Iron Ore Beneficiation in the U.S.A.:
Past and Future

COLERAINE MINERALS RESEARCH LABORATORY

May 2, 2000

By Iwao Iwasaki
Iwao Iwasaki
Senior Research Associate
Endowed Taconite Chair

Approved by Ronald L. Wiegel
Ronald L. Wiegel
Assistant Director – Minerals

CMRL/TR-00-03

NRRI/TR-2000/18

Project #5698106

University of Minnesota – Duluth
Natural Resources Research Institute
5013 Miller Trunk Highway
Duluth, Minnesota 55811

Iron Ore Beneficiation in the USA: Past and Future

I. Iwasaki
Coleraine Minerals Research Laboratory, University of Minnesota-Duluth
Coleraine, Minnesota, USA

ABSTRACT: The iron ore mining industry in the U.S. is facing strong competition from high-grade overseas sources. In order for the American iron ore industry to remain competitive, research on low-cost beneficiation methods that ensure high-quality and uniform-quality products must be maintained in order to prepare for ever-tightening specifications on ironmaking raw materials for blast furnaces and for direct reduction processes. In this article, some of the past developments are reviewed and future prospects are discussed with a special emphasis on flotation technology.

1 INTRODUCTION

With the dwindling reserves of high-grade, direct-shipping natural ores in the USA, various beneficiation methods based on sizing and gravity separation were developed on intermediate- and low-grade ores in an attempt to meet the rapidly growing demand for steel following World War II. During that period, flotation technology on oxidized ores received considerable attention as a primary means of concentration. The worldwide exploration efforts at that time led to the discovery of vast sources of high-grade ores. As a result, the flotation processing of low-grade hematitic iron ores became no longer an attractive target. Current interest in the USA centers on upgrading magnetic taconite concentrates which, when ground to 80% -44μm (-325 mesh), still contain 5-7% SiO_2 due to locked siliceous middlings that cannot be removed by repeated magnetic or hydraulic separation. Fine screening and cationic silica flotation have received considerable attention by the iron ore industry of the Lake Superior Region, particularly by the plants producing fluxed pellets. The present practice demands a uniform silica product of typically 4% for providing adequate slag volume for sulfur control.

The current trend in the steel industry is in favor of increased electric furnace steel production and gradual reduction of integrated steelmaking based on blast furnace-coke oven technology. This is because the cost of steel produced in minimills, based on iron and steel scrap, is significantly lower than that produced in integrated mills. Though scrap quality and quantity will eventually become a limiting factor in this trend, recent technological advances in thin-slab casting and direct rolling through the use of direct reduced iron (DRI) in electric furnace-based minimills are encroaching into the traditional markets of integrated steelmakers. This trend would result in attendant decrease in the demand for oxide pellets. The taconite industry in the Lake Superior Region should, therefore, aim at some flexible product mix that will provide some metallic feedstock along with oxide pellets to survive and prosper into the 21st century. Feed materials to direct reduction should preferably contain less than 2% SiO_2.

In this article, some of the parameters that were identified to influence the removal of siliceous gangue from hematitic iron ores are reviewed first, and then some future directions for development in upgrading magnetic taconite concentrates are discussed. It is these high-grade concentrates that are necessary to permit the continuing production of oxide pellets and provide feedstock for direct reduction facilities.

2 BENEFICIATION OF IRON ORES

The iron ores in the Lake Superior Region is a typical example of banded iron formation (BIF).

BIF is a sedimentary rock deposited about 2 billion years ago with layers of iron oxides, either hematite or magnetite, alternately banded with layers of silica and silicates, analyzing normally 20-30%Fe. By the action of meteoric water, the leaching of siliceous components led to the oxidation of magnetite and enrichment of iron, thereby forming hematite and goethite deposits. Ore grades in the enrichment zone tend to decrease with depth and eventually reach the protore as mining proceeds.

In the late 1950s, a term 'semi-taconite' was coined by the Minnesota Legislature to provide favorable taxation policy to promote the development of lower grade oxidized material of the Mesabi Range. Semi-taconite was defined as iron-bearing material which was oxidized and partially leached, and which could not be made merchantable until it was ground finer than 20 mesh and concentrated by methods other than washing, jigging, heavy-media separation, or cyclone. This legislation prompted research activities on flotation upgrading of oxidized iron ores.

3 FLOTATION OF OXIDIZED IRON ORES

Iron ores may be upgraded by flotation of either iron oxides or siliceous gangue using either a cationic or anionic collector as shown in Table 1. Each method has its own optimum operating conditions, and well illustrates the complexity of the chemistry involved. The choice of a flotation method for a given iron ore involves a careful assessment of various parameters.

Table 1. Classification of iron ore flotation methods

	Iron Oxide Flotation	Siliceous Gangue Flotation
Anionic Collector	1. $RCOO^-$ (pH 6-9) 2. RSO_3^-, RSO_4^- (pH 2-4) 3. $RSO_3^- + RCOO^-$ (pH ~ 5.5)	$RCOO^- + Ca^{++}$ (pH 11-12)
Cationic Collector	$RNH_3^+ + F^-$ (pH 2-4)	RNH_3^+ (Lab pH ~ 6) (Plant pH 8-11)

R = Paraffin chain containing 12-18 carbon.

The mineralogy of the ore is by far the most important. Hard martite ores consisting of approximately equal amounts of hematite and siliceous gangue may be upgraded by floating either iron oxides or silica. For specularite ores, the anionic flotation of the hematite would be preferable by taking advantage of its readily floatable surface property. A hydrophobic coating on iron oxides, however, causes moisture accumulation in the drying stage in pelletizing, and also lowers the decrepitation temperature, both leading to difficulties in induration furnaces. For magnetic taconite concentrates, only a small amount of locked siliceous gangue is left after magnetic separation and, therefore, the cationic silica flotation would be the method of choice. Limonitic iron ores with porous and easily abrading surfaces are extremely difficult to process.

A positive control of concentrate grades is another important parameter in meeting the product specifications for iron ores. Cationic silica flotation is amenable to automatic control in conjunction with neutron activation analysis for silica, but it may be difficult with anionic silica flotation. In the development of the Tilden, Michigan, flowsheet, both calcium-activated anionic silica flotation and cationic silica flotation following the selective flocculation step (vide infra) were evaluated. Cationic silica flotation was chosen because of the reagent cost for maintaining the pulp pH near 10.5 with amine as against 11.5 in the anionic silica flotation. Another factor in favor of amine was the ability to exercise grade control via the amount of cationic collector added (Nummela and Iwasaki 1986). Those processes that require highly acidic pulps have serious equipment corrosion problems and the plant effluent becomes of environmental concern.

4 PROBLEMS IN OXIDIZED IRON ORE FLOTATION

The selectivity of flotation separation, as shown in Table 1, is influenced by a complex combination of mineralogical, chemical, physical and engineering parameters. In an attempt to unravel the complex flotation behaviors, intensive research efforts have been made on the surface chemistry of iron oxides and quartz, which are the major constituents of oxidized iron ores. The principles and industrial practice of iron ore flotation have been reviewed extensively (Houot 1983, Iwasaki 1983, 1989, Nummela and Iwasaki 1986, Uwadiale 1992). The research topics are divided into three categories, namely, the selectivity of collector action, the effect of soluble salts and the effect of slimes.

4.1 *Selectivity of collector action*

The theoretical foundation leading to the selectivity of adsorption of flotation reagents on oxide and

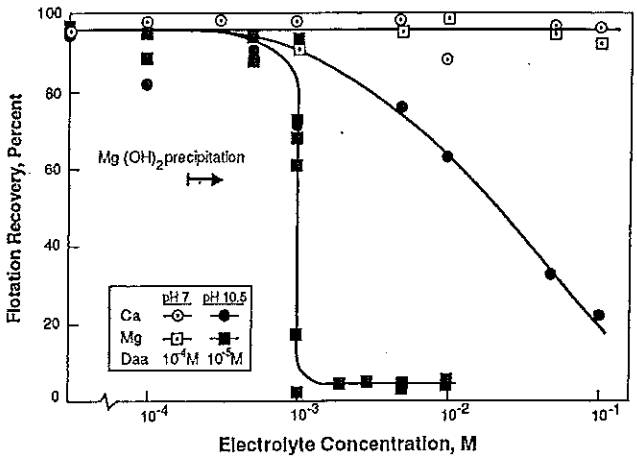

Figure 1. Flotation of quartz as functions of calcium and magnesium chloride concentrations at pH 7 and 10.5 (Iwasaki et al. 1980).

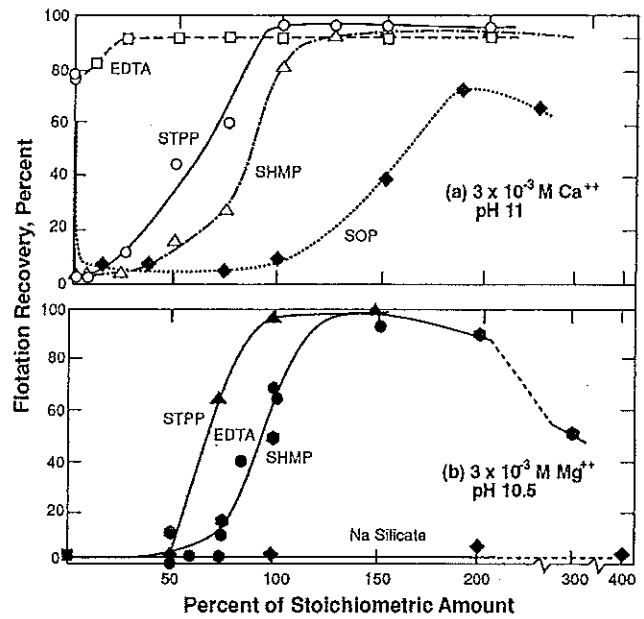

Figure 2. Flotation recovery of quartz at 10^{-5} M dodecylammonium acetate as functions of stoichiometric amounts of complexing agents (Heerema et al. 1982, Iwasaki et al. 1980.)

silicate minerals has been a subject of intensive research over the years and a number of comprehensive reviews are available (Aplan & Fuerstenau 1962, Fuerstenau 1970, Fuerstenau & Fuerstenau 1982, Fuerstenau & Palmer 1976, Smith & Akhtar 1976). It is now clearly established that for oxide minerals, H^+ and OH^- are the potential-determining ions and control the surface charge, which, in turn, govern 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.

4.2 *Effects of soluble ions*

The importance of water quality has long been recognized in the desliming and flotation of iron ores. In fresh water supply, Na^+, K^+, Ca^{++} and Mg^{++} are most commonly found, Al^{3+}, Fe^{2+} and Fe^{3+} may occur in acidic water, whereas anions include HCO_3^-, $SiO_3^=$ and sometimes $SO_4^=$ when sulfides and gypsum are present. Oxidized iron ores ground in distilled water typically release 10^{-3} to 10^{-4}M of Ca^{++} and Mg^{++} at near neutral pH. These ions cause not only the accidental activation of siliceous gangue in the fatty acid flotation of iron oxides, but also the depression of siliceous gangue in cationic silica flotation. In the other extreme, Ca^{++} may be intentionally added at highly alkaline pH to activate siliceous gangue for flotation using fatty acid collectors.

From adsorption measurements, streaming potential measurements and flocculation tests, it was postulated that at neutral pH, calcium ion is adsorbed as hydrated Ca^{++}, whereas at pH 11 as a hydroxy complex $CaOH^+$ (Iwasaki et al. 1980). By correlating with the flotation behaviors, the flotation of Ca-activated quartz with fatty acid collectors involves $CaOH^+$ as the effective form for activation (Clark & Cooke 1968). The hydroxy complex $CaOH^+$ appears to play a role that differs from hydrated Ca^{++} in the cationic silica flotation as well, as shown in Figure 1. At neutral pH, the recovery is unaffected by increased Ca^{++} and Mg^{++} concentrations, while at pH 10.5, the flotation recovery decreases gradually with increasing concentration of calcium ion, implying that strongly adsorbed $CaOH^+$ may have influenced the adsorption of the collector.

The adverse effect of $CaOH^+$ can be remedied by the use of complexing agents, see Figure 2a (Iwasaki et al. 1980). In the presence of 10^{-3} M $CaCl_2$, the flotation recovery with amine at pH 10.5 is lowered to about 80%. With EDTA, virtually full recovery is obtained at as low as 25% of the stoichiometric amount. An addition of a small amount of sodium tripolyphosphate (STPP) or sodium hexametaphosphate (SHMP) forms precipitates, which results in a marked drop in flotation recovery to near zero. These phenomena are attributable to the heterocoagulation of quartz with calcium polyphosphate precipitates, resulting in slime coating. At higher levels of their addition, nearly full recoveries are obtained above the stoichiometric amounts, suggesting that calcium as

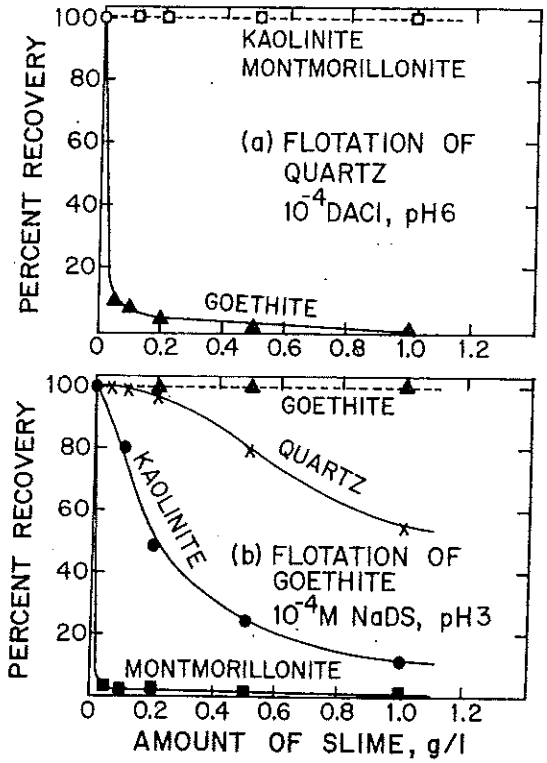

Figure 3. Effect of montmorillonite, kaolinite, quartz and goethite slimes on flotation of iron ore minerals (Iwasaki et al. 1962a)

well as polyphosphates has been removed from the quartz surface.

These observations suggest that the types of complexing agents and the manner in which these reagents are 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 present in iron ore pulps and the flotation behavior of quartz is affected differently. With magnesium ion, the flotation recovery in the region where $Mg(OH)_2$ precipitates, say above pH 10, the flotation recovery drops to nil. Such a flotation behavior is attributable to slime coating caused by the heterocoagulation of $Mg(OH)_2$ precipitates on the quartz surfaces.

When the same complexing agents, EDTA, STPP and SHMP, are added in excess of stoichiometric amounts, all the complexing agents restore the flotation of quartz particles. Apparently, the $Mg(OH)_2$ precipitates are dissolved and the quartz surfaces are made accessible to the collector ion. Sodium silicate, however, is ineffective in restoring the floatability when the $Mg(OH)_2$ coating is present.

4.3 *Effect of slimes*

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. The detrimental effect of slimes is twofold. The presence of slimes leads to high reagent consumption because of high specific surface. When montmorillonite clays are present and when cationic collectors are used, abstraction of the collector by ionic exchange accentuates this effect. Attempts to compensate by addition of large amounts of collectors result in only partial correction. Slime coatings on granular particles, which interfere with the bubble-mineral contact, are another effect. It is now well established that the electrostatic interaction between slimes and mineral particles governs the slime coating. The nature of slime coating may be interpreted by the heterocoagulation theory (Fuerstenau et al. 1958; Usui 1972).

Conventional Desliming: The electrostatic nature of slime coating phenomena was illustrated in the roles that different mineralogical components play in the flotation separation of oxidized iron ores (Iwasaki et al. 1962a). The effect of slimes is well illustrated in Figure 3. 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 goethite slimes coat the particles and prevent the attachment of air bubbles to quartz surfaces. In the anionic flotation of goethite, goethite slimes are the reagent consuming species, but they do not interfere with the flotation so long as sufficient anionic collector is added. In this case, negatively-charged quartz and particularly clay slimes coat the positively-charged goethite surfaces 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.

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 sodium silicate as dispersants. In pilot and commercial

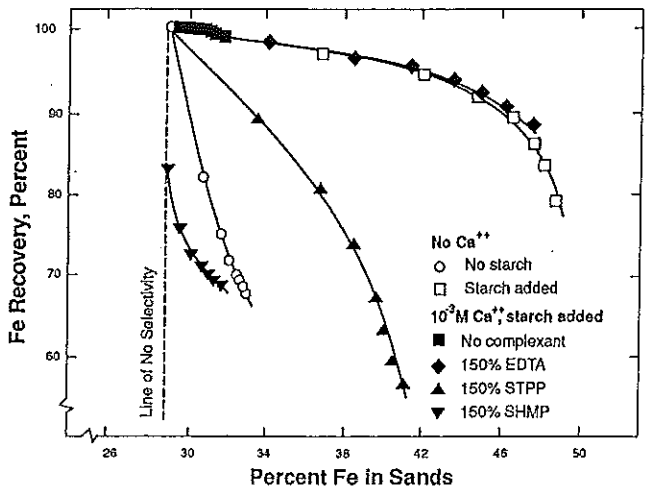

Figure 4. Selective desliming results on an artificial mixture of goethite and quartz at pH 11 (Heerema et al. 1982)

plants, hydrocyclones are used for desliming at 5 to 20 μm. Normally, dispersants are not required. Besides slime coating and reagent consumption, fine particles are known to cause problems in flotation by entrainment and slower flotation.

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 (Colombo 1980). The selective flocculation is brought about by the use of a proper combination of a dispersant and a starch flocculant. The deslimed products are further upgraded by cationic flotation of the remaining siliceous gangue. The process has been in commercial operation on a Michigan hematitic ore (Villar & Dawe 1975).

To achieve the full benefit of selective flocculation, ground pulps must be properly dispersed prior to the addition of a starch flocculant. The optimum conditions, however, are quite sensitive to the mineralogical characteristics of the ore and the types and amounts of soluble salts in pulp solutions. Figure 4 shows the results of selective desliming tests on an equal weight mixture of goethite and quartz, plotted as grade-recovery curves (Heerema et al. 1982). The vertical line drawn at the head grade of 28.5% Fe represents no selectivity of separation, corresponding to the conventional desliming on a fully dispersed pulp. In the absence of Ca^{++}, an addition of corn starch shows high selectivity of separation. In the presence of Ca^{++}, however, the pulps are totally flocculated with or without starch addition, and very little slimes are removed. Therefore, the control of the calcium ion is the key to a successful selective flocculation of iron ores.

Calcium ion may be deactivated in several ways. When calcium ion is fully complexed with EDTA, the selectivity of separation is restored. STPP is only partially effective, while SHMP indiscriminately disperses the pulp and is totally ineffective. It is evident that selective flocculation is quite sensitive to the nature of calcium compounds formed with these complexing agents. The use of montmorillonite, with a large cation exchange capacity, or chemical precipitation with, say, a carbonate salt, in conjunction with ultrasonic treatment, are reported to show considerable promise in controlling Ca^{++} in pulp solutions (Arol & Iwasaki 1987, Manukonda & Iwasaki 1987).

As briefly reviewed here, the electrical double-layer theory is applicable to clarifying the seemingly complex flotation behaviors of iron ore minerals with respect to the selectivity of collector action, the effect of soluble salts, and the effect of slimes. The theory is also useful in approaching the problems associated with flocculation and selective flocculation.

5 SILICA CONTROL OF MAGNETIC TACONITE CONCENTRATES

Currently, nine concentrator-pelletizing plants are in operation in the Lake Superior Region with a total annual pellet production capacity of 65 million tons. Four plants in Minnesota and two plants in Michigan practice cationic silica flotation of magnetic concentrates to lower the SiO_2 to about 4% for blast furnace use, except for a plant in Michigan which operates with a hematitic ore a part of the year.

5.1 *Mineralogical characteristics of magnetic taconite*

The feeds to the concentrators, magnetic taconite, consist in the order of abundance of quartz, silicates, magnetite, siderite and other carbonates and hematite (Gruner 1946). It analyzes about 30%Fe with about 75% of the iron in the form of magnetite and the remainder largely as iron carbonate and iron silicate minerals including: minnesotaite

$Fe_3Si_4O_{10}(OH)_2$

stilpnomelane

$(K,Na,Ca)_{0\sim1}(Fe,Mg,Al)_{7\sim8}Si_8O_{23\sim24}\cdot2\sim4H_2O$

and greenalite

$Fe_6Si_4O_{10}(OH)_8$.

Cummingtonite $(Fe,Mg)_7Si_8O_{22}(OH)_2$ occurs only in the eastern part of the Mesabi Range, resulting from the action of the gabbro intrusion. Except for SiO_2, magnetic taconite is essentially free of such impurities as P, S, Cu, Ti and V.

Magnetic taconite, in general, is quite fine grained and even when it is ground typically to 80% -44μm (325 mesh), siliceous gangue is not fully liberated. When magnetic concentrates are screened into different size fractions and analyzed for SiO_2, the size fractions coarser than 52 μm (270 mesh) become progressively higher in SiO_2, and over 50% of the SiO_2 is in the +52μm (270 mesh) fractions as middlings in about 10% by weight of the material. Sizing with a cyclone tends to force large and light siliceous gangue particles to go to overflow due to fine magnetite particles acting as heavy media within the cyclone. Microscopic observations indicate that if 5 to 10% by volume of magnetite is present in siliceous gangue particles, they are picked up by magnetic separators, and repeated cleaning will not remove them.

There are two ways to remove these locked siliceous gangue particles, namely, fine screening and cationic flotation.

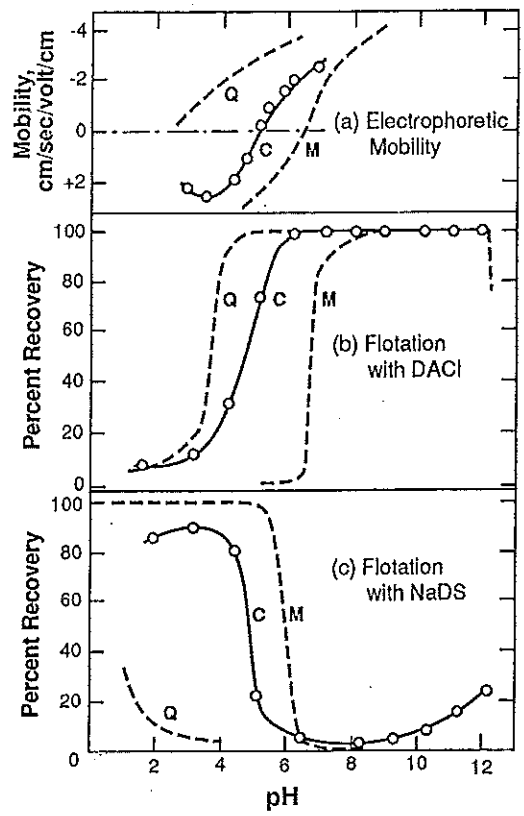

Figure 5. a) Electrophoretic mobilities of magnetite(M), cummingtonite(C), and quartz(Q) as a function of pH. b) Flotation of magnetite, cummingtonite, and quartz with 10^{-4} M dedecylammonium chloride. c) Flotation of magnetite, cummingtonite, and quartz with 10^{-4} M sodium dodecylsulfate (Iwasaki et al. 1961)

5.2 *Fine screening*

About 30 years ago, stationary screens were developed for the fine screening of magnetic concentrates in industrial scale (Healy et al. 1967). With fine screens, however, blinding is a serious problem. In order to get around the blinding problem, a rapper was installed. When the rapper hits the screen, it works for a while, but gets blinded soon afterwards. Sandwich deck screens, consisting of two screen cloths of larger mesh sizes have been developed and are available to nominally 37 μm (400 mesh), and they can operate effectively on a commercial scale (Derrick et al. 1989). The separation is made by two wires of the top screen and two wires of the bottom screen, thereby the blinding is alleviated. Here, magnetite particles act as heavy media on the vibrating screen and encourage siliceous gangue particles to 'float' and report to the oversize, a feature diametrically opposite to hydrocyclones. In plant operations, fine screening precedes flotation.

5.3 *Cationic silica flotation*

A common interest among the concentrator operators is to reduce iron losses in cationic silica flotation. The iron losses appear to be related to silicate mineralogy, particle size distribution and plant water chemistry.

Silicate Mineralogy: Figure 5 shows the electrophoretic mobilities and flotation characteristics of quartz, cummingtonite and magnetite (Iwasaki et al. 1961). Their points-of-zero-charge (PZC) are seen to be located at pH near 2, 5 and 6.5, respectively. The intermediate behavior of cummingtonite suggests that there will be difficulty in achieving high selectivity of separation, either by insufficient removal of the siliceous gangue, or by excessive loss of iron units. A customary way to improve the selectivity of flotation separation in such a case is to use a depressant for making magnetite less floatable.

In the flotation of oxidized iron ores, starches and starch derivatives are used successfully as depressants for iron oxides. When these starch depressants were tested on magnetic taconite concentrates, however, they had virtually no effect on the selectivity of separation. Cursory flotation tests were performed on a magnetite-quartz mixture in the absence and presence of dextrin, and the

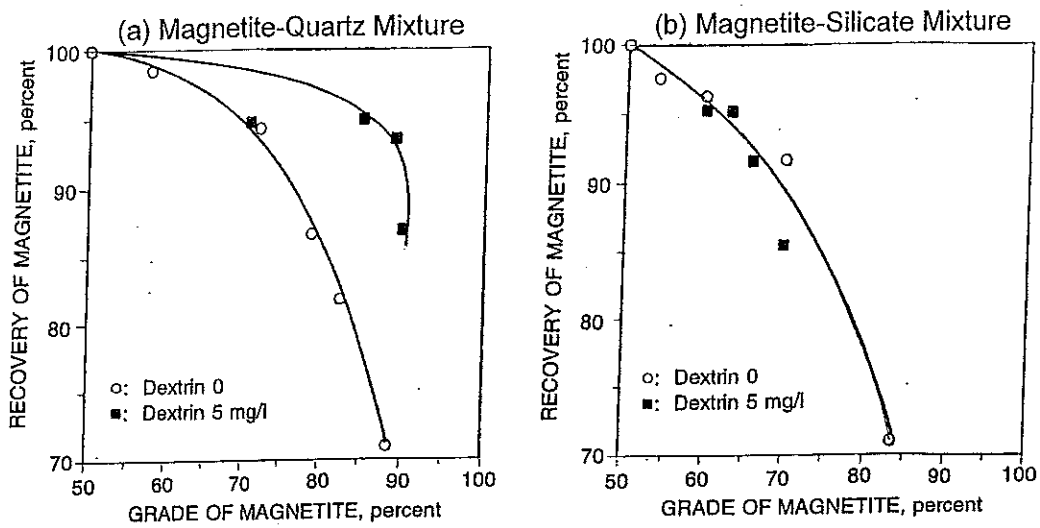

Figure 6. Grade-recovery curves showing the effect of dextrin on cationic silica flotation of magnetite-quartz and magnetite-silicate mixtures. (1:1 mixture, 200/270 mesh, pH 7)

results are plotted in Figure 6a as grade-recovery curves. A marked improvement in the selectivity of separation by the addition of dextrin is evident. This is to be expected since the three iron oxides, hematite, goethite and magnetite, have their PZCs within a narrow pH range of 6.5 to 6.7, and their flotation characteristics are reported to be quite similar (Iwasaki et al. 1962b). Similar tests performed on a mixture of magnetite and nonmagnetic minerals separated from taconite had virtually no effect on the selectivity of separation by the addition of dextrin, see Figure 6b. The nonmagnetic minerals consisted mainly of silicates. Apparently, the silicate minerals are depressed along with magnetite by dextrin.

An investigation was initiated on the use of chelating agents for iron ions, well known in analytical chemistry, as magnetite depressants. Some chelating agents are known to function as effective collectors or depressants in sulfide mineral flotation. Figure 7 shows that 8-quinolinol made the magnetite surface more negative, allowing it to float along with quartz, while 1,10-phenanthroline made the surface charge of magnetite reverse to positive and repelled the cationic collector, thereby helping the selectivity of separation (Dho & Iwasaki, 1996). Such an observation suggests that further research on chelating agents as a potential depressant may be promising. However, their costs and environmental effects become of concern.

Particle Size Distribution: On well-sized, slime-free particles, the selectivity of flotation separation from artificial mixtures may be related to the difference in their PZCs. In the processing of magnetic taconite, however, fine siliceous fractions in ground products are well liberated and removed by magnetic separation, while locked siliceous

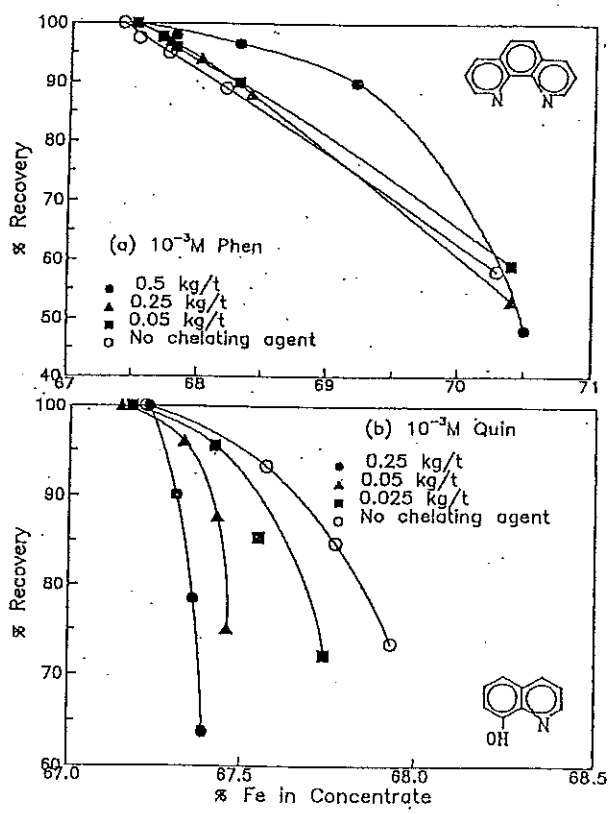

Figure 7. Effect of chelating agents on cationic silica flotation of magnetic taconite concentrates: a) 1, 10 phenanthroline, b) 8-quinolinol. (Dho & Iwasaki, 1996)

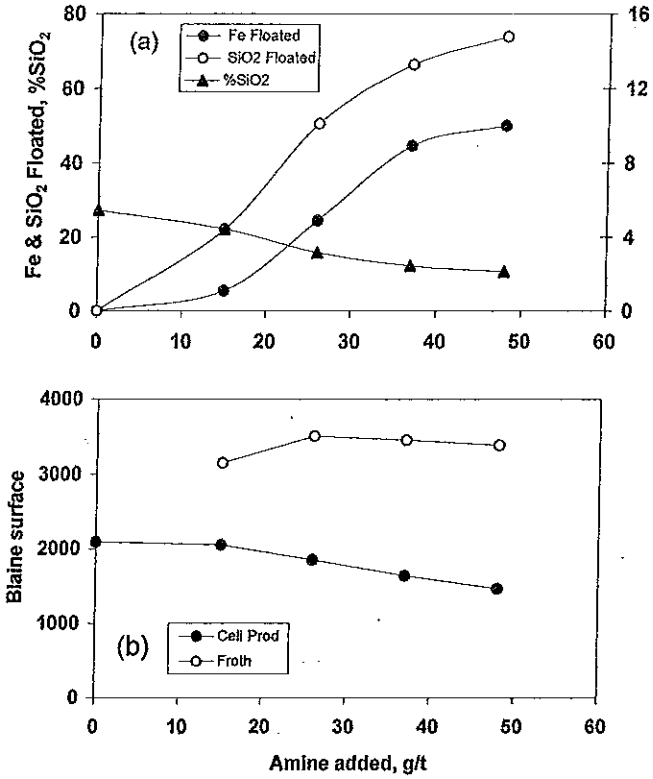

Figure 8. a) Iron and silica recoveries, and % SiO_2 in cell products in cationic silica flotation of a magnetic taconite as functions of amine addition. b) Blaine surface areas of froth and cell products as functions of amine addition.

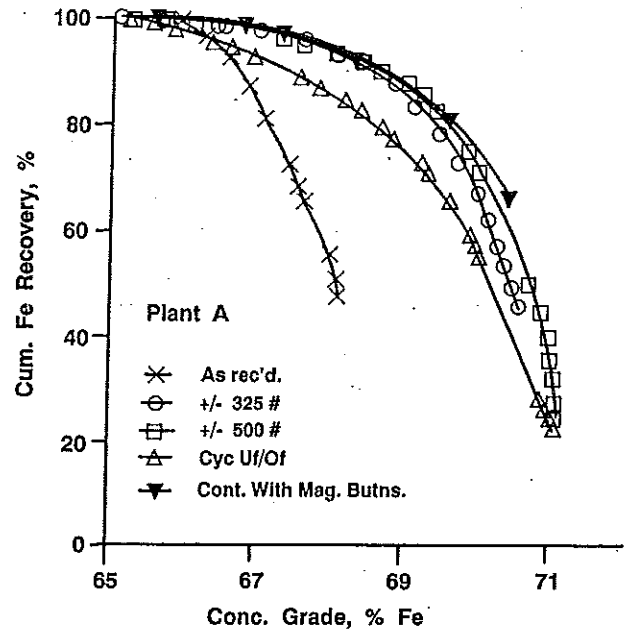

Figure 9. Grade-recovery curves of cationic silica flotation results on as received, screen undersize and oversize, and cyclone overflow and underflow samples of a magnetic taconite concentrate. Also included is a grade-recovery curve showing the effect of magnetic field on flotation results.

gangue fractions are concentrated in the coarse fraction. 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. Here, coarse gangue particles have the same floatabilities as fine magnetite particles, and attempts to remove siliceous gangue by increased addition of the collector lead to flotation of fine magnetite as well.

Figure 8a shows the flotation recoveries of SiO_2 and Fe into froths when an amine collector is added in stages of 15, 11, 11 and 11 g/ton (0.033, 0.025, 0.025 and 0.025 lb/lt). With increasing addition of the amine, SiO_2 is removed and the SiO_2 contents in cell products decrease from 5.5% to 2.1%, but Fe is also lost proportionately in the form of fine magnetite. Figure 8b shows the changes in Blaine surface areas of the froths and cell products. As more SiO_2 is removed, the Blaine surface areas of cell products decrease from 2000 to 1400. The Blaine surface areas of froths remain in the range of 3200 to 3500 indicating that fine magnetite particles are lost into froths along with siliceous gangue particles. This behavior becomes more critical when the siliceous gangue is in the form of ferromagnesian silicates with their PZCs between quartz and magnetite as in the case of cummingtonite.

One way to get around this problem is to size a concentrate into coarse and fine fractions, either with a screen or a hydrocyclone, and float them separately. The results obtained in this manner are plotted in Figure 9. Combination of the concentrates from the two flotation circuits shows higher grade concentrates than when an unsized sample is processed directly.

Yet another approach is to apply a magnetic field in a flotation cell to hold back magnetite particles. The results obtained in a laboratory flotation cell converted into a continuous flotation unit and using increasing amounts of an amine collector, are included in Figure 9. Fine magnetite particles are effectively depressed and the results are markedly improved, and, in fact, were even somewhat better than when a concentrate was pre-classified into coarse and fine fractions for flotation. The use of a magnetic field is inexpensive and environmentally sound. Further development of such a concept becomes of interest.

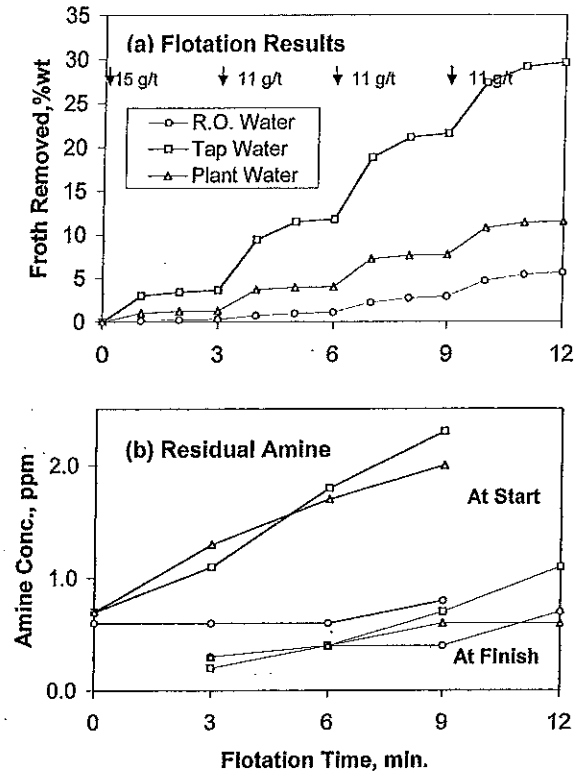

Figure 10. Weight recoveries of froth products from a magnetic taconite concentrate as functions of amine addition and flotation time.

Plant Water Chemistry: In many taconite plants, the process waters appear to be either at the solubility limit or even super-saturated with respect to Ca^{++} and HCO_3^- for $CaCO_3$ precipitation. In some plants, the waters are also super-saturated with respect to Ca^{++} and $SO_4^=$ for possible gypsum ($CaSO_4 \cdot 2H_2O$) formation. Production of fluxed pellets increases the concentrations of Ca^{++} and Mg^{++} in process waters due to the recycling of agglomerator return water.

Solutes in super-saturated solutions in the meta-stable region may not precipitate spontaneously in aqueous phase, but may nucleate at mineral surfaces and form precipitates on the surfaces. The precipitate coatings, like slime coatings, physically prevent air bubbles from establishing contacts with siliceous gangue surfaces, thereby adversely affecting their flotation recoveries.

In an attempt to test if the adverse effect of Ca^{++} may be alleviated by softening the process water, a comparison was made by performing flotation tests using reverse osmosis (R.O.) water, a tap water and a plant water (analyzing <0.01, 70 and 120 ppm Ca^{++}, respectively). The weight recoveries into froths as a function of flotation time when an amine collector was added in stages of 15, 11, 11 and 11

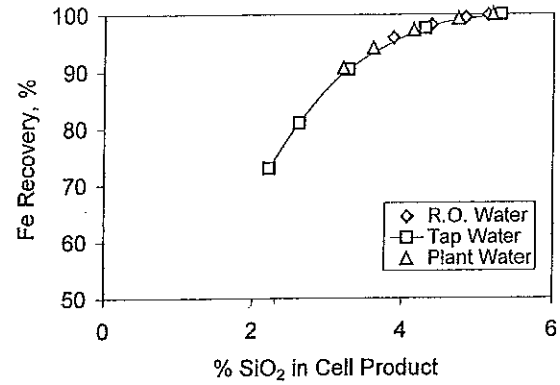

Figure 11. Grade-recovery curves of cationic silica flotation results using reverse osmosis water, tap water and plant water on a magnetic taconite concentrate.

g/ton (0.033, 0.025, 0.025 and 0.025 lb/lt), are plotted in Figure 10a. Contrary to the expectation, however, very little floated in R.O. water, good recoveries were obtained in the tap water, while the recoveries were notably less in the plant water. Residual amine concentrations in flotation pulp waters are shown in Figure 10b, which indicates that virtually all the amine was adsorbed in R.O. water, while a substantial amount of amine was left in the other two waters. When the test results were plotted as grade-recovery curves, as shown in Figure 11, the data points followed an identical curve indicating that the use of the three different types of waters simply affected the weight recoveries, but not the selectivity of separation.

These seemingly complex flotation behaviors may be reconciled if layered clay minerals are assumed to consume inordinately large amounts of amine collectors via cation exchange mechanism according to

$$\boxed{Ca^{++}, Mg^{++}, Na^{+}} + RNH_3^+ = \boxed{RNH_3^+} + Ca^{++}, Mg^{++}, Na^{+} \quad (1)$$

In waters free of inorganic ions, the cations within the layers will be replaced by RNH_3^+ and very little amine will be left in pulp solutions for the flotation of quartz and silicate minerals. The tap water had sufficiently high Ca^{++} ion concentration, thereby shifting the equilibrium to the left to have high enough RNH_3^+ concentration left in pulp solutions for flotation. In the plant water super-saturated with Ca^{++} and HCO_3^- and/or $SO_4^=$, surface precipitation of $CaCO_3$ and/or $CaSO_4 \cdot 2H_2O$ adversely affected the flotation recoveries.

Taconites from the east end to the west end of the Mesabi Range differ appreciably in their silicate mineralogy. It becomes of interest to identify and estimate the amount of amine-consuming layered

clay minerals at each mine location that will remain in flotation feeds after magnetic separation, and establish the roles played by Ca^{++} and Mg^{++} ions in affecting the amine adsorption as well as in causing the surface precipitation. The use of blinding agents that retard the exchange reaction of amine collectors with the alkaline earth ions, becomes of interest.

6 SUMMARY

In order for the iron ore industry of the USA to remain competitive with high-grade overseas sources, it is important to ensure a supply of uniform- and high-quality products for the Nation's blast furnaces and for direct reduction processes. Current interest centers on the cationic silica flotation of magnetic concentrates in which the selectivity of separation can be improved, particularly in the presence of ferromagnesian silicate minerals, while protecting the environment.

While the surface chemistry plays a fundamental role in the selection of a proper combination of reagents, attention should also be paid to the engineering aspects, such as flotation machine type, design and operation, pre-classification of flotation feed and application of magnetic field in flotation cells.

7 REFERENCES

Aplan, F.F., & D.W.Fuerstenau 1962. Principles of Nonmetallic Mineral Flotation.In D.W.Fuerstenau (ed), *Froth Flotation:* 170-214. New York: AIME.

Arol, A.I., & I.Iwasaki 1987. Control of Montmorillonite via Complexation and Ultrasonics in the selective Flocculation of Iron Ores. *Miner. Metall. Process.*, 4: 82-87.

Clark, S.W., & S.R.B.Cooke 1968. Adsorption of Calcium, Magnesium, and Sodium Ion by Quartz. *Trans. SME-AIME*, 241:334-341.

Colombo, A.F. 1986. Concentration of Iron Oxides by Selective Flocculation-Flotation. P.Somasundaran (ed), *Advances in Mineral Processing:* 695-713. Littleton, Colorado: SME.

Derrick, H.W., J.E.Wennen & W.J.Nordstrom 1989. Applications of Fine Screens in Taconite Ore Concentration. *Proceedings of the 62nd Annual Meeting of the Minnesota Section AIME and 50th Annual Mining Symposium*, University of Minnesota-Duluth.

Dho, H., & I.Iwasaki 1996. Chelating Modifiers in the Cationic Silica Flotation of Magnetic Taconite Concentrates. *Miner. Metall. Process.* 13:65-68.

Fuerstenau, D.W. 1970. Interfacial Processes in Mineral/Water Systems, *Pure and Applied Chemistry*. 24:135-164.

Fuerstenau, D.W., & M.C.Fuerstenau 1982. The Flotation of Oxide and Silicate Minerals. In R.P.King (ed), *Principles of Flotation:*, 109-158. Johannesburg: S. Afr. Inst. Min. Metall.

Fuerstenau, M.C., & B.R.Palmer 1976. Anionic Flotation of Oxides and Silicates. In M.C.Fuerstenau (ed), *Flotation, A.M.Gaudin Memorial Volume*: 148-196. New York: AIME

Gruner J.W. 1946. *Mineralogy and Geology of the Mesabi Range*. St. Paul, Minnesota: Iron Range Resources and Rehabilitation.

Healy, J.H., A.J.Carlson, M.L.Hovland & G.M. Marincel 1967. Erie Mining Company Patents New Method for Screening Ores in Very Fine Size Range. *Mining Eng.* 19: 4: 65-70.

Heerema, R.H., & I.Iwasaki 1980. Chemical Precipitation of Alkaline Earth Cations and its Effect on the Flotation and Flocculation of Quartz. *Trans. SME-AIME*, 268:1510-1516.

Heerema, R.H., R.J.Lipp & I.Iwasaki 1982. Complexation of Calcium Ion in Selective Flocculation of Iron Ores. *Trans. SME-AIME*. 272: 1879-1884.

Hogg, R., T.W.Healy & D.W.Fuerstenau 1966. Mutual Coagulation of Colloidal Dispersions. *Trans. Faraday Soc.*, 62:1638-1651.

Houot, R. 1983. Beneficiation of Iron Ore by Flotation. *Intern. J. Miner. Process.* 10: 183-204.

Iwasaki, I. 1983. Iron Ore Flotation, Theory and Practice. *Mining Eng.* 35: 622-632.

Iwasaki, I. 1989. Bridging Theory and Practice in Iron Ore Flotation. In S.Chander & R.R.Klimpel (eds), *Advances in Coal and Mineral Processing Using Flotation:* 177-190. Littleton, Colorado: SME.

Iwasaki, I., S.R.B.Cooke, & H.S.Choi 1961. Flotation of Cummingtonite. *Trans. SME-AIME*. 220: 394-395.

Iwasaki, I., S.R.B.Cooke, D.H.Harraway & H.S.Choi 1962a. Iron Wash Ore Slimes---Some Mineralogical and Flotation Characteristics. *Trans. SME-AIME*, 223:97-108.

Iwasaki, I., S.R.B.Cooke & Y.S.Kim 1962b. Some Surface Properties and Flotation Characteristics of Magnetite. *Trans. SME-AIME.* 223: 113-120.

Iwasaki, I., K.A.Smith, A.S. Malicsi & H.Sato 1980. Effect of Calcium and Magnesium Ions on Selective Desliming and Cationic Flotation of Quartz from Iron Ores. In P.Somasundaran(ed), *Proceedings of the International Symposium on Fine Particle Processing, Las Vegas, Nevada:* 1057-1082. Littleton, Colorado: SME.

Manukonda, V.R. & I.Iwasaki 1987. Control of Calcium Ion via Chemical Precipitation-Ultrasonic Treatment in Selective Flocculation. *Miner. Metall. Process.* 4: 216-222.

Nummela, W. & I.Iwasaki 1986. Iron Ore Flotation. In P.Somasundaran (ed), *Advances in Mineral Processing:* 308-342. Littleton, Colorado: SME.

Smith, R.W., & S.Akhtar 1976. Cationic Flotation of Oxides and Silicates. Flotation, A.M. Gaudin Memorial Symposium, In M.C.Fuerstenau (ed), *Advances in Mineral Processing*: 87-116. New York: SME.

Usui, S. 1972. Heterocoagulation. In J.F.Danielli, M.D.Rosenberg & D.A.Cadenhead (eds), *Progress in Surface and Membrane Science, Vol. 5:* 223-266. New York: Academic Press.,

Uwadiale, G.G.O.O. 1992. Flotation of Iron Oxides and Quartz---A Review. *Miner. Process. Extr. Metall. Rev.* 11:129-161.

Villar, J.W., & G.A.Dawe 1975. The Tilden Mine---A New Processing Technique for Iron Ore. *Mining Congress J.*, 61:40-48.