BRIDGING THEORY AND PRACTICE IN IRON ORE FLOTATION

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Abstract. Iron ores may be upgraded by flotation of iron oxides or siliceous gangue using either cationic or anionic collectors. The electrostatic mechanism of adsorption can account for the complex chemistry involved. In industrial practice, only cationic silica flotation is used at present in North America. Some of the seemingly paradoxical phenomena of cationic silica flotation behaviors in meeting the demand for low silica concentrates are reviewed.

INTRODUCTION

Low-grade iron ores that occur in vast quantities in North America are, in general, intimately associated with silicious gangue and require fine grinding for liberation. Earlier, prompted by the dwindling reserves of direct shipping and easily concentratable wash ores in the Lake Superior and Birmingham, Alabama districts, the research efforts were directed towards the development of flotation technology on oxidized iron ores as a primary means of concentration. The principles and industrial practice of iron ore flotation have been reviewed extensively (Houot, 1983; Iwasaki, 1983; Nummela and Iwasaki, 1986).

Due to an excess capacity in the world at present, the flotation processing of low-grade hematitic iron ores is no longer an attractive target. A major interest has recently been directed towards upgrading magnetic taconite concentrates which, when ground to 80-90% -44 µm (-325 mesh) or even finer, still contain locked siliceous middlings to the extent of 5-9% SiO₂ that cannot be removed by repeated magnetic or hydraulic separation. The development of low silica concentrates by cationic silica flotation, therefore, is receiving increasing attention by the iron ore industry, particularly for the production of fluxed pellets, to improve the productivity and energy efficiency of blast furnaces. The present practice demands a uniform silica product typically in the range of 4 to 5% for providing sufficient slag volume for sulfur control. Direct reduction-electric furnace smelting may be economically competitive with the conventional blast furnace - BOF steelmaking under certain specific circumstances. Feed materials for direct reduction should preferably contain less than 2% SiO₂. Future technologies of direct iron- and steelmaking may impose yet lower gangue requirements, either in concentrates or in pellets.

In this review, an emphasis was placed on some of the parameters that influence the flotation removal of siliceous gangue from hematite and magnetite concentrates in order to meet the increasingly critical demands of the steel industry.

CHOICE OF FLotation METHODS

Iron ores may be upgraded by flotation of either iron oxides or siliceous gangue using either a cationic or anionic collector as illustrated in Table 1. Each method has its own optimum operating conditions, and well illustrates the complexity of the chemistry involved. The theoretical foundation leading to the selectivity of adsorption of flotation reagents on oxide and silicate minerals has been a subject of intensive research over the years and a number of comprehensive reviews are available (Aplan and Fuerstenau, 1962; Fuerstenau, 1970; Fuerstenau and Fuerstenau, 1982; Fuerstenau and Palmer, 1976; Smith and Akhtar, 1976). It is now clearly established that for oxide minerals, hydrogen and hydroxyl ions are the potential determining ions and control the surface charge, which, in turn, governs the selectivity of collector adsorption. The selectivity of flotation separation may then be related to the difference in the points-of-zero-charge (PZC) of the constituent minerals in ores. An extensive list of the PZC's of solid oxides and hydroxides is available in which the effects of cationic charge, hydration, impurities and nonstoichiometry on PZC's are also discussed (Parks, 1965). Lists of the PZC's of silicate minerals and their relations to flotation are also available (Fuerstenau and Palmer, 1976; Fuerstenau and Raghavan, 1978).

The iron ore flotation methods interpreted in this manner may be theoretically simple, yet they are
ADVANCES IN COAL AND MINERAL PROCESSING USING FLOTATION

SELECTIVITY OF FLOTATION SEPARATION

Figure 1 shows the electrophoretic mobilities and the flotation characteristics with dodecylammonium chloride and sodium dodecylsulfate on quartz, magnetite and cummingtonite \((\text{Fe,Mg})_2\text{Si}_8\text{O}_{22}(\text{OH})_2)\), which are the three major constituent minerals in magnetic taconite of the East Mesabi Range, Minnesota. It is apparent in the figure that the floatabilities of the three minerals using these collectors correlate well with their surface electrical conditions and suggest that the selectivities of flotation separation may be related to the difference in the PZC’s of the constituent minerals. The intermediate behavior of cummingtonite indicates the difficulty of achieving high selectivity of separation by the cationic silica flotation either by insufficient removal of siliceous gangue or by excessive loss of the iron units.

![Figure 1: Electrophoretic Mobilities and Flotation Characteristics](image)

The three iron oxides, hematite, goethite and magnetite, have their PZC’s within a narrow pH range of 6.5 to 6.7, and hence their flotation characteristics of well-sized and hard varieties are indeed quite similar both with the cationic and anionic collectors (Iwasaki, Cooke and Choi, 1961). The influence of pH on the selectivity of flotation separation of iron ores may be demonstrated on an artificial mixture of well-sized goethite and quartz with the cationic and anionic collectors in terms of selective indices (Gaudin, 1957), as shown in Figure 2. With dodecylammonium chloride,
BRIDGING THEORY AND PRACTICE IN IRON ORE FLOTATION

the maximum selectivity of separation was obtained in the range of pH 6 to 7, whereas with sodium dodecylsulfate, it was approximately at pH 2 in good agreement with the flotation characteristics of the single mineral systems presented in Figure 1.

The flotation separation can then be achieved in the pH range bracketed by the PZC's of the two minerals, where they are oppositely charged. However, this pH range also corresponds to the condition where heterocoagulation of the two minerals can occur and the flotation separation becomes more difficult as the particle size becomes finer. Usui and Takeda (1983, 1983a) made a detailed study of the flotation behaviors of hematite and quartz in three size fractions (149/210, 53/44 and -10 μm) both individually and as equal weight mixtures. Figure 3 shows the flotation results as a function of the collector concentration in acid pulps. When the two minerals were floated individually, all three size fractions of quartz particles responded to flotation similarly while very little hematite floated as expected. When the equal weight mixtures of the respective size fractions of quartz and hematite were floated, an excellent separation was obtained on the coarsest mixture and a reasonably good separation on the intermediate size mixture near M, but the -10 μm mixture showed very little selectivity indicating that heterocoagulation of hematite and quartz overshadowed the difference in the adsorption behaviors of the cationic collector.

In a moderately alkaline pulp of near pH 10, both hematite and quartz are negatively charged and adsorb cationic collectors. Since the amines are not particularly selective for the flotation separation of siliceous gangue at this pH, a suitable hematite depressant is needed for satisfactory separation. Starches and their derivatives are commonly used for this purpose. Nonionic polyacrylamide also appears to act as a depressant for hematite (Somasundaran and Lee, 1982). In fact, the earthy hematite ores at the Sept-Iles plant were processed at a pH of 10 to 10.5 using a diamine as a collector and a wheat dextrine as a depressant for iron oxides (Bunge et al., 1977). The pulp pH of the cationic silica flotation at the Tilden concentrator is also reported to be in the range of 10 to 11 because of the caustic soda carried over from the selective desliming step (Villar and Dawe, 1975). Apparently, a combined use of a moderately alkaline pH and a starch depressant is preferable to the simple control of pulp pH between the PZC's of hematite and quartz in order to circumvent heterocoagulation.

Coburn (1985) reported, however, that, in the cationic flotation of finely ground oxidized iron ores, free iron oxide particles were recovered in the froth due to co-flocculation (or heterocoagulation) of iron oxide to quartz-covered bubbles even at a pH near 10. Small additions of decyl alcohol, dodecylsulfate or EDTA with dodecylsulfate was noted to increase double layer repulsion between the particles thereby diminishing the co-flocculation.
EFFECT OF WATER QUALITY

The importance of water quality has long been recognized in the desliming and flotation of iron ores. In fresh water supply, \( \text{Na}^+ \), \( \text{Ca}^{2+} \), and \( \text{Mg}^{2+} \) are most commonly found, \( \text{Al}^{3+} \), \( \text{Fe}^{2+} \), and \( \text{Fe}^{3+} \) may occur in acidic water, whereas anions include \( \text{CO}_3^{2-} \), \( \text{SiO}_4^{4-} \) and sometimes \( \text{SO}_4^{2-} \) when sulfides and gypsum are present. Oxidized iron ores ground in distilled water typically release \( 10^{-3} \) to \( 10^{-4} \) M of the alkaline earth ions at near neutral pH. These ions cause not only the activation of siliceous gangue in the fatty acid flotation of iron oxides, but also the depression of siliceous gangue in the cationic silica flotation, thereby contaminating the iron concentrates in both methods. For this reason, the selectivity of the anionic flotation of iron oxides is known to improve by using either softened water or ion exchange resins in pulps.

Cationic silica flotation is more tolerant of water quality than the fatty acid flotation of iron oxides, but an extensive recycle of water in flotation plants may lead to a buildup of soluble salts, flotation reagents, products of vegetation decomposition, and even micro- and macrobiological species in tailing ponds. Developmental work in the laboratory and pilot plant is often carried out with distilled or tap water totally unrelated in quality to the eventual commercial operation. A final evaluation with plant water, therefore, is essential in the development of a flotation flowsheet.

From adsorption measurements, streaming potential measurements and flocculation tests, it has been postulated that at near neutral pH, calcium ion is adsorbed as hydrated \( \text{Ca}^{2+} \), whereas at pH 11 as a hydroxy complex \( \text{CaOH}^+ \) (Iwasaki, et al., 1980). By correlating with the flotation behaviors, the flotation of Ca-activated quartz with fatty acid collectors was postulated to involve \( \text{CaOH}^+ \) as the effective form for activation (Clark and Cooke, 1968). The hydroxy complex \( \text{CaOH}^+ \) appears to play a role that differs from hydrated \( \text{Ca}^{2+} \) in the cationic silica flotation as well, as shown in Figure 4. At neutral pH, the recovery was unaffected by increased \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) concentrations.

FIGURE 4. Flotation of Quartz as Functions of Calcium and Magnesium Chloride Concentrations at pH 7 and 10.5 (Iwasaki, Smith, Lipp, and Sato, 1980).

Earlier, Onoda and Fuerstenau (1964) reported that in the flotation of quartz with dodecylammonium acetate, inorganic ions depress flotation of quartz through ionic competition at low collector concentrations, but they have little effect at high collector concentrations where the collector is strongly adsorbed through a hydrocarbon chain interaction. At pH 10.5, however, the flotation recovery decreased gradually with increasing concentration of calcium ion implying that strongly adsorbed \( \text{CaOH}^+ \) may have influenced the adsorption of the collector.

The adverse effect of \( \text{CaOH}^+ \) can be remedied by the use of complexing agents, as shown in Figure 5a. In the presence of \( 10^{-3} \) M \( \text{CaCl}_2 \), the flotation recovery was lowered to about 80%. An addition of a small amount of sodium tripolyphosphate (STPP) or sodium hexametaphosphate (SHMP) formed precipitates, which resulted in a marked drop in recovery to near zero. This phenomenon is attributable to the heterocoagulation of quartz with the precipitates, resulting in slime coating. At higher levels of their addition, nearly full recoveries were obtained. In the case of STPP, full recovery was obtained at the stoichiometric amount suggesting that nearly all calcium and tripolyphosphate had been removed from the quartz surface. SHMP, however, did not reach full recovery until 125% of the stoichiometric amount. The flotation recovery curve for EDTA shows virtually full recovery at as low as 25% of the stoichiometric amount. Apparently, this complexing agent not only removed the calcium ion from quartz surface, but also was attracted to the calcium ion on the quartz surface and aided the flotation of quartz with the cationic collector.

These observations suggest that the type of complexing agents and the manner in which these
Perhaps chemical precipitation, say with soda ash, reagents may be used should be carefully assessed. Perhaps chemical precipitation, say with soda ash, followed by high solid scrubbing or ultrasonic treatment, as will be discussed under selective desliming, may alleviate the adverse effects of calcium ion without introducing environmentally sensitive chemicals to the pulp.

Magnesium ion is also found in iron ore pulps though not in as high a concentration as calcium ion, and it appears to affect the flotation behavior of quartz differently. With magnesium ion, the flotation recovery dropped abruptly to nil above $10^{-3}$ M, as shown in Figure 4. In the region where the flotation recovery was nil, white precipitates were observed. Such a flotation behavior was attributed to a slime coating caused by the heterocoagulation of magnesium hydroxide precipitates on the quartz surfaces.

When the same complexing agents, EDTA, STPP and SHMP, were added in excess of stoichiometric amounts, all the complexing agents restored the flotation of quartz particles, as seen in Figure 5b. Apparently, the magnesium hydroxide precipitates were dissolved and the quartz surfaces were made accessible to the collector ion. Sodium silicate, however, is ineffective in restoring the floatability when the magnesium hydroxide coating is present.

**EFFECT OF PULP TEMPERATURE**

The effect of temperature on the fatty acid flotation of oxidized iron ores was investigated by Cooke et al. (1960). The selectivity indices of the flotation separation on a deslimed ore increased linearly with the pulp temperature, and even an undeslimed sample was shown to produce reasonably good separation at 70°C. At room temperature, the undeslimed ore was totally unresponsive to collection of the iron oxide minerals with fatty acids, irrespective of the addition levels of the collector. The increase in selectivity index, when iron ores are floated at higher temperatures, may be interpreted on the basis of the floatabilities of hematite and of calcium-activated quartz which are, respectively, positively and negatively temperature-dependent at pH 6. The temperature-dependence may then be due either to diminished calcium adsorption, or to a lower calcium-soap solubility.

The hot flotation, that was in practice at the Republic Mine in Michigan, involved regrinding of the specularite concentrate floated with a fatty acid collector followed by re-conditioning near boiling point with steam injection. The re-conditioning at an elevated temperature rejected the silicates in the subsequent flotation.

The information on the effect of temperature on the cationic silica flotation is sparse due presumably to the relatively minor effect this parameter has to the selectivity of separation. Hruz (1954) investigated the effect of temperature on the flotation of an oxidized iron ore using primary amine collectors with ten to eighteen carbons. All the collectors showed improved effectiveness with an increase in temperature and the amounts of the collector required in each case to float 90% of the quartz at 51°C were reduced by half. In the hot flotation of a deslimed oxidized iron ore, the concentrate grade was improved, but at the expense of the iron recovery, implying that the effect of pulp temperature on the selectivity of separation was minor.

In a pilot plant study on the cationic silica flotation of a deslimed oxidized iron ore at the MRRC in the mid 1960’s, the selectivity of separation was reported to suffer progressively as the pulp temperature fell from fall to winter and virtually no separation was obtained when the temperature reached near 5°C. Such a flotation behavior was thought to be related to the solubility of the collector at lower temperatures. Heating of the process water to room temperature by steam injection restored the effectiveness of the flotation separation.

**DESILING**

**Conventional Desliming**

In the flotation of oxidized iron ores, desliming is essential to successful separation, irrespective of whether the iron oxide or siliceous gangue minerals are floated, although anionic silica flotation appears to be less sensitive to the presence of slimes. The detrimental effect of slimes is twofold. The presence of slimes leads to a high reagent consumption because of high specific surface. When clays are present and when cationic collectors are used, abstraction of the collector by ionic exchange accentuates this effect. Table 2 presents the chemical composition of the slime fraction of an oxidized iron ore sample fractionated into three size ranges. It is apparent that iron and alumina increased in the finer size ranges, whereas silica decreased. From x-ray diffraction analyses, differential thermal analyses and electron microscopy, the slime fraction was shown to consist of hematite, goethite, quartz and kaolinite. It is interesting to note that the -1 μm fraction was particularly high in goethite and kaolinite.

**Table 2. Analysis of an Oxidized Iron Ore Slimes**

<table>
<thead>
<tr>
<th>% Fe</th>
<th>% SiO₂</th>
<th>% Al₂O₃</th>
<th>% H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head</td>
<td>18.68</td>
<td>69.80</td>
<td>0.26</td>
</tr>
<tr>
<td>20/5 μm</td>
<td>19.63</td>
<td>67.92</td>
<td>0.43</td>
</tr>
<tr>
<td>5/1 μm</td>
<td>24.06</td>
<td>64.60</td>
<td>0.75</td>
</tr>
<tr>
<td>-1 μm</td>
<td>56.71</td>
<td>11.70</td>
<td>2.68</td>
</tr>
</tbody>
</table>

Iwasaki, Cooke, Harraway and Choi (1962)

Attempts to compensate by the addition of large amounts of collectors result in only partial correction. Table 3 shows an example of the flotation results on an oxidized iron ore using dodecylammonium chloride as a collector. When the same amount of amine was added to the deslimed and undeslimed samples, the collector was consumed by the slimes and the recovery of the siliceous gangue was markedly reduced. When the amount of the collector addition to a deslimed ore was reduced to one half, the solution concentration of the amine was nearly identical with the undeslimed sample, yet the floatability of the siliceous gangue was not as severely affected. Apparently, slime coating on granular particles interfered with the bubble-mineral contact. It is now fairly well established that the electrostatic interaction between slimes and mineral particles governs the slime coating, and that the nature of the slime coating may be interpreted by the heterocoagulation theory (Fuerstenau et al., 1958; Usui, 1972).
Table 3. Cationic Silica Flotation Results on an Oxidized Iron Ore Using Dodecylammonium Chloride.

<table>
<thead>
<tr>
<th>Collector Addition</th>
<th>Flotation Products</th>
<th>Pct Wt</th>
<th>Pct Fe</th>
<th>Pct Insoluble</th>
<th>Pct SiO₂ Recovery in Flotation</th>
<th>Pct SiO₂ Concentration After Conditioning, mg per L</th>
<th>Pct Abstraction of Amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15 kg/t (deslimed)</td>
<td>Fe conc.</td>
<td>20.43</td>
<td>59.61</td>
<td>10.56</td>
<td>96.52</td>
<td>10.0</td>
<td>70.7</td>
</tr>
<tr>
<td></td>
<td>SiO₂ froth slime</td>
<td>14.22</td>
<td>25.21</td>
<td></td>
<td>59.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.075 kg/t (deslimed)</td>
<td>Fe conc.</td>
<td>57.54</td>
<td>24.49</td>
<td>62.41</td>
<td>43.33</td>
<td>3.5</td>
<td>79.5</td>
</tr>
<tr>
<td></td>
<td>SiO₂ froth slime</td>
<td>28.81</td>
<td>2.25</td>
<td>95.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15 kg/t</td>
<td>Fe conc.</td>
<td>84.93</td>
<td>19.01</td>
<td>71.44</td>
<td>16.48</td>
<td>3.4</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>SiO₂ froth</td>
<td>15.07</td>
<td>12.83</td>
<td>79.46</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Iwasaki, Cooke, Harraway and Choi (1962)

An elegant method of verifying the heterocoagulation theory was reported by Usui et al. (1967) by using twin mercury droplet electrodes. By varying the polarization potentials of the mercury droplets in potassium fluoride solutions, they established the critical potentials for their coalescence. The results are shown in Figure 6. The curves drawn through the experimentally observed critical potentials represent the potentials at the outer Helmholtz plane ($$\psi_0$$) calculated independently from the differential capacity data.

The electrostatic interaction model of slime coating on quartz by ferric oxide slimes, shown in Figure 7, may be compared with the domains of coalescence in Figure 6. The applied potentials, $$E_1$$ and $$E_2$$, may be assumed to represent the surface potentials ($$\psi_0$$) of quartz and hematite, respectively, by

$$\psi_0 = 59.2(pH_{PZC} - pH) \text{ mV}$$

The pH axis in the figure was drawn in such a manner that when the quartz is at its PZC (pH 3.7 in Fuerstenau et al. (1958)), the surface potential of the ferric oxide slimes with the PZC of pH 8 is +278 mV. Conversely, when the ferric oxide is at its PZC, the surface potential of the quartz is -278 mV. The intersections with the critical potential curves in the first and third quadrants define the pH range where heterocoagulation can occur. Although further refinement is necessary in view of the dissimilar surfaces with different Hamaker coefficients (Usui, 1972), it is interesting to note that the ferric oxide coating density on quartz in Figure 7 with a maximum near pH 6 is in good agreement with the twin mercury droplet interaction data, and that the slime coating can occur even when the two minerals are similarly charged. Coagulation of the ferric oxide slime tends to shift the maximum of the apparent coating density curve to near the PZC of the slime.

The sizes of goethite slime particles attached to quartz surfaces that interfere with cationic flotation were determined under a scanning electron microscope to be essentially less than 1 μm and most are smaller than 0.5 μm in discrete particles (Tippin, 1974). Usui and Takeda (1983) also reported that hematite slime particles of less than 0.3 μm were observed on coarse quartz particles. It follows then, that quartz particles with iron oxide slime coating and with natural stains can be removed by high solid scrubbing with either sulfuric acid or caustic soda in view of the coating behaviors shown in Figures 6 and 7.

The principles described here were well illustrated in the roles that different mineralogical components play in the flotation separation of oxidized iron ores (Iwasaki...
FIGURE 7. Effect of Slime Concentration and pH on the Ferric Oxide Slime Coating Density on Quartz in the Absence of Collector (Fuerstenau, Gaudin and Miaw, 1958).

et al., 1962). In the cationic flotation of siliceous gangue at near neutral pH, clay slimes are the reagent consuming species, but if enough amine collector is added so that the solution concentration is maintained, the clay slimes do not interfere with the flotation. Conversely, goethite slimes do not consume the amine collector, but they seriously interfere with the flotation of quartz particles because the goethite slimes coat the particles and prevent the attachment of air bubbles to the quartz surface. In the anionic flotation of goethite, the goethite slimes are the reagent consuming species, but they do not interfere with the flotation so long as sufficient dodecylsulfate collector is added. In this case, negatively-charged quartz and particularly clay slimes coat the positively-charged goethite surface and interfere with flotation.

The optimum pH for anionic silica flotation is over 11, so both iron oxide slimes and quartz particles are negatively charged. Here, the slime interference is much less pronounced. It is interesting to note that apparently cationic silica flotation at pH 10-10.5 along with a starch depressant is also more tolerant of slimes. Bunge et al. (1977) reported that the Sept-Iles plant operated successfully without desliming on the Knob Lake hematite ore ground to -149 µm (100 mesh).

Desliming in laboratory flotation tests is commonly carried out by repeating the agitation-settling-decantation procedure at 10 to 20 µm quartz equivalent using caustic soda and/or sodium silicate as dispersants. In pilot and commercial plants, hydrocyclones are used for desliming at 5 to 20 µm. Normally, dispersants are not required. Any attempt to develop a desliming device capable of splitting at a finer size than 10 µm is subject to the success of flotation separation in the size range of 10/1. µm. Besides slime coating, reagent consumption and heterocoagulation (or co-flocculation), particles in this size range are known to cause problems in flotation by entrainment, slower flotation rate and more reactive surfaces (Warren, 1984).

Selective Desliming

When finely disseminated ores are ground to liberation, conventional desliming leads to an excessive loss of iron units. Selective flocculation of iron oxides followed by the removal of dispersed siliceous slimes offers one of the most promising approaches for the treatment of finely disseminated, oxidized iron ores (Frommer, 1964; Colombo, 1986). The selective flocculation is brought about by the use of a proper combination of dispersant and a starch flocculant, and the deslimed products are further upgraded by the cationic flotation of the remaining siliceous gangue. The process has been successfully applied to a Michigan hematitic ore (Villar and Dawe, 1975).

High intensity magnetic separation is also capable of functioning as a selective desliming device for oxidized iron ores, rejecting siliceous gangue particles as well as slimes, while retaining fine iron oxide particles. The magnetic concentrate thereby obtained can then be upgraded by a combination of cationic and anionic silica flotation (Lawver et al., 1965).

To achieve the full benefit of selective flocculation, the ground pulp must be properly dispersed prior to the addition of a starch flocculant, but the optimum conditions are extremely sensitive to the mineralogical characteristics of the ore and the type and amounts of soluble salts in pulp solutions (Iwasaki, 1979; Paananen and Turcotte, 1980). For some iron ores, caustic soda alone is sufficient and for others, a combined use of caustic soda and sodium silicate works well. However, more generally, sodium tripolyphosphate in combination with caustic soda and sodium silicate may be necessary.

The alkaline earth cations in pulp solutions may be deactivated in several different ways. Sodium silicate is a nonselective dispersant, but can be used effectively in selective desliming when calcium ion concentration is low, say less than 20 ppm. At low silicate additions, calcium silicate precipitates coat the surfaces of both quartz and iron oxides, but the hydrophilic patches on the minerals are sparse and starch molecules can be adsorbed with little hindrance from the precipitate coating. At higher levels of sodium silicate, however, a thick coating of the precipitates on iron oxide surfaces shields starch molecules from adsorption (Krishnan and Iwasaki, 1982). Sodium tripolyphosphate (STPP) and sodium hexametaphosphate (SHMP) behave in a similar manner as sodium silicate below stoichiometric addition. They form calcium polyphosphate precipitates that coat both quartz and iron oxide surfaces and interfere with the starch adsorption. At higher concentrations of polyphosphates, most of the precipitates are detached through complexation and dissolution. Sufficient amounts of the calcium polyphosphate precipitates, however, remain on the iron oxide surface and interfere with selective flocculation (Heerema, et al., 1982).

Figure 8 shows the results of selective desliming tests on an equal weight mixture of goethite and quartz, plotted as grade-recovery curves. The vertical line drawn at the head grade of 28.5% iron represents no selectivity of separation corresponding to the conventional desliming on a fully dispersed pulp. In the selective desliming, the selectivity of separation improves.
as the curve extends farther to the right. The curve with no Ca$^{2+}$, but with corn starch, shows high selectivity of separation. In the presence of Ca$^{2+}$ with or without starch addition, the pulp was totally flocculated and very little slimes were removed. The effects of EDTA, STPP and SHMP are compared at 150% of the stoichiometric addition for $10^{-3}$ M Ca$^{2+}$. The selectivity of separation can be fully restored by complexing the calcium ion with EDTA. STPP is seen to be only partially effective whereas SHMP fully disperses the pulp and is totally ineffective. It is evident that selective flocculation is appreciably more sensitive to the nature of calcium compounds formed with these complexing agents than cationic silica flotation.

In the presence of calcium ion in pulp solutions in excess of, say 20 ppm, therefore, the selective flocculation of iron ores can be implemented satisfactorily with the use of a strong complexing agent, such as EDTA and NTA (Learmont et al., 1984). With some iron ores containing gypsum, the calcium ion concentration may reach several hundred ppm. Their dosage rates would then become prohibitively high and also the complexed calcium ion would accumulate in recycled water. Furthermore, the use of these complexing agents may be undesirable for their toxicological and ecological properties.

Clay minerals, particularly montmorillonite, with large cation exchange properties may be added to remove calcium ion in solution, although their presence appears to make selective flocculation more sensitive to operating conditions. In the presence of calcium ion, montmorillonite causes indiscriminate dispersion of both hematite and quartz, and hematite particles do not flocculate upon addition of starch. Heterocoagulation of hematite and montmorillonite may be intensified in the presence of calcium ion. It is interesting to note in Figure 9 that ultrasonic treatment of the pulp markedly improves the flocculation of hematite when starch is added to the pulp before the treatment, but no beneficial effect may be observed when starch is added after the ultrasonic treatment. Apparently, the ultrasonic treatment leads to the replacement of montmorillonite particles by starch molecules at the hematite surface. The addition of starch after the ultrasonic treatment does not aid flocculation since montmorillonite particles redeposit on the hematite surface and prevents the starch adsorption (Arol and Iwasaki, 1987).

Chemical precipitation per se is ineffective due to surface precipitation as well as heterocoagulation of the precipitates with quartz particles (Heerema and Iwasaki, 1980; Krishnan and Iwasaki, 1986). However, chemical precipitation of calcium ion as a carbonate salt followed by mechanical cleaning of the surface precipitates through ultrasonic treatment shows considerable promise in controlling calcium ion in pulp solutions (Manukonda and Iwasaki, 1987). A quartz suspension in the presence of as high as 400 ppm Ca$^{2+}$ dispersed fully with about a half of the stoichiometric amount of bicarbonate after ultrasonic treatment. The dissolution of quartz might have been accelerated at the prevailing pH of 11 by the ultrasonic treatment, thereby precipitating the remaining Ca$^{2+}$ with the silicate ion. Scanning electron microscope observations of ultrasonically dispersed quartz samples show no precipitate coating. Selective flocculation tests, conducted on a hematite-quartz mixture in the presence of 400 ppm Ca$^{2+}$ and ultrasonic treatment following an addition of the stoichiometric amount of bicarbonate produced satisfactory separation.

**EFFECT OF PARTICLE SIZE**

As mentioned earlier, on well-sized, slime-free particles, the selectivity of flotation separation from artificial mixtures may be related to the difference in their PZC's. However, the role that particle size plays in the flotation separation of oxide minerals with paraffin-chain collectors is often overlooked. In the processing of magnetic taconite, fine siliceous fractions are well liberated and removed in the magnetic separation step, while the size fractions coarser than 44 μm (325 mesh) become progressively higher in the SiO$_2$ contents, and more than half of the silica is in the +44
Table 4. Screen Analyses of a Magnetic Taconite Concentrate and Its Flotation Concentrate. The Effect of Particle Size on Flotation Removal of Silica is Included.

<table>
<thead>
<tr>
<th>Screen Size, Mesh</th>
<th>Magnetic Concentrate</th>
<th>Flotation Concentrate*</th>
<th>SiO₂ Floated %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% wt Fe % SiO₂</td>
<td>% wt Fe % SiO₂</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.70 35.94 40.08</td>
<td>0.60 36.27 40.48</td>
<td>13</td>
</tr>
<tr>
<td>200</td>
<td>6.22 55.79 16.89</td>
<td>4.03 51.79 21.16</td>
<td>19</td>
</tr>
<tr>
<td>270</td>
<td>8.89 61.59 10.11</td>
<td>7.52 62.90 8.91</td>
<td>25</td>
</tr>
<tr>
<td>325</td>
<td>8.54 65.35 7.41</td>
<td>9.34 67.15 5.09</td>
<td>25</td>
</tr>
<tr>
<td>400</td>
<td>12.50 67.96 4.52</td>
<td>10.33 69.27 2.90</td>
<td>43</td>
</tr>
<tr>
<td>500</td>
<td>10.79 67.64 4.52</td>
<td>11.83 70.42 1.73</td>
<td>58</td>
</tr>
<tr>
<td>500</td>
<td>10.79 67.64 4.52</td>
<td>11.83 70.42 1.73</td>
<td>58</td>
</tr>
<tr>
<td>Composite</td>
<td>100.00 67.28 4.91</td>
<td>79.56 68.34 3.97</td>
<td>36</td>
</tr>
</tbody>
</table>

* Cleaner concentrate at point A in Figure 10.

μm (+325 mesh) fractions. Table 4 shows a typical example of the screen analysis on a magnetic taconite concentrate. Therefore, the cationic silica flotation of magnetic taconite concentrates involves the flotation of coarse and locked siliceous gangue particles from the full size range of magnetite particles.

Figure 10 shows the cationic silica flotation results on the magnetic concentrate. With increasing addition of the collector at the natural pH of 8.5, the iron recovery drops precipitously at about 3.6% SiO₂ in the flotation concentrate. The screen analysis of the cleaner concentrate in Table 4 shows that the SiO₂ contents in the size fraction coarser than 44 μm (+325 mesh) remained quite high and the SiO₂ recoveries in the cationic silica flotation in the +44 μm (+325 mesh) fractions were notably poor. This is because the coarse gangue particles have the same floatabilities as the fine magnetite particles, and further addition of the collector floats both together indiscriminately. In fact, the flotation results are seen to be less selective than simply screening out the coarse fractions. This behavior becomes more critical when the siliceous gangue is in the form of ferromagnesian silicates with their PZCs between quartz and magnetite as shown in Figure 1.

Frothers can reduce the amount of cationic collectors approximately weight-for-weight, but with very little effect on selectivity. Kerosene and fuel oil are used effectively as an extender in the anionic flotation of oxidized iron and phosphate ores, but their use along with cationic collectors will not float coarse siliceous gangue in magnetic concentrates. The effect of pH, as seen in Figure 10, is relatively minor though somewhat higher selectivity was obtained at pH 10 than at 8.5 and 5.5. High solid scrubbing with caustic soda at pH 12.3 followed by desliming and flotation at pH 10 appeared to improve the selectivity of flotation separation (Anon, 1977).

To search for more selective collectors, both company and university laboratories have carried out a large number of flotation tests with different types of amines (Bleier et al., 1976; Cronberg and Lentz, 1968; Freyberger et al., 1981; Jacobs, et al., 1978; Smith, 1973). Certain amines are somewhat more selective than others, and in commercial plants, ether amines and diamines with the following formulas

**Ether Primary Amine**

\[ R-\text{O-}(\text{CH}_2)\alpha-N \]

where \( R \) is \( C_\alpha/C_{10} \) hydrocarbon in a ratio of 60/40

**Ether Diamine**

\[ R-\text{O-}(\text{CH}_2)\alpha\text{HN-}(\text{CH}_2)\alpha-N \]

where \( R \) is a \( C_{13} \) branched hydrocarbon chain
are used for ease of feeding, metallurgical efficiency and cost. The diamines are used as partially neutralized with acetic acid, or unneutralized. The optimum pH for the cationic silica flotation of oxidized iron ores is in the range of 10 to 11, while the flotation of magnetic taconite concentrates is carried out at the natural pH of near 8.5.

Another approach to this problem would be to search for more selective depressants for magnetite. Starches and starch derivatives have been used successfully in the flotation of oxidized iron ores. In Figure I(a), the effect of various starch depressants is shown as grade-recovery curves, replotted from Chang, Cooke and Huch (1953). The figure shows that certain starches are more effective than others. When the starch depressants were tested on magnetic taconite concentrates, however, they had virtually no effect on the selectivity of separation as shown in Figure I(b).

Derrick sandwich deck screens are available to 37 μm (400 mesh) and they can operate effectively on a commercial scale (Derrick et al., 1989). Because of the heavy media effect on the vibrating screen, the siliceous gangue particles tend to float and report selectively to the oversize. It becomes of interest then to study the effects of screening a flotation feed into coarse and fine fractions, and carrying out the flotation tests on the two size fractions separately as described earlier.

In the selective desliming-silica flotation applied to oxidized taconites, the concentrate grade could be improved by adding more amine collector to ensure the flotation of coarse gangue particles. The increased addition of the collector causes the flotation of fine iron oxides leading to a loss of iron units. Wet high-intensity magnetic separation of the cationic silica flotation froths was reported to recover the fine iron oxides, which was recycled to the overall flotation circuit.

The size dependence of their floatabilities may be utilized in the upgrading of a magnetic taconite concentrate. When a concentrate is sized into coarse and fine fractions with a laboratory sieve and they are processed separately, the combined concentrate from the coarse and fine circuits is markedly higher in grade than when the unsized magnetic taconite concentrate is floated directly (Figure 10). Conventionally, hydrocyclones are used in commercial operations, but cyclones classify on the basis of particle size and specific gravity, and closing of a grinding circuit with a cyclone forces coarse siliceous gangue into the overflow fraction. The replacement of a cyclone by a Rapifine screen reportedly minimized coarse silica and resulted in a better flotation response for the Knob Lake hematite ore (Major-Marothy, 1972). Thereby increasing the overall iron recovery by 2 percent with no adverse effect on the concentrate grade (Hopstock, 1979). The effectiveness of fine screening the froth product may also merit attention.

DUPLEX FLOTATION

The size dependence of the floatabilities of iron oxides and siliceous gangue may be utilized in the combination or duplex process applied to low-grade oxidized iron ores. Fatty acid flotation of iron oxides following desliming results in an appreciable contamination of the concentrate by fine-sized siliceous gangue due presumably to the accidental activation by calcium ion. This is exactly opposite in behavior to the cationic flotation of siliceous gangue from magnetic...
concentrates in which silica froths were contaminated with fine magnetite. Therefore, if the fatty acid coating on iron oxides can be removed, the fine siliceous gangue can be removed by the cationsic silica flotation by taking advantage of the differences in the floatabilities between coarse and fine particles in both steps. This combination process is successfully applied to the beneficiation of Florida phosphate ores in which the fatty acid coating is removed by acid scrubbing. However, acid scrubbing is totally ineffective on iron ores.

Two methods have been proposed for removal of the hydrophobic coating of fatty acids from iron oxide concentrates. In one method, activated carbon with a large specific surface of the order of 600 m²/g was used to remove the adsorbed collector by distribution over its enormous surface area. An oxidized iron ore, analyzing 37% iron, was ground to -149 µm (~100 mesh), deslimed and upgraded by flotation using 0.25 kg/ton fatty acid. The concentrate analyzed 44% iron, which was heavily contaminated with fine siliceous gangue. The concentrate coated with fatty acid was then conditioned with 1.5 kg/ton activated carbon. The activated carbon was then removed by flotation without any addition of collector, followed by the cationic flotation of siliceous gangue with 0.3 kg/ton British gum as a depressant for iron oxides. The final concentrate analyzed 62.5% iron with 69% iron recovery (Iwasaki, Zetterstrom and Kalar, 1967).

The second method involves the use of ozone for decomposing the fatty acid coating. Ozone can oxidize organic compounds rapidly without leaving potentially hazardous by-products. A hematite ore, analyzing 36% iron, was processed by the same flowsheet as shown in Figure 12. The iron concentrate with fatty acid coating was treated by bubbling ozone. The hydrophobic coating was completely destroyed with 0.25 kg/ton ozone. The amine flotation of siliceous gangue from an ozonated pulp produced a final concentrate analyzing 65% iron at an overall iron recovery of 70%. This duplex flotation process appears to be capable of producing a concentrate with similar grade and recovery at much coarser mesh-of-grind than the conventional or selective desliming-cationic silica flotation process.

**SUMMARY**

North American iron ores are low in grade and finely disseminated, but are relatively free from such impurities as sulfur, phosphorus and titania. In order to remain competitive with high-grade overseas sources, the investigations on low-cost beneficiation methods that insure high quality and uniform quality products must be continued in order to prepare for ever tightening specifications on ironmaking raw materials for blast furnaces and also for the future iron- and steelmaking processes that can directly utilize the finely ground concentrates.

In this article, a major emphasis was placed on the problem areas of interest at present in the cationic silica flotation. Some of the seemingly paradoxical behaviors may be related to the effects of surface contamination, inherently caused by natural processes or by unintentional pretreatments, as well as to the effects of minor impurities or lattice defects as reported on other oxide minerals (Aplan and Spearin, 1980; Balachandran et al., 1987; Mular, 1965; Roy and Fuerstenau, 1972). The development of more specific collectors or depressants becomes of interest in improving the selectivity of separation. Perhaps, flotation reagents with chelating groups may provide an approach to this problem (Fuerstenau et al., 1967; Marabini et al., 1983; Pradip, 1988), although the effect of residual reagents on the environment should be carefully assessed.

Besides silica, many other minor impurities are becoming of concern for improving the productivity and product quality in ironmaking and steelmaking. The removal of alkali metals, sulfur and phosphorus from iron ores, that are often directly amenable to conventional flotation, has been reviewed recently (Nummela and Iwasaki, 1983). The attention should also be directed towards removing more refractory impurities which are either intimately associated or chemically combined, such as arsenic, zinc, tin, nickel and titania.

While the surface chemistry plays a fundamental role in the selection of a proper chemical combination, attention should also be paid to the engineering aspects of the mineral-reagent as well as mineral-bubble contacts. The importance of conditioning has been well recognized in the anionic flotation of iron oxides (Arbiter and Williams, 1983; Chi and Young, 1962; Li, Livingston and Lemke, 1960). In the cationic silica flotation, capillary condensation of undissociated amines may play a similar role in alkaline pulps (Takeda and Usui, 1987). The effect of flotation machine design and operation has not been fully explored and warrants both theoretical as well as developmental research (Beebe, 1965). Column flotation with less vigorous agitation than mechanical cells and the effect of bubble size distribution on the selectivity of separation merit attention (Szatkowski and Freyberger, 1988).

**FIGURE 12. Duplex Flotation of a Hematite Ore Involving Fatty Acid Flotation of Hematite, Ozone Treatment and Cationic Silica Flotation (after Iwasaki and Malicsi, 1985).**
REFERENCES


BRIDGING THEORY AND PRACTICE IN IRON ORE FLOTATION


