Methods of Flotation of Iron Ores, Recent Developments in the Iron Ore Flotation Industry

Djaksimuratov Karamatdin Mustapaevich
Candidate of Natural Sciences, Nukus Mining Institute

Joldasbaeva Ayzada Baxitbay qizi, Maulenov Nurlibek Axmet o'g'li,
Joldasbayeva Aysulu Baxitbay qizi
Student of Karakalpak State University named after Berdak

Abstract: With the depleting reserves of high-grade iron ore in the world, froth flotation has become increasingly important to process intermediate- and low-grade iron ore in an attempt to meet the rapidly growing demand on the international market. In over half a century's practice in the iron ore industry, froth flotation has been established as an efficient method to remove impurities from iron ore. In this chapter, the industrial practice and fundamental research activities of iron ore flotation are reviewed. The latest innovations in iron ore flotation at major iron ore operations around the world are introduced. The development of flotation routes from direct anionic flotation to reverse cationic flotation, and the rising of reverse anionic flotation in China in recent years is discussed. Although direct anionic flotation was the first flotation route employed in the iron ore industry, it was later largely replaced by the more efficient reverse cationic flotation route. The application of reverse anionic flotation in China in recent years effectively overcomes some flaws of reverse cationic flotation such as high reagent cost and high metal loss in desliming. The reagents used in iron ore flotation, including starch, amines and fatty acids, and the mechanisms of their interactions with the minerals in iron ore are examined. The presence of some specific impurities other than quartz in iron ore, such as alumina containing minerals, i.e. kaolinite and gibbsite, and phosphorous, is detrimental and attracts penalties. The removal of these specific impurities has received increasing attention in the iron ore industry. The industrial practice and latest research activities in this area are closely reviewed.

Keywords: Iron Ore Flotation, Reverse Cationic Flotation, Reverse Anionic Flotation, Alumina Removal, Phosphorus Removal.

1. Introduction

With the depleting reserves of high-grade iron ore in the world, various beneficiation methods have been employed to process intermediate- and low-grade iron ore in an attempt to meet the rapidly growing demand. The current trend in the steel industry is in favour of increased direct reduction coupled with electric furnace production which requires iron ore containing less than 2% SiO_2. In practice, iron ore often contains a few percent SiO_2, even after repeated magnetic or hydraulic separation, due to the presence of locked siliceous gangue minerals. To further upgrade the concentrate, froth flotation has been established as an efficient method to remove impurities from iron ore in half a century's practice around the world.

2. Iron Ore Flotation Routes

Although the reverse cationic flotation route has become the most popular flotation route in iron ore industry, the direct flotation of iron oxides still appears desirable for some low grade iron ores that contain a vast amount of quartz. For example, at Republic Mine, Michigan, U.S.A., a hematite ore is upgraded from 36.5% Fe to 65.4% Fe with a Fe recovery of 82.5% using the direct flotation route. Fatty acids (a distilled tall oil containing approximately 91% oleic and linoleic acids, 6% rosin acid and 3% unsaponifiables) are used as the collector of iron oxides, the dosage of which is usually in the range of 0.45-0.67 kg/t. Conditioning was reported to be of critical importance for the direct flotation process. Intense conditioning can reduce reagent cost as much as 50%. Prolonged conditioning was also found beneficial to the direct flotation route but was not economically justified. The adsorption of fatty acids on hematite plays a key role in the direct flotation route. In the literature, it is generally accepted that fatty acids adsorb on the surfaces of hematite through chemical bonding. Based on infrared studies, Peck et al. established that oleic acid/sodium oleate chemisorb on hematite. Using the technique of microelectrophoresis, Han et al. demonstrated the chemisorption of oleic acid and lauric acid on hematite. Buckland et al. also confirmed chemisorption of lauric acid on hematite surfaces. In addition to chemisorption, fatty acids can also adsorb on mineral surfaces through surface precipitation. It is noteworthy to mention that hydroxamates, which behave similarly to fatty acids in solution, were used successfully in the laboratory as collectors for hematite and goethite flotation, with better performance than fatty acids. The adsorption mechanism of hydroxamates on hematite was classified as classical chemisorption. Reverse cationic flotation removes quartz using ether amine as a collector, while depressing iron oxide with the use of corn starch in alkaline pulp adjusted by NaOH. In most cases, the pH ranges from 10 to 10.5. In early years, primary fatty amines such as dodecylamine were used in reverse cationic flotation. The fatty amines were of low solubility in pulp and were replaced by more soluble ether amines later. Papini et al compared the efficiency of various cationic collectors including fatty monoamine, fatty diamine, ether monoamine and ether diamine. It was found that ether amines are generally more efficient than fatty amine and ether monoamines achieved superior performance than ether diamines. In recent years, quaternary ammonium compounds have been reported to be more selective than primary amines in iron ore flotation. The classical theory about the adsorption mechanism of amines on quartz is electrostatic in nature, stabilized by hydrophobic association of the hydrocarbon chains. This point of view was broadly supported in the literature. For example, Gaudin and Fuerstenau, Fuerstenau , Iwasaki et al, Somasundaran et al and Smith et al. observed that the flotation of hematite/quartz using amines only occurred when the oxides were negatively charged and thus proposed that the ammonium ions at the oxide−water interface are electrostatically held in the Stern layer as individual counterions behaving almost like an indifferent electrolyte. However, a recent study using infrared spectroscopy demonstrated that amine cations form strong hydrogen bonds with the surface silanol groups of quartz. The depressant of iron oxides that is widely used in the reverse cationic flotation is typically corn starch. Corn starch is not soluble in cold water and must be put into solution in a process known as gelatinization. Starch gelatinization can be realized by thermal gelatinization or alkali gelatinization. The physicochemical fundamentals of starch gelatinization are still not fully understood and different theories have arisen. In the thermal gelatinization process, it is generally agreed that as temperature increases starch molecules vibrate more vigorously, thus breaking the intermolecular hydrogen bond and allowing penetration of water. In the iron ore processing industry, thermal gelatinization has become less popular due to the hazards of employing hot water and the associated energy cost in heating. In comparison with thermal starch gelatinization, much less is known about alkali gelatinization.

3. Removal of Specific Impurities in Iron Ore Flotation

In addition to quartz, the most common gangue mineral in iron ore, other impurities, such as alumina containing minerals and phosphorus, are also found in iron ores. The surface properties of alumina containing minerals and phosphorus are different from that of quartz and have to be studied separately for the successful removal of these impurities.

3.1. Alumina Removal

Alumina containing minerals in iron ore are detrimental to blast furnace and sinter plant operations. In the literature, silica removal has been studied extensively, while alumina removal has received limited attention. The reverse cationic flotation route widely used in the iron ore industry is less selective for alumina/hematite separation than for quartz/hematite separation. Das et al.studied the beneficiation of some alumina-rich iron ores and reported that to reduce alumina content by 4%, as much as 45% Fe has to be lost in the beneficiation process. Most of the studies in the literature were based on a "trial-and-error" approach, because the underlying mechanisms of the interactions between iron ore flotation reagents and the alumina containing minerals were largely unknown. Systematic research on kaolinite, a major alumina containing mineral in Australian iron ore, has been conducted at CSIRO, with the aim to provide an in-depth understanding of the flotation mechanism of kaolinite in iron ore flotation and a scientific basis for kaolinite removal research. So far, a series of findings have been developed at CSIRO on kaolinite removal from hematite ore. Kaolinite removal in iron ore flotation mainly involves three interactions, i.e. collector-kaolinite interactions, depressant-kaolinite interactions, and dispersant-kaolinite interactions. For collector-kaolinite interactions, it was found that the flotation behavior of kaolinite is opposite to that of silica. For example, ether diamine, a strong collector for silica, does not induce any flotation of kaolinite at pH 10. The pH dependence of kaolinite flotation is also opposite to that of silica, which explains why it is difficult to remove kaolinite in iron ore flotation. For depressant-kaolinite interactions, it was found that selective depression of hematite against kaolinite largely depends on strict pH control in iron ore flotation circuits and the level of ionic strength in iron ore flotation pulp. The presence of calcium and magnesium is particularly detrimental to kaolinite removal from iron ore. For dispersant-kaolinite interactions, it was found that sodium silicate, a standard dispersant widely used in iron ore flotation for silicate gangue minerals, is inadequate to disperse kaolinite. A low molecular weight polyacrylic acid was found to induce full dispersion of kaolinite particles, in the presence of calcium and magnesium ions in alkaline pulp. In addition to kaolinite, gibbsite, of general chemical formula $Al(OH)_3$, is also a common alumina containing mineral in iron ore. Separation of gibbsite from iron oxides such as hematite and magnetite is known to be extremely difficult due to the similarities in their surface properties. In recent years, Indian researchers reported a bioprocessing method for hematite–corundum (Al_2O_3) separation. It was reported that through the use of corundum-adapted strains and metabolites of paenibacillus polymyxa, efficient separation of corundum from iron oxides can be achieved. However, the procedure to prepare the bacteria was reported to be complicated and industrial application of this method has not been reported.

3.2. Phosphorus Removal

Phosphorus (P) in steel increases its hardness, strength, fluidity and brittleness, while reducing its melting point and carbon solubility. Depending on the use intended for the steel, these effects are either beneficial or detrimental. In general, phosphorus is considered as a gangue mineral in iron ore because it makes steel brittle. High levels of phosphorus in iron ore attract a penalty and reduces the profit margin substantially.The mineralogy of phosphorus in iron ore depends on the type of iron minerals. In magnetite, phosphorous is often found in the form of discrete phosphorus containing minerals, which are referred to as apatite. Apatite is a group of phosphate minerals including

hydroxylapatite, fluorapatite, chlorapatite, collophane and bromapatite. This type of phosphorus containing minerals can be removed by physical methods such as flotation. For example, the magnetite ore at LKAB (Luossavaara-Kiirunavaara AB) in Kiruna, Sweden, contains about 1 wt% phosphorus, which is removed by magnetic separation in combination with flotation. In hematite and goethite ores, phosphorous tends to be dispersed and incorporated into the lattice of iron minerals. For example, more than 80% of Western Australian iron ore contains an average of 0.15% phosphorus. The phosphorus in Western Australian goethite ores occurs in the form of solid solution. The distribution of phosphorus in goethite crystals prevents the effective use of physical beneficiation methods. This type of phosphorus containing minerals can be rejected by chemical methods. Apatite minerals are readily floated using anionic collectors such as fatty acids. At LKAB (Luossavaara-Kiirunavaara AB) in Kiruna, Sweden, the dephosphorization of a magnetite ore is conducted using magnetic separation and flotation. In the flotation process, the apatite minerals are floated with a fatty acid based collector. Sodium silicate is also used in this process as a dispersant of fine particles. The phosphorus content can be easily reduced to an acceptable level of less than 0.025 wt% P by increasing collector dosage. But increasing collector dosage also results in collector adsorption on the surfaces of magnetite which increases metal loss and reduces the strength of pellets. It was reported that these problems can be resolved to some extent by optimizing reagent dosage, pH and pulp temperature.

4. Recent Developments in the Iron Ore Flotation Industry

4.1. Reverse Anionic Flotation

Reverse cationic flotation is currently the most widely used flotation route in the world. However, the iron metal loss in the de-sliming stage, which is an essential step in reverse cationic flotation, and the high reagent cost of amine collector are the common problems of reverse cationic flotation. Reverse anionic flotation rejects quartz by first activating it with the use of lime, and then floating it using fatty acids as collectors. The advantages of reverse anionic flotation, in comparison to reverse cationic flotation, include its relatively lower sensitivity to the presence of slimes and the lower reagent cost for the fatty acid collectors, which are the main components of waste from the paper industry. This was demonstrated in an investigation by the U.S. Bureau of Mines and has been generally accepted in the literature thereafter . In recent years, reverse anionic flotation has been successfully applied in China's iron ore industry and achieved excellent results. In 1998, three reverse anionic flotation circuits were built in China's major iron ore area, Anshan. In 2003, these circuits processed 6.77 million tons of iron ore, with a feed grade of 29.9% Fe, a concentrate grade of 67.5% Fe, a tailings grade of 8.31% Fe, and a Fe recovery of 82.1%. A significant advantage of reverse anionic flotation circuits is the omission of de-sliming prior to flotation attributed the higher tolerance to slimes using reverse anionic flotation to the increased surface charges on the oxides at higher pH (pH 11~12). The electrostatic repulsive force between mineral particles and slime coatings is so strong at this pH level that de-sliming is no longer necessary. It is noteworthy to point out that in Anshan, China, magnetic separation is often used in combination with reverse anionic/cationic flotation to upgrade low grade iron ore from ~29% Fe to ~50% Fe before flotation. Such a configuration has the advantage of removing some of the slimes in the magnetic separation stage. For the reverse cationic flotation circuits once popular in this area, the de-sliming effect of magnetic separation was not adequate and typically produced concentrate of 65.22% Fe grade at a recovery of 78.42% from a feed of 29.16% Fe. The iron ore in USA and Anshan are both of Lake Superior type. The de-sliming effect of magnetic separation prior to reverse cationic flotation was also found to be insufficient at Groveland Mine, Michigan, United States. The superior performance of reverse anionic flotation circuits in Anshan demonstrated their better tolerance towards slimes.

4.2. Column Flotation

The application of column cells in the mineral processing industry has gone from virtually zero in 1983 to wide acceptance in 1990[55-57]. The major operating difference between column flotation cells and mechanical flotation cells is the lack of agitation in column flotation which reduces energy and maintenance costs. The practice of froth washing in direct flotation increases concentrate grades without significant recovery losses. In the reverse flotation of iron ores, froth washing was found effective in reducing the loss of FINE iron oxide particles to froth. It was reported that the cost of installing a column flotation circuit is approximately 25% - 40% less than an equivalent flotation circuit of mechanical flotation cells. Industrial application of column cells in iron ore processing has been reported in several Brazilian operations and Sydvaranger mine in Norway. Samarco is the first Brazilian producer to use column cells to increase its flotation capacity as part of a plant expansion program. Other companies using column cells at present include CVRD (Companhia Vale do Rio Doce), CSN (Companhia Siderúrgica Nacional), and MBR (Minerações Brasileiras Reunidas). However, negative reports on the use of column cells were also found in the literature. According to Dobby, there were several failures in the application of column cells in the iron ore industry. At CVRD's Samitri (Alegria) concentrator in Brazil, after three column flotation stages, i.e. rougher, cleaner and re-cleaner, a secondary circuit of mechanical cells was still installed to produce the final concentrate. Despite the advantages of column flotation reported in the literature, the use of column cells in iron ore flotation has mainly been reported in South America. In a typical mill in North America, the iron ore flotation section consists of mechanical flotation cells arranged in rows.

5. Summary

The flotation of iron ore started with the direct flotation of iron oxides using anionic collectors, but was latter largely replaced by reverse cationic flotation which has become the most widely used flotation route in the iron ore industry. The successful application of reverse anionic flotation in China's iron ore industry in recent years offers a good opportunity to reduce costs while increasing iron recovery at the same time since desliming is not essential in the reverse anionic flotation circuits. Column flotation cells have been used at a couple of iron ore operations, mainly in Brazil. Various advantages of the column flotation cells have been reported, but a negative report on the column flotation of iron ore was also found in the literature. With the depletion of high grade iron ore, the removal of alumina containing minerals and phosphorous from low grade iron ore has received increasing attention in iron ore industry. The flotation behaviour of kaolinite was found to be opposite to that of quartz and special care has to be taken for the successful removal of the clay mineral. The surface properties of gibbsite are similar to that of iron oxides which makes it refractory to treatment using conventional flotation methods. The mineralogy of phosphorus in iron ore depends on the type of iron minerals. In magnetite, phosphorous is often found in the form of discrete apatite minerals which can be removed by flotation using anionic collectors. In hematite and goethite ores, phosphorous tends to be incorporated in the lattice of iron minerals and has to be rejected by chemical methods. The author would like to thank CSIRO National Research Flagship for support of this work.

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