Iron Ore Flotation—1969[1]

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Abstract

Current flotation practice in the iron ore industry is reviewed with special attention given to gains made since the 1966 AOCS meeting. Known applications are described with estimates of tonnage treated, the degree of beneficiation achieved, and the quantity and types of reagents used. Apparent trends and prospects for new applications of flotation in the iron ore industry are discussed.

Introduction

The primary intention of this paper is to show the magnitude of the market for flotation chemicals in the iron ore industry by examining current practices and the potential for additional growth.

Statistical information on flotation practice was obtained from the major iron ore producers. Such basic information was obtained readily, although various company policies stipulated that their organization should not be identified, or that they should not be placed in a position of endorsing any reagent by brand name. Because of its competitive value, information on the prospects for future flotation application could not be obtained directly, and the projections presented here are my own.

At the 1966 AOCS Annual Meeting, the author presented a paper entitled "Iron Ore Flotation: Practice, Problems and Prospects" in which the then current status of iron ore flotation was reviewed. The present paper provides a somewhat different perspective, while at the same time updates the statistics.

Basics, Iron Ore Flotation

Iron ore flotation is generally concerned with the separation of the iron oxide minerals from those containing silica. Iron minerals often occur with titanium, phosphorus, sulfur and alkaline earth minerals; however, for simplicity, this discussion is limited primarily to the siliceous ores. For these ores the flotation method employed may be that which recovers iron minerals in the froth (direct flotation), or, alternatively, that by which the siliceous gangue is contained in the froth product (reverse flotation).

Flotation of any ore requires that certain physical conditions be met; one minimal condition is grinding the ore to about minus 65 mesh. Actually, finer grinding is often necessary to achieve adequate mineral liberation. Coarse particles are not effectively floated because the air bubbles to which they must become attached do not impart sufficient buoyancy. On the opposite end of the size scale, extremely fine particles (slime) are equally reluctant to float, but for various other reasons, less well defined than those for the coarser sizes.

After grinding, the ore is slurried with water and conditioned with reagents to provide selectively coated hydrophobic surfaces on one of the mineral species. Upon introduction of air, these reagent-coated minerals attach themselves to air bubbles, rise to the surface, and are subsequently removed from the system. The reagent suite employed may be simple or complex depending upon the demands of the system, but basically the reagents accomplish two purposes, collection and collection modulation.

Because collectors are the most important reagents in any flotation system, it is worthwhile to list some of their properties and other desirable features. The two main classes of nonsulfide collectors (1) are as follows: (a) Anionic. Organic acids containing a hydrocarbon group, and/or the ammonium, potassium, or sodium salts of these acids. In iron ore flotation the important reagents in this group would include the straight chain fatty acids and soaps, and the alkyl aryl sulfonates. Naphthenic acids and their soaps also fall into this category but have not been extensively used because of limited availability. (b) Cationic. Organic bases containing a hydrocarbon group, and the salts of these bases, usually chlorides or acetates. This group includes the primary aliphatic amines, diamines, quaternary ammonium salts and the newer beta-amine and ether amine products. These reagents are generally used to float siliceous minerals.

Both classes of collectors consist of hydrocarbon chains attached to a charged polar group, are ionizable, and are at least partially miscible or soluble in water. At an air-water interface, the polar end of the compound, being water soluble, is oriented toward the water phase and the nonpolar hydrocarbon end toward the air phase. Attraction between polar groupings of the reagent and polar mineral surfaces results in adsorption, leaving the long chain nonpolar hydrocarbon end oriented away from the mineral surface. Bubble attachment occurs at the nonpolar segment of the collector ion, thereby completing the mechanism by which the mineral particle is rafted to the surface of the pulp.

In iron ore flotation we are dealing with oxide systems (2,3) and a knowledge of the condition of the mineral surfaces is essential to an understanding of the flotation process. Both silica and iron oxides acquire a surface charge in aqueous environments through acquisition of hydroxide or hydronium ions at the fractured bond sites, with the sign and magnitude of the charge being dependent on the pH of the system. For example, at about pH 2, silica is electroneutral; at a lower pH, silica surfaces exhibit a net positive charge, and above pH 2, the silica surface carries a net negative charge. Similarly, iron oxides accumulate a net excess of either positive or negative surface charges, with the obtained condition again being dependent on the pH. A pH of about 7 is usually reported as the point at which electroneutrality occurs at the various iron oxide surfaces (4).

The fact that the mineral surfaces are subject to a varying surface charge influences the pH at which flotation is performed through the choice of the collector. Anionic collectors are the logical choice when the pH of the system is such that the mineral to be collected bears a net positive charge; cationic collectors are selected when the opposite condition of surface charge prevails. However, it should also be noted that these observations pertain to an ideal system, and that in treating ores as opposed to purified minerals, actual conditions may produce a deviation from the expected behavior.

Various inorganic anions and cations may be re-

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TABLE I

Cationic Flotation of Silica From Magnetic Concentrates: Estimates for 1969

Location	Annual production[a]	Consumption of collector, lb/yr	Consumption of frother, lb/yr
Ontario	1,600,000	170,000	85,000
Ontario	1,150,000	52,000	34,500
Ontario	1,200,000	175,000	80,000
Ontario	650,000	19,500	39,000
Michigan	3,850,000	71,500	95,600
Missouri	1,500	3,000	None
Total	8,451,500	491,000	334,100

[a] Long tons of concentrate.

TABLE II

Cationic Flotation, Nonmagnetic Ores: Estimated for 1969

Location	Annual production[a]	Mineral floated	Reagents, lb/yr collector
Missouri	163,000	Hematite	75,000[b]
Liberia	2,000,000	Silica	250,000
Total	2,163,000		325,000

[a] Long tons of concentrates.
[b] Other reagents, lb/yr: H_2SO_4, 413,000; NaF · HF, 108,000.

leased from the ore or be present in the water, and these ions may be closely adsorbed by mineral surfaces in a manner such as to influence the magnitude and sign of the effective surface charge (5,6). For example, it is an established fact that clean, negatively charged quartz cannot be floated with fatty acid collectors. However, in the presence of calcium ion at pH 10 to 12, effective flotation of quartz does occur with fatty acids, and much of our research at the Bureau of Mines had taken advantage of this phenomenon (7,8).

In the flotation of iron ores, certain fatty acids and alkyl aryl sulfonates are effective anionic collectors. The fatty acids used are generally mixtures of oleic, linoleic, linolenic and rosin acids. These fatty-acid mixtures are usually obtained as by-products of the wood pulp industries because of lower costs. Structurally, the major constituents of commercial fatty acids contain 18 carbon atoms in an aliphatic chain, which have one or more carbon-carbon double bonds. The common unsaturated fatty acids are liquid at room temperatures, a factor which facilitates their use.

In the flotation of iron minerals, fatty acids are best employed in a pH range near that giving electroneutrality of the iron surfaces. Below a pH of about 5.5, the fatty acid remains undissociated, so that the effective pH range that can be employed is quite narrow. However, anionic sulfonate collectors may be used in the lower pH ranges where fatty acids are ineffective.

Cationic collectors find their greatest utility in flotation of the siliceous constituents. In some instances they are effective at the natural pH of the ore which is usually around 7 to 8. In other instances, pH regulation to 9 or 10 has been found to be advisable. The cationic collectors are normally used in a neutralized form, and in systems of a pH 10 or above, the neutralized salts may revert to the less effective free amines.

In some applications, fuel oil seems to increase collector effectiveness and for this reason can be considered as an extender. Frothers are also important in flotation systems; these may be added separately, but with the type of collectors we have been discussing, the collectors themselves often have ample frothing power.

Frothers and collectors are directly involved in the collection mechanism. Collection-modulation is achieved through use of pH regulators, activators, depressing agents and dispersants. Depressing agents and dispersants may include sodium silicate, soluble phosphates, wood and vegetable extracts, starches and cellulosic products, fluorides, and many other compounds and materials that have been found to be beneficial on occasion. When effective, these reagents increase selectivity, but the exact manner in which they achieve this result is at best poorly understood. Some of the mechanisms proposed to explain their effect includes the complexing of activating ions, prevention of slime coatings, blocking of surfaces, repression of surface ionization, and reverse conditioning. In any event, their utility is determined by empirical testing.

Current Practice

Iron ore flotation practice may be categorized in several different ways, as shown by the following examples: (a) by collector type, i.e., anionic or cationic; (b) by direct or indirect (reverse) flotation, depending on whether the iron minerals or the gangue constituents are made to report in the froth; and (c) by predominant iron mineral type, which in most instances would result in classifying the ore body as being either magnetic or nonmagnetic. Ore bodies containing magnetite are susceptible to primary concentration on magnetic separators. The nonmagnetic ore bodies contain hematite, martite and goethite, usually in varying proportions. An evaluation of current practice shows that cationic flotation predominates in the treatment of magnetic ores, and that anionic flotation is the most common flotation method applied to nonmagnetic ores.

Although not included in this presentation, there is some production of by-product iron ore derived from flotation and oxidation of pyrites from base-metal sulfide deposits. Additionally, several iron ore producers recover pyrite as a by-product from their ores, using flotation methods. However, such practice may be categorized as sulfide flotation rather than iron ore flotation, and, from a viewpoint of reagent use, it consumes only a small portion of the total of xanthates and similar type collectors.

Since 1966, there has been a substantial increase in the number of installations employing cationic flotation. Most of these plants treat a magnetic taconite-type of ore by magnetic separation, with further improvements in concentrate quality being obtained by flotation of silica from the magnetic concentrates. The amount of silica removed by flotation varies, but generally accomplishes a reduction of 2 to 5 percentage points in silica content of the magnetic concentrate. Recovery of iron from feed entering the flotation process is usually above 95%. These applications are tabulated (Table I) to give estimated tonnages of final product and consumption of reagents.

In addition to cationic flotation of silica from magnetic concentrates, two installations are employing cationic flotation to upgrade hematitic feeds. At the Missouri location cited in Table II, a tailing from magnetic separation is first serially floated to remove sulfides and apatite. The remaining hematitic-silicious residue is then conditioned with reagents so as to favor the flotation of iron minerals with a cationic collector. This application is unique in present day iron ore flotation practices and is a radical departure from the fatty acid flotation formerly employed. Apparently,

TABLE III

Anionic Flotation of Iron Oxides: Nonmagnetic Ores

Location	Annual production[a]	Reagents, lb/yr[b]		
		Fatty acid	Petroleum sulfonate	Frother
Michigan	2,140,000	1,960,000	4,930,000	....
Michigan	3,850,000	9,500,000	....	46,500
Michigan	960,000	4,000,000	....	63,000
Other	4,000	273,000[c]	....	37,000[d]
Total	6,954,000	15,733,000	4,930,000	146,000

[a] Long tons of concentrate.

[b] Also includes the following totals, lb/yr: H_2SO_4, 12,600,000; NaF, 15,000; Fuel oil No. 2, 8,700,000; Sodium silicates, 3,270,000.

[c] Includes almost 241,000 lb. of distilled tall oil (70% fatty acid) used to remove apatite from iron-bearing feeds at Missouri location.

[d] Used with 104,700 lb. of Pot. amyl xanthate to remove pyrite prior to recovery of hematite.

in this instance, the former use of fatty acids to float the hematite adversely affected the quality of pellets made from the hematite concentrates.

At the Liberian location, hematitic fines from a washing and screening plant are subjected to cationic silica flotation to reduce the silica content below 5%. With the consumption of cationic collector estimated at 250,000 lb/yr, this operation is presently the largest single user of this reagent in the iron ore industry.

From data in Tables I and II, it can be seen that about 816,000 lb. of cationic collectors are expected to be consumed by the iron ore industry during 1969. However, this total is at best a tenuous estimate, since parts of the projected consumption may represent temporary conditions, the correction of which may result in either increased or decreased consumption.

It is also interesting that of the total of cationic collectors used in the iron ore industry, the overwhelming preponderance comes from a single supplier. Thus, most of the collector use is from a class of ether amines, one of which is described as N-tridecoxy-N-propyl-1,3-diamine monoacetate (9) and the other is a mixture of somewhat related compounds. The success of these reagents may be attributed to (a) their high selectivity for silica, thereby obviating the need for iron depressants; (b) their low cost and related cost-effectiveness; and (c) handling advantages due to their liquid properties as acetate salts. However, the iron ore industry is continually examining new reagents as a means of improving present operations, which means that the favorite reagent of today would be readily replaced if some better alternative should be forthcoming.

Table I also shows that approximately 334,000 lb/yr of frother are consumed in the cationic flotation of silica. In the majority of instances the frother is methyl isobutyl carbinol (MIBC), although some pine oil, higher alcohol and synthetic water-soluble types are also being used.

The first commercial applications of flotation in the iron ore industry were to the hematitic jaspers of the Marquette range. The ores are of the nonmagnetic type, and the anionic method for flotation of iron minerals is used (10). Table III shows that Michigan continues to be the focal point of flotation applications to ores of this type and that the anionic method for flotation of iron minerals continues as the preferred mode for the flotation processing of nonmagnetic ores. Annual collector consumption amounts to over 15,700,000 lb. of fatty acids, and to almost 5,000,000 lb. of water-soluble petroleum sulfonates. To these totals must be added a sizable quantity of various modulating agents and also 146,500 lb. of frother of the various types previously described.

TABLE IV

Summation of Estimated Reagent Consumption and Values

Reagent	Pounds per year	Estimated unit costs, dollars	Estimated total value
Cationic collectors (all types)	816,000	0.38	310,000
Fatty acids	15,733,000	.08	1,258,600
Petroleum sulfonate	4,930,000	.05	246,500
Frothers, all types	480,600	.15	72,000
Fuel oil	8,750,000	.016	140,000
H_2SO_4	13,000,000	.016	280,000
Sodium silicates	3,300,000	.018	59,400
NaF	15,000	.16	2,400
NaF · HF	108,000	.21	22,680
Total	....	....	2,319,580

The fatty acids used in these applications are supplied by a number of different manufacturers and generally fit the following description: (a) byproducts of the paper-pulp industry, i.e., tall oil based fatty acids; (b) contain 5% to 7% rosin acids and 4% to 5% unsaponfiables; (c) balance of fatty acid content composed of approximately equal amounts of oleic and linoleic acids; (d) average iodine and acid values of approximately 130 and 190, respectively.

Table IV summarizes the total reagent consumption for all of the types of flotation listed but excludes sulfide collectors, or reagents for such purposes as flocculation, or water reclamation.

On this basis, the estimated total of 17,570,000 tons of iron ore receiving some form of flotation treatment requires an expenditure of approximately $2,320,000 for reagents. Of these total costs, $1,887,000 are allocated to collectors and frothers.

Projections

By scanning the list of taconite producers whose concentrates contain more than 5% silica, plus the potential production from new properties, it could be predicted that a doubling of the 17,570,000 tons of concentrates presently receiving flotation treatment could be attained within the next five years. However, such predictions could not be made with certainty. It is apparent that many of these same producers are investigating the flotation process, but it is equally apparent that they are in no great rush to install flotation in their present operations.

Since taconite plants are usually built only after reaching a long-term agreement between producer and consumer with respect to quality of the product, it would appear that the older producing units are not experiencing the same competitive crunch as are those more recently activated. Many of these newer plants must assure their customers of a product containing less than 5% SiO_2, and flotation processing gives them the flexibility to meet these goals. These newer plants are often designed with thought given to introducing flotation as needed for quality control.

Alternate processes, such as fine screening, magnetic roasting, high intensity magnetic separation and direct reduction continue to be considered along with flotation as a means either of primary concentration or of upgrading the primary concentrates. Further, a body of informed opinion considers that the super-carrier may be able to deliver very high grade ore and concentrates from overseas to consumers in the United States at a price cheaper than the comparable product can be produced domestically. Any tonnage of such imports would correspondingly reduce the need for flotation applications on the North American continent.

Nevertheless, the author is optimistic in expecting that flotation application in the iron ore industry will follow the recent trend and show a modest increase during the next five years. One application which possibly has potential is in the production of superconcentrates containing less than 2% silica from present concentrates containing about 5% SiO_2. These superconcentrates would then be pelletized, prereduced, and utilized in a local market for production of electric furnace steel. Several existing operations are favorably located and are presently producing a product that could be converted to superconcentrates by intensive use of flotation. As an example of such an application, The Meramec Mining Co. produces 1500 tons/yr of Supermagnetite. However, the supermagnetite is not used for steelmaking, but instead is used in the manufacture of components for the electronics industry. Because of the favorable mineralogical characteristics of the deposit, it is possible to produce the Supermagnetite with a guaranteed analysis of less than 0.25% SiO_2.

REFERENCES

1. Sutherland, K. L., and I. W. Wark, "Principles of Flotation," Australian Institute of Mining and Metallurgy, Melbourne, Australia, 1955, p. 68–77.
2. Gaudin, A. M., and D. W. Fuerstenau. Trans. Amer. Inst. Min. Metal. Eng., SME *202*, 66–72 (1955).
3. Parks, G. A., and P. L. de Bruyn, J. Phys. Chem. *66*, 967–973 (1962).
4. Parks, G. A., Chem. Rev. *65*, 177 (1965).
5. Parks, G. A., and P. L. de Bruyn, J. Phys. Chem. *66*, 967–973 (1962).
6. Sennet, P., and J. P. Oliver, Ind. Eng. Chem. *57*, 33–50 (1965).
7. Colombo, A. F., R. T. Sorensen and D. F. Frommer, Trans. Amer. Inst. Min. Metal. Eng., SME *232*, 100–109 (1965).
8. Frommer, D. W., M. M. Fine and L. Bonicatto, BuMines Rept. of Inv. 6399 (1964).
9. Cronberg, A. D., and T. H. Lentz, SME, Preprint 68-B-340, Amer. Inst. Min. Metal. Eng., 1968.
10. Erck, L. J., Quart. Colo. Sch. Mines *56*, 387–416 (1961).

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