Iron Ore Flotation: Practice, Problems, and Prospects[1]

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Abstract

The significant applications of iron ore flotation are reviewed along with an abbreviated discussion on theory and reagent use. Problems or conditions which have militated against a widespread adoption of the flotation process by the iron ore industry, are discussed in contextual relationship to supply, economics, alternatives, and process limitations. Prospects for increased use of secondary flotation are shown to be excellent, but to be less certain for primary flotation.

Introduction

IRON ORE FLOTATION is a subject intriguing to many investigators, past and present. Speaking facetiously for a moment, investigations have been so numerous and extensive that the weight of the research papers engendered has almost equaled the weight of the flotation concentrates. This unfavorable balance persisted until about 12 years ago when the first commercial iron ore flotation plant became a reality, thereby yielding the first tangible benefits from over 25 years of industry and government research. Presently, over 5 million tons of iron ore concentrates annually receive some form of flotation treatment, but this amount is still only a small percentage of total production. It would seem, then, that the iron ore industry is a reluctant participant in a process that has found widespread application in other segments of the mineral industry.

Practice

As could be inferred from the introductory statement, commercial practice of iron ore flotation is quite limited. Therefore, we propose to define terminology, discuss the theoretical and functional aspects of iron ore flotation as oriented towards reagent applications, and evaluate the existing plants in the context of this background material.

Iron ore flotation processes generally are concerned with the isolation of the iron oxide minerals from those containing silica. While it is recognized that iron minerals often occur with titanium, phosphorus, sulfur, and the alkaline earth mineral constituents, for simplicity, this discussion is limited primarily to the siliceous ores. Within these limitations, the flotation method may be employed that recovers iron minerals in the froth (direct flotation), or alternatively, the method by which the siliceous gange is contained in the froth product (reverse flotation) may be used.

Flotation of any ore requires that certain physical conditions be met, such as grinding to about −65 mesh as a minimum. Actually, finer grinding is often necessary to achieve adequate mineral liberation. Extremely 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 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 reagents accomplish two purposes—collection and collection modulation.

As collectors are the most important reagents in any flotation system, it is worthwhile to list some of their properties and other desirable features. The main classes of collectors (15) are:

1) *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. Napthenic acids and their soaps also fall into this category, but have not been extensively used because of limited availability.

2) *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 amine salts, and the newer beta-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, they 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 (7,12) 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 hydrogen 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 (11).

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

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the pH of the system is such that the mineral to be collected bears a net positive charge and cationic collectors 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, conditions may produce a deviation from the expected behavior. Various inorganic anions and cations may be released from the ore or be present in the water, and these ions may be closely absorbed by mineral surfaces in a manner such as to influence the magnitude and sign of the effective surface charge (7,14). 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 has taken advantage of this phenomenon (1,4,5).

In the flotation of iron ores, experience has shown that certain fatty acids and alkyl aryl sulfonates are effective anionic collectors. The fatty acids used are generally mixtures of oleic, linoleic, linolenic, and resin 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 the commercial fatty acids contain 18-carbon atoms in a chain-type hydrocarbon radical, 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 effectively employed in a pH range near that giving electroneutrality of the iron surfaces. Below a pH of about 5.5, the fatty acid hydrolyzes 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. The last two named 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 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.

Flotation may be a primary method of concentration. Examples of such application are in practice at the Republic and Humboldt plants (3) on the Marquette range of Michigan. These plants, which were also the first commercial examples of iron ore flotation, utilize an ore body containing 30% iron. The ore is a cherty, specular hematite with some chlorite and sericite. Adequate liberation is obtained by grinding to −65 to −100 mesh. After light desliming the minerals are reagentized with 1.25 to 2.0 lb of fatty acid per ton of feed, floated, and the rougher froth subjected to several cleaning stages. This simple procedure gives a concentrate containing 63% Fe and about 8% SiO_2. Recently, an innovation, which consists of regrinding the concentrate, heating the pulp to near boiling, and then refloating, has been employed at the Republic mill. This procedure has permitted the production of concentrates containing about 66% Fe and 4% SiO_2.

Both the Humboldt and Republic mills are using direct, anionic flotation of iron minerals, and the usual practice at these sites is to add only the one reagent—the fatty acid collector. Natural conditions are such that no pH regulators, activators, or depressants need to be added.

In the Marquette range there is also an example of what will be referred to as secondary flotation. At the Empire site, primary concentration of a magnetite ore body is being achieved with magnetic separators (2). The final magnetic concentrate is deslimed to give a product containing about 64% iron. This product is next subjected to amine flotation to raise the grade to about 66% iron. According to previous definitions, this is cationic, reverse flotation because the silica is being removed in the froth. Again, as at Republic and Humboldt, the collector is the only reagent used, although it is likely that reagents to modulate collection would be beneficial. Apparently the present system achieves the desired results at lower cost.

As will be discussed again later, there seems to be an assured future for the use of secondary flotation to improve the grade of a primary concentrate made by magnetic separation.

There is yet another class of flotation application to iron ores which will be called intermediate flotation. As an example, The Hanna Mining Co.'s Groveland mill near Iron Mountain, Mich. (8) uses spirals to recover a gravity concentrate from the coarse fractions of the ground feed. The finer fractions are deslimed, and the iron minerals floated with anionic collectors. However, flotation in this instance employs a more complex reagent suite than the examples previously cited because of special conditions imposed by ore mineralogy. The ore contains hematite, magnetite, quartz, some calcite and dolomite, and iron-bearing silicates.

Sulfuric acid and sodium silicate are used in conditioning to regulate the pulp pH at about 5.5 and to depress and prevent activation of silica by calcium and magnesium salts. Flotation is next achieved by a combination of a petroleum sulfonate, fatty acid, and fuel oil. This combination would seem to seek synergistic effects to offset the difficulties imposed by a pH which is high for petroleum sulfonates and low for fatty acids. It is probable that a lower pH would be difficult to maintain in the presence of lime- and magnesia-bearing mineral constituents, and conversely a higher pH would allow for undesirable activation of the silica and silicates.

Intermediate flotation is also being employed at the Meramec Mining Co. at Pea Ridge, Mo. This extremely rich, mixed ore body is processed over magnetic separators to produce a concentrate, but hematite is lost to the tailings. Moreover, the tailing also contains apatite, sulfides, and silica. Progressive stages of flotation are being explored to recover an apatite concentrate, a sulfide concentrate, and finally to separate the hematite from the siliceous gangue.

Problems

There are a number of conditions that have militated against a widespread adoption of flotation processes by the iron ore industry. Some of these conditions, which are in the nature of problems that either have existed or continue to exist, will be discussed under the following headings: 1) Abundance of Ore from Other Sources; 2) Economics; 3) Attractive Alternatives; and 4) Process Limitations.

Abundance of Ore from Other Sources

Flotation processes in general had their commercial beginnings over 50 years ago and in the interim have been adopted by many segments of the mineral industry. In fact, it is difficult to visualize the copper industry, for example, without thinking of flotation at the same time. However, this is not true with the iron ore industry, where flotation is the exception rather than the rule. The difference is that within the copper industry the major tonnage of ore being mined contains only about 1% copper. Obviously copper ores must be beneficiated, and the flotation process has been found to adequately satisfy that requirement. Until World War II, quite a different set of conditions existed with respect to iron ore, and much of the needs of the iron and steel producers were met by direct shipping ores, containing a minimum of 51.5% iron. In those instances where beneficiation was needed, the simple forms employing washing or gravity separations were adequate. After World War II, with the Mesabi range nearing depletion, the iron ore industry focused its attention on high-grade foreign deposits and the low-grade domestic and Canadian sources. With the exceptions previously noted, flotation processes once again missed the opportunity to play a role in the new developments. Beneficiation was necessary in treatment of low-grade ores, but the character of the ore permitted electrostatic, magnetic, and gravity methods to be given preference.

Economics

Iron ore is a cheap commodity, being valued at the lower Great Lakes ports at about $12.75 per long ton containing 61% iron. With the low-grade ores, where flotation might be the most attractive, concentration ratios vary between 2 to 1 and 3 to 1 so that ultimate value contributed per ton of ore would be between about $4.20 and $6.40 for concentrates containing 61% iron. Against these values must be assessed mining costs, taxes, royalties, investment returns, shipping cost to lake head ports, and the cost of concentration. If flotation is considered, the cost of reagents comes under consideration, and possibly additional grinding and other costs attendant to the process. Although there is no official position in respect to reagent cost, about 75 cents per ton of concentrate would appear to be near the upper limit. Unfortunately, ore bodies that respond to effective, cheap flotation systems are rare.

Such factors as location, grade of ore, a favorable concentration ratio, and mineralogy may coincide to produce conditions favorable to the flotation process. Such conditions obviously are obtained at the site of the Republic and Humboldt operations. In other instances, where flotation might have been applied, there existed a satisfactory and cheaper alternate process which was adopted, with virtually any one of the magnetic taconite plants as an example. As a net result, the more costly and difficult-to-beneficiate ores may be expected to remain dormant until such time as a more favorable economic climate arrives.

Attractive Alternatives

Any consideration of primary flotation of iron ores is faced with competition from magnetic separation processes. In treatment of magnetic ore bodies, the preference for magnetic separation is so strong that flotation should hardly be considered. Magnetic separation allows for good recoveries, and the major operating cost can be allocated to crushing and grinding. By use of multistage processing steps, substantial portions of gangue minerals can often be rejected at sizes as coarse as 10 mesh. Therefore, the necessity for grinding all of the ore to final liberation size as in flotation is obviated to the significant advantage of the magnetic separation process. Furthermore, slime is less of a problem in magnetic separation than in flotation.

Because of the attractive features of magnetic separation, most of the new production in taconite is from the magnetic ore bodies. Secondary flotation is an attractive remedy in those cases where the fine-grained nature of the taconite contributes to high-silica content in the magnetic concentrates.

Although the magnetic ore bodies are presently given preference, the nonmagnetic taconite reserves are huge and eventually will have to be considered. It is to this particular body of iron ores that the Bureau of Mines has devoted considerable flotation research. Significant deposits have been studied on both bench and pilot plant scale, and the anionic method for flotation of calcium-activated silica has been shown to yield excellent results in many instances. Although reagent costs are still high in relation to the previously discussed criteria, they may not be out of line on favorably located ores having a moderately high grade.

Even if the primary flotation process is considered an unqualified success, there is a sizeable segment of informed opinion that favors roasting the nonmagnetic ores to synthetic magnetite as the first step in processing. This opinion persists despite the fact that primary flotation and reductive roasting-magnetic separation may be on a comparable economic basis—both too costly at the present time. Reductive roasting-magnetic separation facilities involved higher capital costs than for flotation, and the fuel costs may equal or exceed flotation reagent costs. However, part of the fuel costs incurred in magnetic roasting may be recouped in firing to oxide pellets. In addition, the magnetic oxides are generally easier to pelletize. Thus, because of the inherent advantages of a magnetic treatment, plus the grade control possible through secondary flotation, primary flotation may once again prove to be second best. However, since large-scale utilization of nonmagnetic taconites is still some years off, there is time for this position to change through continued research.

Process Limitations

Iron ores are notorious for their variability, and it sometimes seems that every shovelful is different from the preceding one. Mineralogically, iron ores may contain hematite, goethite, and magnetite, singly or in combination. Carbonates and silicates may occur, as well as a variety of other gangue minerals. Even if discussion is limited to those ores in which a cherty or quartz gangue predominates, the several iron species may be expected to possess different surface characteristics and therefore respond individualistically to flotation. Water supplies may vary with the season, and carry more or less of soluble constituents that consume fatty acid collectors, affect the pH, and influence surface charges.

In the face of such variability, the primary flotation processes might be expected to exhibit corresponding variations in outcome. A present lack of methods to instantly recognize and adjust to variable conditions may be considered a deterrent, particularly in the primary flotation of more complex or difficult ores. Bureau research on anionic flotation of calcium activated silica, especially when coupled with selective flocculation of iron oxides and decantation of slimes, has demonstrated that it is generally the most applicable and effective flotation method for nonmagnetic ores. However, the necessity of obtaining a favorable balance between the four chief reagents under conditions of varying demands from a changing ore body also introduces process uncertainties. This fact is recognized in current Bureau research which seeks to develop methods of process control through analytical techniques and instrumentation.

Slime is detrimental to every type of flotation, and iron ore flotation is no exception because iron ores contain more slime than many other ores. Slimes cause a difficult recovery problem in flotation of iron minerals, and if present in quantity, result in a lowering of concentrate grade when employing silica flotation methods. Effective use of petroleum sulfonate and cationic collectors in primary flotation is dependent on essentially complete slime removal.

Mention has already been made of the fact that the finely ground iron ore concentrates need to be pelletized before use in the blast furnace. This consideration also poses some limitations on flotation systems. Heavy fatty-acid coatings on iron mineral surfaces contribute to difficulties in pelletizing; other reagents may produce the same effect indirectly by making effective filtration difficult to accomplish.

It can be argued that many of the factors listed as deterrents also exist in other segments of the mineral industry, and that these other industries are successfully employing flotation. Again, the difference is that the iron ore industry has not been forced to make a commitment to flotation because of ample supplies and alternative processes.

Prospects

The prospects for increased flotation applications to iron ore appear to be excellent.

Increased flotation usage can be expected to follow the trend towards better concentrate grade. In the late 1950's, the output from the taconite plants created a demand for concentrates containing 60 to 65% iron, which resulted in the closing of many mines delivering the lower grade direct-shipping ores. At that time, talk in informed trade circles suggested that concentrates containing 6 to 8% SiO_2 might soon be the norm. These predictions seem to have been verified at the 7.5% level of silica, as a quick check of statistical sources will show (9). Such values for silica content reflect the combined output of both the concentration plants and those direct-shipping mines that continue to operate. As of 1963, the United States combined area produced a total of 72 million tons of ore and concentrate averaging 57% Fe and 8.0% SiO_2 and the Canadian combined area produced 27 million tons averaging 59% Fe and 6.2% SiO_2. Of these totals, approximately 54 million tons (10) were considered to be high-iron concentrate that averaged 6.0% SiO_2.

Future trends are suggested in statements by Reno and Brantley (13), namely, that iron ores will not find a ready market unless they are high grade (65 to 70% Fe, and 1.5 to 2.0% SiO_2). Already projections are being made, showing that by 1970, 60 to 80 million tons of iron ore having a silica content of less than 3% will be available from sources in North and South America. Availability of super-grade ores and concentrates cannot help but exert competitive pressure on installations producing at a lower quality level.

It can be assumed that the net effect of super-grade ore and concentrates will be to establish a new average specification for iron ores, perhaps at about the 4% SiO_2 level. If this trend is established, it will sound the final death knell of those direct-shipping ores that cannot be adequately beneficiated and force more rigorous measures on those plants whose current output does not meet the silica specification.

Evaluation of the 54 million tons of production considered to be high grade in 1963 will show that perhaps as much as two-thirds of this production will no longer be so considered by the projected 1975 standards for silica content. Some additional concentration beyond the presently used spiral, magnetic, or electrostatic separations will be necessary, and a substantial portion of the new burden may be expected to be assumed by flotation. The anticipated applications may be expected to be largely in the secondary flotation category, and it does not seem unreasonable to assume that as much as 40 million tons of concentrates annually may be receiving such treatment by 1975.

While the trend to the super-grade concentrate would seem to impart surety to the role of secondary flotation, the outlook for primary flotation is less certain. Briefly, under these conditions, instead of primary flotation, the better approach might be magnetic roasting and separation followed by secondary flotation for reasons of economics, flexibility, and control of product quality.

REFERENCES

1. Colombo, A. F., R. T. Sorensen and D. W. Frommer, Trans. AIME, SME v. 232, June 1965, p. 100–109.
2. Coyle, D. S., "The Empire Concentrator—Iron Ore's First Two-Stage Autogenous Grinding Flowsheet," Twenty-sixth Anniversary Mining Symposium, Center for Continuation Study, General Extension Division, University of Minnesota, 1965, p. 9–13.
3. Erck, L. J., "Flotation of Iron Ore," Quart. Colo. School Mines *56*, 387–416 (1961).
4. Frommer, D. W., M. M. Fine and L. Bonicatto, Anionic Flotation of Silica from Western Mesabi and Menominee Range Iron Ores. BuMines Rept. of Inv. 6399, 1964, 25 pp.
5. Frommer, D. W., USBM Tests on Selective Iron Ore Flotation Point Way to Greater Recoveries. Mining Engr. *16*, 67–71, 80 (1964).
6. Fuerstenau, D. W., Correlation of Contact Angles, Adsorption Density, Zeta Potential and Flotation Rate. Trans. AIME, SME, *208*, 1365–1367 (1957).
7. Gaudin, A. M., and D. W. Fuerstenau, Trans. AIME, SME *202*, 66–72 (1955).
8. Heising, L. F., "Open-Pit Iron Mining, Milling and Costs," Groveland Mine, The Hanna Mining Co., Dickinson County, Mich., BuMines IC 8181, 1963, 37 p.

9. Iron Ore. Sec. VI; Grade Name and Analyses; Sec. VII; Average Analyses and Tonnage by Grade Classification. Am. Iron Ore Assoc. 1964, pp. 70–100.

10. McComb, J. B., "Iron Mining and Taxes in Minnesota," Bull. 13, Bureau of Economic Studies, Macalester College, St. Paul, Minn., 1963, Table 11, p. 16.

11. Parks, G. A., The Isoelectric Point of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems, Chem. Rev. *65,* 177 (1965).

12. Parks, G. A., and P. L. de Bruyn, J. Phys. Chem. *66,* 967–973 (1962).

13. Reno, H. T., and F. E. Brantley, "Problems Facing the North American Iron Mining Industry," Presented at Annual Meeting of Minnesota Section of AIME, Duluth, Minn., Jan. 10, 1966.

14. Sennett, P., and J. P. Olivier, Colloidal Dispersion, Electrokinetic Effects and the Concept of the Zeta Potential. Ind. Eng. Chem. *57,* 33–50 (1965).

15. Sutherland, K. L., and I. W. Wark, "Principles of Flotation," Australian Institute of Mining and Metallurgy, Melbourne, Australia, 1955. p. 68–77.

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• *Addendum*

JAOCS *44,* 26 (1967). "Methods of Isolation and Identification of Volatile Compounds in Lipids," by Pio Angelini, D. A. Forss, M. L. Bazinet and Charles Merritt, Jr.

On page 27, lines 10 and 11 of the second paragraph under Sampling Techniques, the quantity "2 μg each" should read "2 μl each."