td>
<td>13.27</td>
<td>95.3</td>
</tr>
<tr>
<td></td>
<td>Size (at 65 mesh)/cleaner</td>
<td>30.48</td>
<td>10.48</td>
<td>95.0</td>
</tr>
<tr>
<td></td>
<td>Size (at 48 mesh)/cleaner</td>
<td>30.71</td>
<td>9.55</td>
<td>94.7</td>
</tr>
<tr>
<td>Coarse feed</td>
<td>Rougher 1 with silicate</td>
<td>29.74</td>
<td>12.71</td>
<td>95.0</td>
</tr>
<tr>
<td></td>
<td>Bulk cleaner</td>
<td>31.52</td>
<td>7.65</td>
<td>89.8</td>
</tr>
</tbody>
</table>

exists in all flotation processes, it is more remarkable in anionic flotation of phosphate. For example, to reduce the Al in the concentrate from 10% to 6% would generally sacrifice recovery by up to 10%. Coarse phosphate particles are the main reason for the big gap between recovery and grade. Over-reagentizing in rougher flotation could ensure better recovery of coarse phosphate particles, but would also make it impossible to achieve low Al product in cleaner flotation. On the other hand, if reagent starvation were practiced in rougher flotation, coarse phosphate particles would not float in cleaner flotation. Another problem with some of the previous processes is the high cost for purer and more expensive collectors. The FIPR/SAPR (single-collector, all-anionic phosphate recovery) process (Zhang, Yu, and Bogan 1997) offers solutions to both of the above-mentioned problems. In this process, a relatively pure, selective, yet inexpensive, collector is mixed with a typical low-cost fatty acid collector used by the phosphate industry. The mixture boosts selectivity and the recovery of coarse phosphate with a reasonable reagent cost.

Comparative flotation tests showed that a mixture of iso-stearic and iso-oleic acids is the optimal collector for this process in terms of selectivity and coarse phosphate flotation. Sodium silicate was also found to be beneficial to this process. Table 16 summarizes some typical laboratory results.

**REVERSE CRAZO PROCESS**

Recently, FIPR developed the reverse Crago process (i.e., reverse of the conventional “double float” process). The first stage is employed to pre-float fine quartz particles with a minimum dosage of amine as collector. The dewatered sink product is then conditioned with a mixture of fatty acid, surfactant, and fuel oil to float the phosphate particles (Zhang, Yu, and Bogan 1997; Zhang and Yu 2000). This process could simplify the current flowsheet by eliminating the acid-scrubbing circuit, reducing the sizing section, and reducing the amount of reagents used when compared to the Crago process (Zhang, Yu, and Bogan 1997). The new process (reverse Crago) was evaluated in pilot-scale experiments at two Florida operating plants. A comparison for the reverse Crago process was accomplished in parallel with the conventional Crago flowsheet using mechanical flotation cells. Table 17 shows the comparison for pilot-plant results obtained for both procedures (Zhang and Yu 2000).

**NEW FLOTATION REAGENTS**

One of the recent trends in advancing flotation technology is to search for new reagents of better selectivity that are more economic to treat both siliceous and carbonaceous phosphate ores. In this regard, the success of an amphoteric collector called “Cataflot” to separate dolomite from phosphate of an igneous ore has been reported (Houot et al. 1985). A concentrate containing 0.2% to 0.5% MgO and 31.5% P$_2$O$_5$ was obtained from an ore containing
TABLE 17 Comparison between Crago and reverse Crago processes

<table>
<thead>
<tr>
<th></th>
<th>Unsized Feed (16 x 150 mesh)</th>
<th>Coarse Feed (16 x 50 mesh)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reverse Crago</td>
<td>Crago</td>
</tr>
<tr>
<td>P$_2$O$_5$, %</td>
<td>30.4</td>
<td>32.7</td>
</tr>
<tr>
<td>Al, %</td>
<td>8.6</td>
<td>3.2</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>92.6</td>
<td>90.5</td>
</tr>
<tr>
<td>Reagent cost, $/t</td>
<td>1.2</td>
<td>2.43</td>
</tr>
</tbody>
</table>

TABLE 18 Flotation results of Chinese phosphate using S711 as carbonate depressant

<table>
<thead>
<tr>
<th>Chinese Phosphate Mine</th>
<th>S711 Dosage, kg/t</th>
<th>P$_2$O$_5$, % Feed</th>
<th>Concentrate</th>
<th>% P$_2$O$_5$ Recovery</th>
<th>% MgO Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dayukou</td>
<td>0.35</td>
<td>16.1</td>
<td>32.6</td>
<td>83.2</td>
<td>86.0</td>
</tr>
<tr>
<td>Kunyang</td>
<td>0.90</td>
<td>22.4</td>
<td>32.7</td>
<td>81.9</td>
<td>77.9</td>
</tr>
<tr>
<td>Yichang</td>
<td>0.45</td>
<td>22.0</td>
<td>34.6</td>
<td>89.8</td>
<td>83.0</td>
</tr>
<tr>
<td>Damao</td>
<td>0.12</td>
<td>14.9</td>
<td>30.4</td>
<td>83.6</td>
<td>79.6</td>
</tr>
<tr>
<td>Jinping</td>
<td>0.10</td>
<td>8.1</td>
<td>31.0</td>
<td>98.4</td>
<td>93.9</td>
</tr>
</tbody>
</table>

about 1.3% to 1.6% MgO and 27% P$_2$O$_5$. Dolomite removal ranged from 70.7% to 89.7% (Houot et al. 1985). Such success encouraged some researchers to test a new amphoteric collector (dodecyl-N-carboxyethyl-N-hydroxyethyl-imidazoline) to separate dolomite from sedimentary phosphates (Shao, Jiang, and Parekh 1998). From a mixture of francolite and dolomite containing 26.2% P$_2$O$_5$, a concentrate containing 35.2% P$_2$O$_5$ with a 90% recovery was obtained using 290 g/t of the amphoteric collector. The rejection of MgO was about 81.4%. The results also showed that this collector was not sensitive to dissolved ions in the flotation system (Shao, Jiang, and Parekh 1998).

A series of new depressants (S217, S804, S711, and S808) was described by Lu and Sun (1999) as good depressants for phosphate minerals. The major compounds in all the S-depressants are aromatic sulfonate macromolecules with many -S03H polar groups. Depressant molecules adsorb onto the surface of carbonates with some polar groups and at the same time orient other polar groups toward water, making the surface hydrophilic. Table 18 shows some flotation results for different Chinese phosphate ores using S711 as the carbonate depressant. It appears that such a depressant can significantly improve the selectivity and stability of the flotation process (Lu and Sun 1999). At the same time, its consumption is relatively low (0.1–0.9 kg/t). For this reason, the S711 depressant is commercially applied in the Wangji (China) flotation plant.

Another depressant developed in China (L399), basically contains sodium lignosulfonate where polar (-CH$_2$SO$_3$H) groups are introduced into its molecules. Such polar groups interact with fatty acid to form a complex molecule, promoting the collector adsorption on apatite and, thus, enhancing the wettablity difference between apatite and carbonate gangue (Lu and Sun 1999). Table 19 shows some experimental results using L399 as a depressant.

Meanwhile, comprehensive efforts have been made (Liu and Liu 1992; Luo, Hua, and Hu 1995) to develop new and inexpensive collectors of better selectivity that work at ambient temperature. In these studies, the synergistic effect of mixing surfactants with fatty acids for flotation of salt-type minerals was investigated. Generally, these mixed collectors serve three basic functions to improve fatty acid flotation: (1) they enhance the collector ability
TABLE 19 Flotation results of Chinese phosphate using L399 as depressant

<table>
<thead>
<tr>
<th>Chinese Phosphate Mine</th>
<th>L399 Dosage, kg/t</th>
<th>P$_2$O$_5$, %</th>
<th>Feed</th>
<th>Concentrate</th>
<th>% P$_2$O$_5$ Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jinping</td>
<td>0.3</td>
<td>8.98</td>
<td>38.45</td>
<td>91.98</td>
<td></td>
</tr>
<tr>
<td>Xinpu</td>
<td>0.5</td>
<td>18.3</td>
<td>36.16</td>
<td>88.30</td>
<td></td>
</tr>
<tr>
<td>Huangmailin</td>
<td>0.5</td>
<td>10.79</td>
<td>35.18</td>
<td>85.15</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 20 Pilot-plant flotation results and reagent level for single-stage flotation with Aero 6493

<table>
<thead>
<tr>
<th>Process</th>
<th>Feed P$_2$O$_5$, %</th>
<th>Concentrate P$_2$O$_5$, %</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine feed, 1.78 lb/t feed</td>
<td>9.6</td>
<td>29.6</td>
<td>86</td>
</tr>
<tr>
<td>Coarse feed, 2.65 lb/t feed</td>
<td>12.9</td>
<td>31.55</td>
<td>95</td>
</tr>
</tbody>
</table>

and selectivity of fatty acid; (2) they reduce consumption of fatty acids; and (3) they improve the efficiency of collector at lower temperature (e.g., 10°C) and exclude pulp heating during wintertime (Luo, Hua, and Hu 1995). Some of these new collectors are CCLS (a mixture of fatty acid and amphoteric surfactant in 1:1 ratio), PA31 (fatty acid mixed with 2% nonionic surfactant), MAT (synthesized by esterization of fatty acid with ROH followed by sulfonation) alone or with OP (oxidized paraffin) and Tween 80 (nonionic surfactant). These studies indicated that such mixed collectors give better results than using fatty acids alone. For example, application of Tween 80 increases recovery by about 30% at 10°C, compared to the flotation with oleic acid alone at 40°C (Lu and Sun 1999).

The selectivity of the hydroxamic acid collector for phosphate flotation with respect to dolomite and quartz was revealed by researchers at the University of Utah (FIPR #0002142R). The results from microflotation experiments showed that when the total reagent dosage increased to 400 g/t, the recovery of the coarse phosphate minerals reached 95%, whereas the recovery of dolomite and quartz was insignificant (about 2%). The collector used was Cytec’s Aero 6493, a 30% alcohol solution of hydroxamic acid.

Most importantly, flotation with the hydroxamic acid collector is not particularly sensitive to pH values between 6 and 9. The results for a dosage of 1,200 g/t suggest that the selective flotation of phosphate rock can be achieved without pH adjustment.

Encouraged by the bench-scale laboratory results, FIPR funded a pilot testing program to evaluate the new collector, results of which are shown in Table 20.

A matter of particular concern in the development of the hydroxamic acid collector for phosphate flotation is the higher cost of the new collector chemistry relative to current reagent costs for typical plant operations.

NOVEL PROCESS EQUIPMENT

During the last decade some novel equipment has been developed for the flotation recovery of phosphates. Such efforts are mainly intended to develop more efficient flotation machines. Examples include columns, the air-sparged hydrocyclone (ASH), and the HydroFloat cell.

Column Flotation

Industrial application of column flotation has gone from virtually no use in the 1970s to a wide acceptance in the 1990s. During the last few years, column flotation has replaced conventional mechanical flotation cells in some of Florida’s phosphate plants, particularly for
**TABLE 21** Results of column flotation for different flotation feeds of Florida phosphate

<table>
<thead>
<tr>
<th>No.</th>
<th>Feed Sample</th>
<th>Feed Size, mm</th>
<th>% P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</th>
<th>Al, %</th>
<th>% P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</th>
<th>Al, %</th>
<th>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Belt</td>
<td>(1.2–0.5 mm)</td>
<td>19.7</td>
<td>39.8</td>
<td>34.3</td>
<td>5.2</td>
<td>99.6</td>
</tr>
<tr>
<td>2</td>
<td>Coarse</td>
<td>(0.84–0.5 mm)</td>
<td>18.0</td>
<td>45.4</td>
<td>31.9</td>
<td>12.3</td>
<td>99.5</td>
</tr>
<tr>
<td>3</td>
<td>Fine</td>
<td>(0.5–0.105 mm)</td>
<td>5.9</td>
<td>82.3</td>
<td>32.2</td>
<td>11.4</td>
<td>95.8</td>
</tr>
<tr>
<td>4</td>
<td>Unsized</td>
<td>(1.2–0.105 mm)</td>
<td>8.4</td>
<td>74.2</td>
<td>26.3</td>
<td>31.9</td>
<td>97.0</td>
</tr>
</tbody>
</table>

flotation of coarse phosphate particles (typically 16 x 35 mesh). A research project was conducted by the University of Florida and Jacobs Engineering (United States) to evaluate different air generation systems and frothers at bench and pilot scale to identify the best system for column flotation of phosphate. Different feed sizes including coarse (0.71 + 0.5 mm, or 24 x 35 mesh), fine (0.5 + 0.1 mm, or 35 x 150 mesh), unsized (1.4 + 0.1 mm, or 14 x 150 mesh), and belt feed (1.4 + 0.5 mm, or 14 x 35 mesh) were successfully floated using the column cell (El-Shall, Abdel-Khalek, and Svoronos 2000; El-Shall and Zhang 2004; El-Shall et al. 1999; El-Shall et al. 1998). The results shown in Table 21 indicate that column flotation, depending on the operating conditions, can give phosphate concentrates of high grade (about 31% P<sub>2</sub>O<sub>5</sub>) at recoveries as high as 99%. Such recovery is much better than the current 60% recovery obtained from flotation of coarse feed with mechanical cells at some Florida flotation plants.

**Air-Sparged Hydrocyclone**

The ASH is a novel process for fine particle flotation that has been developed at the University of Utah during the last decade. It combines the advantages of the conventional hydrocyclone and froth flotation into a single piece of equipment with a large specific capacity for the flotation of fine particles. The ASH equipment provides a unique opportunity for the effective flotation of fine hydrophobic particles at a high rate. The design of the ASH for fine particle flotation is based on the proposition that the energy for inertial collision between a fine particle and an air bubble will be increased sufficiently in a strong centrifugal force field, which facilitates film rupture, bubble attachment, and flotation (Das and Miller 1996; Miller and Das 1995). The ASH flotation technology is particularly well suited to handle high volumes of pulp at a specific capacity 50 to 100 times greater than that offered by other flotation machines.

ASH flotation technology has been evaluated for phosphate recovery from the central Florida phosphate deposits in pilot-plant experiments (Miller et al. 1999a). It was demonstrated that the 2-in. ASH system has a high specific capacity of about 435 to 550 gpm/ft<sup>3</sup> in both rougher flotation and amine flotation systems (50 to 100 times higher than that of a traditional flotation cell). In the case of fatty acid flotation, single-stage ASH flotation produced a recovery of 75% to 77% in a rougher concentrate containing 24% P<sub>2</sub>O<sub>5</sub>. In reverse flotation, the ASH system produced a phosphate recovery of 98% with a cleaner concentrate containing 31% P<sub>2</sub>O<sub>5</sub>, as given in Table 22 (Miller et al. 1999a, b).

Based on the pilot-plant research progress, a 6-in. ASH system was fabricated and tested in a central Florida phosphate plant for reverse flotation in the amine flotation circuit (Miller et al. 1999a, b). The high capacity (160 gpm/ft<sup>3</sup>) of the ASH system was again demonstrated for the 6-in. ASH system, which should have a significant effect on capital cost. A single-stage phosphate recovery of 91% was achieved with a concentrate grade of 30% P<sub>2</sub>O<sub>5</sub>,...
However, plant-site continuous operation of the 6-in. ASH was found to be limited to about 6 hours because of crud formation on the inner surface of the porous tube, which caused poor flotation separation, apparently due to inadequate air distribution. This plugging problem was found to be due to the plant water quality, and the composition of the crud was found to consist of about 50% fine quartz/clay and 50% organic (amine, fatty acid, and fuel oil). The effect of pore size (20–40, 40–60, and 70–90 μm) and porous material (plastic, ceramic, and metallic) were examined, but the plugging could not be prevented (Miller et al. 1999a). It seems that porous tube plugging will be the most significant engineering problem for the commercialization of the ASH system for use by the phosphate industry (Miller et al. 1999a).

### HydroFloat Cell

A new separator, known as the HydroFloat cell, has been developed by Eriez Manufacturing to overcome the limitation of traditional flotation equipment in recovering coarse particles (Kohmuench, Luttrell, and Mankosa 1999). This equipment uses a novel aeration system to reduce turbulence, improve attachment, and increase retention time. Thus, the coarse particle recovery can be improved. The separator consists of a rectangular tank subdivided into an upper separation chamber and a lower dewatering cone. During operation, deslimed feed slurry is introduced through a distributor at the top of the separator. The feed particles settle into the separation chamber at a rate dictated by their size and density. The rate of settling is counteracted by means of an upward flow of fluidization water injected evenly across the bottom of the separation chamber through a network of distribution pipes. This action creates a suspended bed of particles (i.e., teeter bed) within the separation chamber that has a higher overall effective density than the fluid. The teeter bed is continuously aerated by injecting compressed gas and a small amount of frothing agent into the fluidization water. The gas is dispersed into small air bubbles by circulating the water through a high-shear mixer in a closed-loop configuration with a centrifugal pump. The air bubbles in the fluidization water become attached to the hydrophobic particles within the teeter bed, thereby reducing their effective density. The lighter bubble–particle aggregates rise to the top of the denser teeter bed and are collected as overflow from the top of the separation chamber. Hydrophilic particles continue to move down through the teeter bed and eventually settle into the dewatering cone. These particles are discharged as a high-solids stream (e.g., 70% solids) through a control valve at the bottom of the separator. The valve is actuated in response to a control signal provided by a pressure transducer mounted to the side of the separation chamber. This configuration allows a constant effective density to be maintained within the teeter bed.

The HydroFloat cell offers several advantages over traditional flotation processes for the treatment of coarse feed streams, including reduced turbulence, improved attachment, reduced aeration rate, and increased retention time. The results from laboratory tests indicate

### TABLE 22 Comparison between the results of an ASH and typical plant performance

<table>
<thead>
<tr>
<th>Circuit</th>
<th>Phosphate Recovery, %</th>
<th>Concentrate Grade P₂O₅, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASH-2C</td>
<td>Plant</td>
</tr>
<tr>
<td>Rougher flotation</td>
<td>76.9</td>
<td>69.3–78.0</td>
</tr>
<tr>
<td>Amine flotation</td>
<td>98.3</td>
<td>96.4–98.0</td>
</tr>
</tbody>
</table>
that the $P_2O_5$ recovery from coarse feed can be increased by about 20%, as shown in Table 23. A pilot-scale test was carried out at a central Florida phosphate plant, and the results (Table 24) indicate that the recovery was increased by more than 20% with +35 mesh (+0.5 mm) plant feed (Kohmuench, Luttrell, and Mankosa 1999).

The primary disadvantage of the HydroFloat cell, however, is the need to effectively deslime the feed to remove fines that would otherwise be carried unselectively into the clean product. So, proper design of the plant classification circuits seems to be a critical factor that will determine the efficiency for flotation of coarse phosphate particles (Kohmuench, Luttrell, and Mankosa 1999).

### Soluble Salts

**J.D. Miller and J. Nalaskowski**

**FUNDAMENTAL CONSIDERATIONS**

The flotation chemistry of soluble salts in their saturated solutions has been investigated by many researchers during the past years (Rogers and Schulman 1957; Singewald 1961; Roman, Fuerstenau, and Seidel 1968; Schubert 1988; Miller, Yalamanchili, and Kellar 1992; Miller and Yalamanchili 1994; Veeramasuneni, Hu, and Miller 1997; Hancer et al. 1997; Hancer and Miller 2000; Hancer, Celik, and Miller 2001). Several explanations have been put forth in the past five decades to explain the mechanism of soluble salt flotation, which has had some success (Rogers and Schulman 1957; Schubert 1988; Roman, Fuerstenau, and Seidel 1968; Miller, Yalamanchili, and Kellar 1992; Miller and Yalamanchili 1994; D.W. Fuerstenau and Fuerstenau 1956; Arsentiev and Leja 1976; Yalamanchili, Kellar, and Miller 1993). Further discussion specifically regarding potash flotation has been given in the literature (Laskowski 1994; Titkov 2004; Monte and Oliveira 2004).

Studies about the dodecyl amine flotation of alkali halide salts and other soluble salts have suggested that flotation took place only after precipitation of the amine hydrohalide collector colloid had occurred and that the flotation response was governed by electrostatic interaction of the colloid with the mineral (Roman, Fuerstenau, and Seidel 1968; Miller, Yalamanchili, and Kellar 1992; Miller and Yalamanchili 1994; Yalamanchili, Kellar, and Miller 1993). The sign of the surface charge had been determined by nonequilibrium laser-Doppler electrophoresis and generally confirmed expectations from lattice ion hydration.
theory. In this way, the classic amine flotation separation of negatively charged KCl from positively charged NaCl was explained. The surface charge–collector colloid adsorption hypothesis is an interesting explanation for the primary amine flotation of alkali halides and the flotation behavior of KCl in particular. Unfortunately, this theory does not explain the fact that KCl is floated equally well or even better with the anionic SDS collector as reported in the literature (Rogers and Schulman 1957; Schubert 1988; Hancer and Miller 2000; Rogers 1957).

The most recent analysis of simple soluble salt flotation systems has explained the flotation of alkali halide and oxyanion salts from their saturated brines with both cationic dodecyl amine hydrochloride (DAH) and anionic SDS collectors according to the hydration behavior of the salt (Hancer and Miller 2000). It seems that salts which can be classified as water structure breakers can be floated with either collector, whereas salts classified as water structure makers stabilize the interfacial water structure so that flotation of these salts with the aforementioned collectors is not possible. For example, the correlation for alkali halides is presented in Table 25. A similar correlation was found for alkali oxyanions (Hancer and Miller 2000).

Some researchers (Rogers and Schulman 1957; Schubert 1988) had recognized the importance of hydration in soluble salt flotation but had not discussed this matter with respect to interfacial water structure nor provided evidence to support such a position. Now, the significance of interfacial water structure has been demonstrated for alkali halides and oxyanions and for more complex double salts (Hancer and Miller 2000).

Surface chemistry studies and analysis of bulk solution properties of various salts have demonstrated that the interfacial water structure and the hydration states of soluble salt surfaces are of considerable importance in understanding their flotation behavior with cationic DAH and the anionic SDS collectors. In particular, the high concentration of ions in these soluble salt brines appears to modify the bulk and interfacial structure of water, and this effect is salt specific. If the salt is a structure breaker, then flotation with either collector can be accomplished. The nature of the collector adsorption reaction requires additional research. In addition to water structure, salt solubility and salt stability must be taken into consideration in the analysis of salt flotation, as indicated in Table 26.

It has been shown that the soluble salt flotation response is largely independent of surface charge and that flotation can be achieved with either the cationic DAH or the anionic SDS collector, depending on the influence of the salt on water structure. For salts that act as structure breakers, flotation with either DAH or SDS is possible, whereas for salts that act as structure makers, flotation with these collectors is not possible. Flotation of soluble salts is dictated by the ability of respective cations and anions to organize the structure of interfacial water at the brine–salt interface. The sign of the surface charge is of little significance in the

### Table 25 Water structure correlation of the flotation response of alkali halide salts using either DAH or SDS

<table>
<thead>
<tr>
<th>Element</th>
<th>Fluoride</th>
<th>Chloride</th>
<th>Bromide</th>
<th>Iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure Makers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium</td>
<td>Flotation</td>
<td>No flotation</td>
<td>No flotation</td>
<td>No flotation</td>
</tr>
<tr>
<td>Sodium</td>
<td>No flotation</td>
<td>No flotation</td>
<td>No flotation</td>
<td>No flotation</td>
</tr>
<tr>
<td>Potassium</td>
<td>No flotation</td>
<td>Flotation</td>
<td>Flotation</td>
<td>Flotation</td>
</tr>
<tr>
<td>Cesium</td>
<td>No flotation</td>
<td>Flotation</td>
<td>Flotation</td>
<td>Flotation</td>
</tr>
<tr>
<td>Rubidium</td>
<td>No flotation</td>
<td>Flotation</td>
<td>Flotation</td>
<td>Flotation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure Breakers</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>No flotation</td>
<td>No flotation</td>
<td>No flotation</td>
<td>No flotation</td>
</tr>
<tr>
<td>Potassium</td>
<td>No flotation</td>
<td>Flotation</td>
<td>Flotation</td>
<td>Flotation</td>
</tr>
<tr>
<td>Cesium</td>
<td>No flotation</td>
<td>Flotation</td>
<td>Flotation</td>
<td>Flotation</td>
</tr>
<tr>
<td>Rubidium</td>
<td>No flotation</td>
<td>Flotation</td>
<td>Flotation</td>
<td>Flotation</td>
</tr>
</tbody>
</table>
TABLE 26  Analysis of soluble salt flotation with DAH and SDS

<table>
<thead>
<tr>
<th>Water structure</th>
<th>For salts if the salt is a structure maker. Flotation is achieved if the salt is a structure breaker.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt solubility</td>
<td>For salts of high solubility, flotation is difficult because of viscosity considerations. Examples include LiCl and NaClO₄. For salts of low solubility (&lt;0.2 M), flotation is influenced by surface charge. Examples include KClO₄, Na₂B₄O₇·10H₂O, and LiF.</td>
</tr>
<tr>
<td>Salt stability</td>
<td>If salt is unstable with respect to hydration or dehydration, flotation will be difficult in the unstable state. Examples include Na₂S₅O₄ which only floats above 32°C where the anhydrous state is stable. Na₂S₅O₄·10H₂O only floats below 32°C where the hydrated state is stable (Hancer et al. 1997).</td>
</tr>
</tbody>
</table>

TABLE 27  Advancing contact angle measurements for saturated brine at the surface of selected alkali halides (no collector present)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Contact Angle, degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI</td>
<td>25 ± 2</td>
</tr>
<tr>
<td>KCl</td>
<td>7.9 ± 0.5 (12.0 ± 1.4°)</td>
</tr>
<tr>
<td>NaCl</td>
<td>0°</td>
</tr>
<tr>
<td>NaF</td>
<td>0</td>
</tr>
</tbody>
</table>

*Measured on the natural cleavage plane of a single crystal.

TABLE 28  Advancing contact angle measurements for saturated brine at the surface of potassium-soluble salts (no collector present)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Contact Angle, degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>KClO₄</td>
<td>26.4 ± 2</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>20.1 ± 2</td>
</tr>
<tr>
<td>KNO₃</td>
<td>15.0 ± 1</td>
</tr>
<tr>
<td>KCl</td>
<td>7.9 ± 0.5 (12.0 ± 1.4°)</td>
</tr>
</tbody>
</table>

*Measured on the natural cleavage plane of a single crystal.

Flotation of soluble salts. Furthermore, the precipitation of the collector colloid is not necessary for flotation to occur. Instead, the flotation response is determined by the salt’s tendency to be a structure breaker or structure maker for water. The significance of interfacial water structure was demonstrated by sessile drop contact angle measurements with a drop of brine in the absence of collector (see Tables 27 and 28). Specifically, the greater the salt’s tendency to serve as a structure breaker, the greater the contact angle of the brine at the salt’s surface. For structure-making salts, the brine completely wets the salt surface.

Experimental results indicate that structure-breaking anions facilitate hydrogen bonding of the primary cationic collector (DAH) at the salt surface. The lack of flotation with comparable secondary, tertiary, or quaternary amine collectors, which do not permit hydrogen bonding, is in accord with this explanation for the adsorption of the primary amine collector. Flotation of many salts that float with the cationic primary amine (DAH) generally is possible with the anionic alkyl sulfate (SDS) collector at concentrations close to the point of collector precipitation. These results with SDS suggest that chemisorption and/or surface aggregation followed by surface precipitation occurs at the surface for structure-breaking salts.

All these results indicate that for a collector molecule to adsorb at the brine–salt interface, it has to displace interfacial water or penetrate through the structure of water. If the structure of water is strongly hydrogen bonded because of the presence of structure-making anions and cations, then collector molecules cannot reach the surface and be adsorbed.
Those ions that have a tendency to destroy the structure of water can create a condition for the adsorption of collector molecules and, subsequently, allow for the flotation of soluble salt minerals.

Of course, when long-chain collectors such as C18 amines are used, the collector invariably exceeds its solubility limit in saturated brines, and the analysis of the flotation becomes complex, even more so when extender oils are used. In the case of flotation with long-chain amines, the amine collector colloid forms and may attach at the salt surface. This is particularly true for potash, in which case the type of amine, the type of oil, the extent of dispersion, and the procedure followed for preparation/conditioning become important (Laskowski and Wang 1997).

**Potash**

Potash production from the great deposits of Saskatchewan is discussed in this section. Other production comes from Russia, Europe, and the United States. For example, potash production at the Dead Sea Works has involved the separation of magnesium chloride (MgCl₂) by crystallization from a concentrated brine containing carnallite (KCl-MgCl₂·6H₂O) and halite (NaCl). Carnallite is converted to KCl, then the mixture of KCl and NaCl in the brine is treated in a flotation plant to separate KCl from NaCl. In addition, substantial quantities of magnesium chloride and bromide salts are recovered from this lake brine.

The Permian Basin, near Carlsbad, New Mexico, has been a source of high-grade sylvinite ores during the last 40 years. As these high-grade sylvinite ores have been consumed, low-grade sylvinite ores containing carnallite and clay are becoming the future source for potash production from this region. It is reported that carnallite must be converted to KCl using various leaching procedures in order to recover potash from such carnallite-containing ores (Foot, Jordan, and Huiatt 1982; Huiatt, Tippin, and Potter 1975).

Other evaporative salt deposits from lake brines contain a mixture of single, double, and hydrated salts, depending on brine composition. These salts are eventually separated and converted into marketable potash products, such as potassium chloride and potassium sulfate. For example, Great Salt Lake Minerals Inc. (GSL) makes such products at their plant in Utah. In the GSL plant, the typical flotation feed material contains 58% halite (NaCl), 38% schoenite (K₂SO₄·MgSO₄·6H₂O), 3% kainite (KCl-MgSO₄·3H₂O), and 1% epsomite (MgSO₄·7H₂O). Schoenite separation from halite and other salts is achieved by flotation using both anionic and cationic collectors (Hancock, Neacham, and McLaughlin 1993).

Schoenite is a hydrated double salt containing K₂SO₄ and MgSO₄ in its chemical structure. Generally, the GSL plant uses a cationic collector (amine) to float schoenite from halite and other salts in a mixed brine. It has been reported that schoenite is successfully being floated using an amine collector with flotation recoveries in the range of 90%–95% (Hancock, Neacham, and McLaughlin 1993). Occasionally, GSL changes its collector from a cationic type to an anionic type, or sometimes even a mixture of these types is used for schoenite flotation. These results are explained from fundamental studies based on water structure theory (Hancer, Celik, and Miller 2001).

**Trona**

Soda ash (Na₂CO₃) produced from the trona deposits of the Green River basin in Wyoming by chemical treatment is used for glass production, chemicals, soap and detergents, fuel gas desulfurization, pulp and paper, and water treatment (Kostick 1998). The total value of this soda ash product amounts to about $800 million per annum. Production of soda ash from trona has completely displaced the production of synthetic soda ash in the United States.
The trona (sodium sesquicarbonate dihydrate, \( \text{Na}_2\text{CO}_3\cdot\text{NaHCO}_3\cdot2\text{H}_2\text{O} \)) reserves of greater than 120 billion tons (20–25 billion tons that are economical to mine) are extensive, covering an area of 3,100 km\(^2\), and will be the most significant source of soda ash in the years to come. It has been estimated that these reserves of trona could satisfy the world’s demand for many centuries (Kostick 1998). The trona beds occur with layers of oil shale, marlstone, and sandstone/mudstone (Kirk, Othmer, and Standen 1963). Insoluble contaminants, in addition to dolomite shales and clays, include many double-carbonate salt minerals.

A preferred processing strategy would be to remove gangue mineral contaminants from the plant feed by flotation prior to chemical processing. Such a processing strategy has been limited by the lack of satisfactory flotation technology. For example, it has been established that successful flotation of soluble salts generally requires the salt crystals or crystal hydrates to be thermodynamically stable (Hancer et al. 1997). Further, the flotation of structure-making salts, such as sodium carbonate salts, is not so easy (Hancer, Celik, and Miller 2001).

The flotation response of sodium carbonate and bicarbonate salts is increasing with respect to the development of flotation technology for the trona industry. For both DAH and SDS, the flotation response of the salt is controlled by the interfacial water structure, the solubility/viscosity of the saturated brines, and the thermal stability of the salt (see Table 26). Only the sodium bicarbonate salt exhibits a strong flotation response with both DAH and SDS collectors. Unlike the structure-making sodium carbonate salts, the bicarbonate salt does not promote water structure and, thus, seems to account for the strong flotation response from its brine (Ozcan and Miller 2002; Nickolov, Ozcan, and Miller 2003). However, the presence of sodium carbonate in the sodium bicarbonate brine appears to stabilize the interfacial water structure and prevents the flotation of sodium bicarbonate. These fundamental results seem to be very important for the development of new flotation technology as a process alternative for the treatment of trona and nahcolite resources. Further application might be extended to synthetic soda production by the Solvay process.

Even at temperatures of thermal stability, flotation of monohydrate and decahydrate sodium carbonate salts is not great. In similar fashion, neither can trona be floated from its saturated brine with either DAH or SDS collectors under typical conditions (Nickolov, Ozcan, and Miller 2003; Ozcan and Miller 2002; Ozcan et al. 2003). Nevertheless, a procedure for the reverse flotation of insoluble gangue minerals from trona ore in a saturated brine has been developed and demonstrated in pilot-plant testing (Wang, Li, and Miller 2002).

**Potassium Flotation Practice**

G. Strathdee, B. Gotts, and R. McEachern

The minerals sylvest (\( \text{KCl} \)) and halite (\( \text{NaCl} \)) are major components of potash ores in the actively mined basins of Canada, Europe, Russia, and the United States. About 90% of the sylvest produced is used in potash (potassium-containing) fertilizer products, and the remainder is recrystallized for industrial applications. Worldwide, about 53 Mt/a of sylvest are separated from ores, primarily by flotation.

The industrial practice of potash flotation was developed in Europe and the United States, and that experience influenced the design of mills that operate in Saskatchewan and New Brunswick, Canada. Improvements have been made (notably, the development of
column cells) during 40 years of operation, but the basic process remains unchanged. This section is based on modern industry experiences in Canada.

**Process Overview**

Ore composition in Saskatchewan and New Brunswick varies but is typically in the range 35% to 40% sylvite (KCl) and 1% to 8% water-insoluble material. The remainder of the feedstock is halite (NaCl). The water-insoluble material is a mixture of low-value minerals including dolomite, quartz, anhydrite, and clays.

Feed rates for current mills are in the range of 600 to 1,400 t/hr. The crystalline ore is dry-crushed using impactors and screened to a typical size of −5 mm. The ore is then slurried with co-saturated (KCl–NaCl) brine and flows through a series of attrition scrubbers to liberate the insoluble material from the surface of the KCl crystals. The scrubbed ore slurry then reports to a closed-circuit crushing and screening circuit where the oversize material is further reduced in size by an impactor or a rod mill.

The crushed and scrubbed ore is deslimed by processing the slurry through a series of hydrocyclones and hydroseparators. Circuit configurations vary but typically involve two or three stages of desliming. The deslimed ore is illustrated in Figure 49, and a typical circuit is presented in Figure 50. The coarse and fine fractions of the ore are reagentized separately; coarse ore slurry is treated in a mixing screw conveyor, a launder, or a drum conditioner; and fines are generally conditioned in a series of agitated tanks. These streams are recombined prior to being pumped to the flotation feed distributor.

The deslimed ore slurry is first treated with additives that depress flotation of residual clays and conserve valuable collector. Depressants in common usage include the natural products such as hydrolyzed pea or wheat starch, guar gum, or CMC. Total depressant dosage is about 200 to 300 g/t of deslimed ore and is added just prior to the conditioner. The cationic collector, a mixture of partially neutralized tallow-based C16–C18 amines, at a ratio of 50 to 60 g/t and an asphaltene-hydrocarbon oil extender (Esso 904 or microflotation oil at 30 to 40 g/t) are added in the conditioner. A volatile frother (MIBC or a mixture

**FIGURE 49** Photomicrograph of +10 mesh potash ore feed after desliming. Liberated sylvite crystals often contain occluded hematite whereas halite is generally clear.
of C6–C10 aliphatic alcohols at 20 g/t) is typically added just prior to the flotation cells. The selective conditioning time in potash is fast, with residence time in conditioners of approximately 2 minutes.

CONVENTIONAL MECHANICAL CELLS AND PROCESS FLOWSHEET

Conventional impeller-agitated mechanical cells used for rougher flotation range in size from 2.8 to 9.9 m³, and each bank consists of 3 to 6 cells in series. Currently, the most popular design in use is the Denver DR series 30-300, but some Fairbanks Morse and Galigher units are also in service in Canada. Overall, rougher flotation yields acceptable recovery (>95%) and grade for intermediate-sized (0.1 to 1.0 mm) particles (Figure 51). Recovery deteriorates inversely with particle sizes >1.0 mm, whereas concentrate grades drop for fine...
(<0.1 mm) particles. The finer particles are easiest to float and report to the concentrate in
the first few cells of a rougher bank, whereas progressively larger particles float as one pro­
ceeds down a bank of flotation cells (Figure 52).

Mills take advantage of the grade-by-size relationship (Figure 53) and screen the
rougher concentrate with a cut point in the range of 0.5 to 0.8 mm. Screen oversize reports
to the product stream whereas undersize material is refloated in a cleaner flotation circuit. In
other mills, the rougher concentrate is refloated to achieve fertilizer product grade of 95% KCl.

Tailings from the rougher circuit are wet-screened with a 0.85-mm (typical) cut point,
and the undersize material is discarded. The oversize material is sent to a closed grinding circuit
using, for example, a 3.0-m-diameter rod mill. The freshly ground material is then deslimed
and conditioned in a manner similar to that of the rougher circuit, and processed through mechanical regrind/refloat cells.

Flotation of the smallest particle-size material is done separately in a scavenger circuit. Feed to the scavenger circuits originates from the effluent of the product centrifuges or, in some cases, from a fine-particle stream from the desliming circuit. Scavenger flotation machines are Denver DR series or Fairbanks Morse units. Concentrate grade from the scavenger circuits is typically low (85% to 95% KCl), and as a result, this material is often sent to a crystallizer circuit for upgrading. The inability of the industry to effectively separate fine (<0.1 mm) particles in any type of cell is caused not only by physical entrainment but also by self-agglomeration of oppositely charged halite (−) and sylvite (+) minerals in co-saturated NaCl–KCl brine (Miller, Yalamanchili, and Kellar 1992; Boutin and Tremblay 1964). The layout of a typical potash flotation circuit is shown in Figure 54.

**FIGURE 54** Simplified rougher, cleaner, and regrind flotation for a modern potash mill

**RECENT DEVELOPMENTS IN POTASH PROCESSING EQUIPMENT**

Most potash flotation plants are mature operations where performance has been improved during decades of production. Consequently, opportunities for process optimization are defined by the limits that have been achieved in practice over a range of operating conditions. For example, grade-recovery data for potash flotation (see Figure 55) illustrate that there is still room for improvement in both fine and coarse particle separations that affect mill economics. In the last decade, applications of column and HydroFloat cell technologies have improved overall separation performance.
Although the concept of column flotation was developed early in the 20th century, it was the invention of practical cell designs that led to widespread mining industry application during the 1980s with installation of column cells in plants processing base metals, coal, and industrial minerals (Petracek and Gotts 1999). Research in Canada on the beneficiation of potash ores using column flotation began in 1995. Pilot-scale testing with a 15-cm-diameter column (Minnovex Technologies) on cleaner feed with about 0.2 to 1.2 mm particle size showed that product-grade concentrate (>95% KCl) could be achieved with good recovery in a single-stage unit operation (Figure 55).

Later, pilot-scale tests with a 60-cm-diameter column in a cleaner application confirmed that grade-recovery performance was comparable to that of a mechanical cell. Less success was achieved with rougher and scavenger feed streams. A PotashCorp–Minnovex Technologies 3.3-m-diameter by 5-m-high production unit (Tartaron, Cole, and Duke 1942) was installed and has operated well.

In the final column cell design (Figure 56) used in production, relatively uniform, shallow subsurface introduction of the feed slurry is achieved through a modified feed header to ensure that the radial distribution of high-velocity feed slurry does not disrupt the concentrate layer on the surface of the cell. Aerated brine injected into the tails collection cone at the bottom of the column has uniform bubble size and satisfactory spatial distribution. The tangentially injected brine induces a slow rotation of the contents of the cell and facilitates the collection of the concentrate froth. Good level control is also required for regulation of the concentrate flow and its collection at the perimeter of the cell. Aeration of the brine is
achieved by aspiration through a set of venturis that avoid orifice fouling by dripping water into the venturi suction to prevent evaporative crystallization.

Experience with production units for column flotation in a cleaner application has shown that the capacity is similar to that achieved by mechanical cells of comparable froth surface area. The stable performance of columns over a wide range of feed rates, together with reduced equipment maintenance, has been found to be attractive by mill operators.

Application of the HydroFloat Cell

In the past 20 years, PotashCorp has evaluated several commercial and prototype flotation cells, including the Jameson, Outokumpu tank, Eriez HydroFloat, and triflow aerated cyclone units. General findings have been that, because flotation of sylvite occurs very rapidly in the particle size range 0.2 to 1.2 mm, all equipment designs can likely be applied in cleaner or scavenger applications. However, only the hydrodynamic flow-assisted HydroFloat cell yielded exceptional coarse (1 to 4 mm) sylvite particle recovery and grade. That technology, therefore, has application in the processing of large (>1.0 mm) primary rougher feed or coarse tailings. Capture of large sylvite crystals is beneficial as it reduces the load on downstream regrind and cleaner circuits, improves concentrate debrining and the related energy demand for drying, and potentially increases flotation circuit capacity.

The enhancement of flotation of coarse particles by use of an upward flow of water in a column cell was initially reported by Barbery, Bouajila, and Soto (1989). The principle has since been applied to coarse phosphate flotation for an FIPR project and to coarse potash flotation in Canada. The aerated classifier design principle of the Eriez HydroFloat cell (Figure 57) has also been successfully applied for large (1 to 4 mm) particle sylvite recovery by PotashCorp. Air spargers installed below a collapsed slurry bed established in a subcritical fluidization flow of brine provide a combination of hindered settling and bubble-assisted particle buoyancy. Eriez and PotashCorp compared the performance of two prototype cells of different scale with a coarse rougher tailings stream that is normally reprocessed in a set of large mechanical Agitair cells. A preclassified feed is required to avoid entrainment of fines into the concentrate, so the full particle size distribution of typical rougher feed must be screened to match the hydraulic conditions of the HydroFloat cell. After superior recovery of high-grade sylkite was demonstrated in mill experimental campaigns, HydroFloat cell technology was applied at full scale.
Process Control

In the last 40 years, there has been ongoing evolution and development of process controls for the special case of potash flotation in saturated NaCl–KCl brine. Technologies for level control, flow control, and valve automation have all undergone substantial improvements. In addition, most flotation circuits are now controlled through a distributed control system (DCS) which monitors and controls circuit performance. As part of the DCS, several mills now have automated control of the various process reagents based on measurement of ore grade and feed rate.

There has been continuous improvement in onstream analysis through the use of gamma radiation detectors for the naturally occurring $^{40}$K isotope and, therefore, KCl grade. The online determination of run-of-mine dry ore grade is common and is often used for mill reagent control. In addition, several installations measure the grade of flotation tails slurries in batch tanks, with results reported automatically to the DCS. Attempts to measure product grade using $^{40}$K technology have been largely unsuccessful because of difficulties in reliably measuring small changes in the low-level, naturally occurring $^{40}$K radionuclide count rates.

Video image collection and pattern-recognition software are being applied to analyze online the important flotation parameters such as bubble size, froth color, and froth velocity. Nevertheless, potash mill process-control applications have not yet been achieved based on this technology.

Alternate Process Flowsheets

Separate conditioning of coarse (+1 mm) and fine (-1 mm) rougher feed fractions has been common practice to achieve a critical threshold collector coverage on large sylvite particles with low specific surface area. Traditionally, the two streams have been recombined prior to rougher flotation, although kinetic separation inversely by size is immediately observed in rougher cell banks. A steady-state process analysis has shown that a potential benefit may be realized by using existing rougher cell capacity to independently process the two separately conditioned rougher streams. As fine sylvite floats more rapidly than course fractions, existing rougher cell bank capacity could be reconfigured and operated in parallel to recover more coarse potash by extension of flotation residence time.
DEVELOPMENTS IN PROCESS CHEMISTRY

Since the empirical discoveries of the effectiveness of both cationic fatty amine collectors (Trocha and Rodrigues 1962) and hydrocarbon extender oils containing asphaltene fractions (Laskowski 1994) by companies operating in Carlsbad, Calif., those reagent classes have become the industry standard throughout the world. This is especially true for enhancement of coarse (+1 mm) particle flotation separation of sylvinite from halite. The following is an industrial state-of-the-art perspective on reagent chemistry in potash flotation.

Collectors

As the critical collector class for potash flotation, fatty amines work rapidly and effectively at addition ratios of about 50 to 60 g/t of deslimed rougher feed. Commercial hydrogenated amines derived from tallow fatty acids are a mixture of 16 to 18 alkyl carbon chain-length fractions with terminal amino functional groups. Mills convert the linear free-amine feedstock into 3% to 4% aqueous dispersions by partial (50% to 90%) neutralization with HCl to yield the cationic process additive, which is then stored above the Krafft point at about 70°C to avoid precipitation and phase separation of this water-insoluble reagent. The structural knowledge of the state of that amino colloid is limited.

The collector is added separately to coarse and fine ore fractions under turbulent, generally aerated conditions in brine that is co-saturated with soluble NaCl and KCl. Sylvinite surfaces become hydrophobic selectively and rapidly at process temperatures of 25° to 35°C, probably within seconds of exposure to the injected and diluted aqueous amine dispersion. There is no published experimental evidence on the mechanism or kinetics of collector—sylvinite—brine interaction during this fast preflotation conditioning stage.

Analysis of the distribution of collector between sylvinite and KCl brine suggests that the deposition of cationic amine onto the mineral surface is relatively weak. Internal data of PotashCorp show that the specific uptake (in micrograms per square meter) of the industry-standard collector Armeen HT by recrystallized sylvinite increases with brine-phase concentration of amine and decreases with temperature. In contrast, the uptake of the higher average molecular weight Armeen HF, derived from fish oil feedstock, is less dependant on conditioning temperature. The results of these studies are consistent with the observed temperature dependence of flotation performance as a function of chain length (Figure 58).

Leja (1982), Laskowski (1994), and others have shown that solubilities of individual long alkyl chain C14 to C18 amines in brine are less than 10^{-6} molar, and have calculated that a classical soluble collector diffusion mechanism is unlikely to create hydrophobic sylvinite during in-process conditioning residence times. Leja proposed that a two-stage process of flotation air—bubble spreading, then bubble-to-particle transfer, might explain sylvinite conditioning. In support of this view, O'Brien, Feher, and Leja (1976) observed that both free and ionic fatty acid solids spread spontaneously and rapidly at the air—water or air—brine interface.

An alternative explanation is that the rapid temperature drop from 70°C to the flotation circuit temperature of about 30°C, through the Krafft temperature of about 55°C, causes phase instability and an instantaneous competition between either co-precipitation of the precursor make-up tank aqueous colloid or its selective deposition onto the sylvinite surface upon addition to the ore slurry in NaCl—KCl brine. Preliminary AFM evidence of the surface of sylvinite exposed to amine collector while immersed in brine suggests the presence of both sparsely deposited microcrystalline and monolayer fatty amine species (Figure 59).
FIGURE 58 Flotation recovery of sylvite as a function of temperature for pure amines of varying chain length

KCl in brine + 1 mL 1% amine for 20 minutes. Interface sucked out. Topography. 1114S00F-HDF

FIGURE 59 AFM image of fatty amine deposit on a KCl sample kept in a brine–amine solution for 20 minutes

Attempts to characterize the cationic collector in brine by laser diffraction have been confounded by deposition of precipitated amine on silica glass cell windows.

Frothers
The standard practice for many years has been the addition of low levels (20 g/t ore) of volatile MIBC as a frother in potash flotation. Complaints from mill operations personnel have led to an ongoing search for less volatile or fragrant frothers, and several mills have switched
successfully to polyglycol ethers. Other mills have been unable to find an acceptable substitute for MIBC because of performance deterioration and/or downstream foaming incidents in process equipment.

Laskowski, Cho, and Ding (2003) have shown that the volatile alcohols that are added as part of the multicomponent reagent sequence may interact with collector amine and function more correctly as nonionic, small-molecule co-surfactants as they are observed to be poor frothers in brine. Their research suggests that low-molecular-weight alcohol frothers in potash flotation help to improve the dispersion of cationic collector amine, resulting in better coverage of the KCl surface.

**Extenders**

Concerns over long-term exposure to the extender oils used in potash flotation have led to the search for non-asphaltene-based alternatives. In spite of a substantial effort during the past 20 years, no significant change in the chemical class or formulation of extender oil composition has provided in-plant coarse particle flotation performance equivalent to that achieved with the industry standard asphaltene-based additive. Pre-emulsified collector-extender oil mixtures can yield high-grade and high-recovery concentrates in the laboratory. However, in-plant tests with those same formulations in operating flotation circuits have not yet been successful. The mechanism of selective potash ore conditioning in co-saturated NaCl–KCl brine is complex and not fully understood. Reformulation and testing of additives in general, and emulsions in particular, has been limited by inadequate knowledge of the multicomponent reagent chemistry potash process brine.

**SUMMARY**

Three approaches have driven developments in potash flotation in Canada: a search for higher concentrate grade and recovery through the full flotation feed particle size range by changing reagent chemistry, by in-plant comparisons of existing and innovative flotation cells, and by reassessment of conventional flowsheets. Any successful option should help to reduce the operating or capital costs of the core flotation or peripheral circuits. Column and HydroFloat cells have proven to be important emerging technologies that likely will find widespread application in the next generation of potash mills. In contrast, two decades of intensive laboratory and mill research on potash collector chemistry has not yet substantially changed conventional practice. Breakthroughs are overdue.

**REFERENCES**


