OPTIMIZING THE USE OF DEPRESSANTS IN IRON ORE FLOTATION [1]

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Abstract

Iron ore concentration through flotation represents an important application of chemicals in minerals processing. Selective separation between iron oxides and siliceous gangue minerals can only be achieved, in most cases, through the proper application of depressants, pH modifiers and collectors. The purpose of the present work is to describe the use of such reagents in iron ore flotation and to discuss optimization alternatives in the case of depressants. Selection of depressants to be use in flotation is a complex issue that demands continuous optimization especially in cases in which the total cost of chemicals is strongly dependant on one class of flotation reagents. To add complexity to this issue, natural organic polymers, such as starch, might present quality and price variations depending on the harvest, the origin of the grains, on the seasonal trading, transportation logistics and other aspects that can influence supply and demand aspects of a given market. Alternatives for replacing natural polymers by synthetic products specifically developed to act as flotation depressants are presented and discussed. This replacement, partial or total, generally leads to improvement of the overall metallurgy.

Key words: Flotation; Depressants; Iron ore.

OTIMIZANDO O USO DE DEPRESSORES NA FLOTAÇÃO DE MINÉRIO DE FERRO

Resumo

A concentração de minérios de ferro por flotação representa uma importante aplicação de reagentes no processamento de minerais. A separação seletiva entre óxidos de ferro e minerais silicosos de ganga pode apenas ser conseguida, na maioria dos casos, através da aplicação adequada de depressores, modificadores de pH e coletores. O objetivo do presente trabalho é descrever o uso desses reagentes na flotação de minério de ferro e discutir alternativas de otimização no caso dos depressores. A seleção de depressores a serem empregados na flotação reveste-se de complexidade que demanda uma otimização contínua na qual o custo total dos reagentes é fortemente dependente da classe dos reagentes de flotação. A complexidade ainda aumenta com o uso de depressores que são polímeros orgânicos naturais, tal como os amidos. Esses produtos podem apresentar variações de preço e de qualidade dependendo da safra, da origem dos grãos, dos negócios numa dada estação, de logística de transporte e de outros aspectos que podem influenciar aspectos de demanda e oferta de uma dada condição de mercado. Alternativas para a substituição dos polímeros naturais por produtos sintéticos especificamente desenvolvidos para agir como depressores na flotação são apresentadas e discutidas. A substituição, parcial ou total, geralmente leva a uma melhoria dos parâmetros de processo.

Palavras-chave: Flotação; Depressores; Minérios de ferro.

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INTRODUCTION

Nowadays flotation technology is the single most used unit operation for the concentration of several types of ores worldwide.(1) Now more than a century old, this technology has even further increased its use in minerals processing applications mostly because of its high efficiency and high flexibility. The wide application of flotation technology is an outcome that deeply relies on the proper selection of flotation chemicals.

Flotation at the early years was basically operated without any fundamental knowledge whatsoever. Reagents started to participate in the process, by trial and error techniques, but soon flotation operators commenced to notice their extreme relevance. As the initial ores treated by flotation were base metal sulfides, chemical differences (and consequently surface chemical differences) between valuable components (sulfides) and gangue minerals (silicates and carbonates) were large. When sulfides needed to be separate from each other, the value of adding reagents to control surface properties was clearly noticed. When separating galena (PbS) from sphalerite (ZnS), the concept of flotation modifiers was created. Unwanted sphalerite flotation called for a modifier that was termed as deactivator (zinc sulfate) and the reagent used to increase flotation of this mineral was named as activator (copper sulfate). Selective separation of lead and zinc minerals by flotation became a reality because proper reagents could be found. Interference of copper and iron sulfides were dealt with by application of another depressant, namely sodium cyanide. It is important to point out however that the discovery of these reagents for this flotation system was made well before the action mechanisms for activation and deactivation were put forward.

As chemists and engineers started to realize the gigantic potential of using chemical reagents of many kinds, specifically designed for each flotation system, the interest in expanding the application of flotation to several types of ores grew considerably. Serious and open-minded applied research efforts in flotation chemicals were then born. Several reagents started to be tested in order to find out the right combination of chemicals to perform all the fundamental roles of reagents to reach the best response possible when ores were subjected to flotation separation. New collectors, frothers and modifiers (depressants, activators and others) are in continuous development as flotation performance significantly relies upon their optimization.

A single example of the impact of reagent research on flotation technology was reported by Fuerstenau(2) in 1999 (quoting a private communication by Harris, G.H. in 1998). In 1979, Z-200 (a thionocarbamate) was introduced as a co-collector or directly as a collector alone for copper sulfide flotation. Copper recovery was increased in average by two percentage points. This gave the world at that time an additional production of 40 million kg of copper metal in one year alone. At currently market copper prices this gain would represent an annual gross revenue increase of approximately 340 million US dollars (550 million R$). The overall cost of reagent that supported this increased revenue, in 2008 costs, would have been about 13 million US$, or roughly 4% of the revenue gain.

New chemicals with application in mining industry must be continuously looked for. A new family of depressants currently being developed is the cationic copolymers of polyamide-polyamine.

In a similar calculation for iron ore, if a new reagent would increase iron recovery by two percentage points, in the course of one year in Brazil alone, the gain in gross annual revenue taking into account exclusively iron ore processed by flotation would be approximately 110 million US dollars. Assuming that this new reagent is a co-depressant (like a polyamide) and it is consumed at a rate of 100g/t of feed to flotation (a dosage much higher than a typical sulfide collector dosage), increased reagent costs associated with the additional revenue would still allow for a net gain in revenue of 83 million US dollars per year.

Adding new reagents to existing operating plants typically increase only the direct operational cost once no extra pieces of equipment and process modifications are required. Increasing recovery by adding new processing steps would always require capital expenditure for acquisition of new equipment and time for their installation. If the same increase in iron recovery shown above had been achieved, for instance, by magnetic separation, capital cost alone would amount approximately 220 million US dollars (taking into account the installation of Jones type magnetic separators to treat flotation tailings and add the extra two percentage points in iron recovery). In summary, optimizing flotation using better chemicals is clearly a much cheaper alternative that can be put into practice almost immediately.

APPLICATION OF DEPRESSANTS IN IRON ORE FLOTATION

As already mentioned, flotation started its industrial application in sulfide ores. Because of its inherent flexibility, flotation soon started to be investigated as alternative for the beneficiation of several other types of ores. Iron ores were also a subject in flotation research efforts.

As flotation depends on a variety of chemicals and, among them, collectors have the responsibility of making surfaces hydrophobic to enable successful bubble contact, research of flotation chemicals is biased towards these reagents. A long table provided by Nagaraj and Ravishankar in 2007(3) illustrates this statement. Their list covers the chronology of reagent development from the early days of flotation until 2004. Out of the 72 entries in the list, 47 (or 65%) represent collectors. Nonetheless, the second most cited type of reagent is the class of depressants, with 15 entries (or 21%).

Two main research lines were established in the beginning of iron ore flotation research: direct flotation of iron oxides and reverse flotation of siliceous gangue minerals. Direct flotation studies were selected as the first choice to treat hematite iron ores because selective flotation of hematite from quartz using anionic collectors, readily available, seemed to be ease to achieve.(4-5) Hematite surfaces were easily made hydrophobic by the adsorption of several chemicals such as alkyl carboxylic acids as well as alkyl sulfates and sulfonates. At the same time, quartz, which is the major siliceous gangue mineral, did not have its surface made hydrophobic by employing these reagents. Although initial industrial application of iron ore flotation started using the direct flotation route, once better reagents for the reverse flotation alternative were discovered almost every single new application of iron ore flotation to remove siliceous gangue minerals adopted this second processing route.(6-9) Nowadays reverse cationic flotation plants are present in several countries treating iron ore in the pellet feed size range from grades as low 25%Fe to as high as 60%Fe. Table 1 shows a summary of such plants around the world. Reverse flotation to remove phosphate and sulfide minerals are also used and for completeness these plants were included in Table 1. is The types of reagents used (in a generic broad chemical family) are also shown in Table 1. The last column indicates the major gangue removed. By analyzing data presented in Table 1, it is very clear that the country with most plants in operation to process iron ores by reverse flotation is

Brazil. Furthermore, in Brazil at least five new flotation concentrators (of very large capacity – 50 to 160 ktpd) have projects already approved and should come on stream until 2012.

Table 1 – Summary of flotation applications in iron ore (reverse flotation).(10)

Country	Number of plants	Collector type	Depressant type	Major gangue minerals floated
Brazil	15	Amine	Polysaccharide	Quartz
India	2	Amine	Do.	Do.
Canada	1	Amine	Do.	Do.
USA	6	Amine	Do.	Do.
Chile	2	Amine	Not used	Do.
China	2 (**)	Amine	Unknown	Do.
Russia	1	Amine	Unknown	Do.
Ukraine	2	Amine	Polysaccharide	Do.
Mexico	2	Sulfate	Sodium silicate	Apatite
Peru	1	Xanthate	Unknown	Pyrite
Iran	2	Sarcosinate	Sodium silicate	Apatite
Sweden	1 (*)	Sarcosinate	Unknown	Apatite
Venezuela	1 (**)	Amine	Unknown	Quartz
WORLD	38			

(*) Actually three flotation plants are in operation at the same mine location, but receiving feed separately.(**) Precise information is not available.

Starches (a natural polysaccharide) can be considered as the most widely used depressants in reverse flotation of iron ores. Starches are extracted from grains, tubers and other materials of vegetal origin. The most common types of starches used in the mineral processing area are those obtained from corn and tapioca (cassava), especially the first. Modified starches can also be used and several types of starch modification obtained by introducing cationic and anionic groups into starch macromolecules (which are non-ionic) have been tested over the years in the search of more efficient and selective depression of iron oxides.

For over 50 years now, the most accepted and employed flotation concentration route for iron ores is the cationic reverse flotation of silicates. The use of this flotation scheme relies on the successful combination of amines as collectors of silicates, mostly quartz, and starches and their derivatives as iron oxide depressants. In most cases, the addition of depressant represents the only way to achieve required selectivity levels with high iron recovery.

Starches are all based on the same monomer, a saccharide (sugar) known as α-D(+) glucose (or glucopyranose). As a polymer, starch macromolecules come in two varieties: linear shaped amylose and branched amylopectin. Most natural starches consist of a higher proportion of amylopectin in comparison to amylose. Amylopectin macromolecules are likely of the largest polymers found in nature with molecular mass of the order of several million Daltons. Amylose macromolecules are considerably smaller with molecular mass of a few hundred thousands Daltons.

Most of the early research on starch adsorption mechanisms evolved because of the application of this polymer in iron ore flotation. With its non-ionic nature, explanation for the selective role of starches in iron ore flotation systems was initially given as being related to the superior hydrogen bonding capability of iron oxide and hydroxide surfaces in comparison to quartz surfaces. This way the larger extension of adsorption of starch onto hematite and goethite, in its non-modified state, was explained by a hydrogen bond mechanism by Iwasaki and his team.(11) Cationic starch was shown to adsorb more strongly on highly negative surfaces of quartz and, on the other hand, anionic modified starch showed stronger adsorption on iron oxides than on quartz. Other early studies on starch varieties and derivatives, for example the work of Chang(12) during the 1950´s, indicated the same direction as to whole starch being the most effective depressant. Much later, studies performed by Pinto and co-workers(13) demonstrated that amylopectin and whole starch performed best the depression role for hematite in comparison to amylose.

Weissenborn and co-workers(14) presented convincing evidence against a hydrogen bond mechanism for the adsorption of non-modified starches onto hematite surfaces. Their work has shown that the most likely mechanism for the adsorption of starch polymers onto hematite surfaces is through chemical bonds taking place between iron sites on the surface of the mineral and the oxygen atoms on the glucose ring of starch. Similar conclusions favoring a more chemical mechanism for starch and starch derivatives adsorption on several mineral surfaces were reached by Qi and Laskowski.(15,16) These latter researchers established a very well sound mechanism based on acid-base relationships in order to explain adsorption of polysaccharides on mineral surfaces. Similar interpretation for the interaction between starch, amylose and amylopectin with the surface of hematite, quartz, calcite, dolomite and apatite was presented by Leal Filho and co-workers(17) who developed a model based on fitting number to explain success or failure of starch on its adsorption on these minerals. Working with apatite and quartz as model minerals, Araujo and co-workers(18) have also favored a chemical mechanism for the adsorption of whole starch, amylopectin and amylose. According to these workers, starch products adsorption on apatite surfaces could be increased significantly if extra calcium ions were added to the system. Furthermore, Ca ions in solution were likely chelated by starch as indicated by electrical conductivity measurements before and after adding starch to the system.

An important development in the use of starches took place in Brazil. All starch in use during the period from 1960 to 1990 was supplied by a single company and was represented by a wet milled cornstarch of high purity. This monopoly led to high prices and the sole iron operator at the time decided to start an investigation of alternative sources of depressants. Tests performed initially at bench scale and later as industrial test runs showed quite clearly that other types of starch products, especially corn grits (with a much coarser size distribution than pure cornstarch), could replace the high purity reagent then used.(19)). These studies were further corroborated by other researchers.(20,21) Efforts to demonstrate that proteins that occurred in a significant quantity on the alternative starches (dry milled and more impure) would hinder the application of the new reagents failed. Further studies developed on the subject proved otherwise. The most commonly found protein in the impure starches was identified as zein. Peres and Corrêa(20) published a very important research paper that clearly showed that actually zein acts as a strong depressant for hematite.

Dudenkov and co-workers(22) have also discussed the possibility of using starch by products as depressants instead of pure starches. During the production of potato starch, a reject stream containing about 40% starch was employed successfully as a depressant in iron ore reverse cationic flotation. Required dosage, when calculated based on the starch content on this reject was found to be similar to that when pure potato starch was used.

As the demand for corn grits increased because of the new iron ore flotation plants that were commissioned in the early 1990s, and also taking into account that retail sales of the product paid better prices for the suppliers, another cornstarch product was introduced as flotation depressant.(23) This product, which is essentially a cornmeal, locally known as *"fubá"*, presented a new challenge for its use. Also derived for dry milled corn, after removal of germen, some suppliers were not able to supply it with low oil content. The presence of oil in quantities above 3% in weight makes the use of *"fubá"* almost impossible in flotation systems. The high amount of oil hinders (sometimes, destroys) the stability of mineralized froths. Currently, all suppliers of *"fubá"* have to ascertain that their products meet the required characteristics in terms of quality that necessarily includes an oil content of less than 1.5%. Figure 1, taken from data presented by Mapa(24) clearly shows the strong deleterious effect of the oil content in cornmeal on the flotation of iron ores.

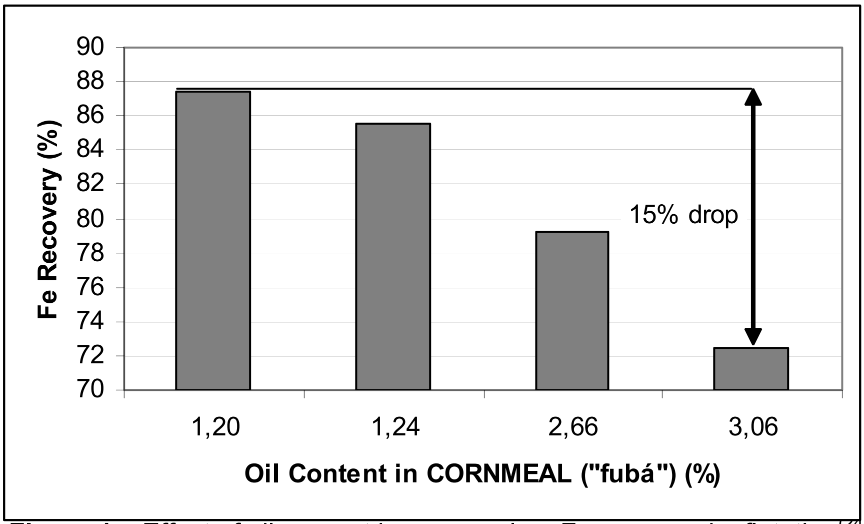

Figure 1 – Effect of oil present in cornmeal on Fe recovery by flotation(24)

Besides cornstarch, several other starches derived from other vegetal sources can be used. The major difficulty facing the use of starches not from corn, especially in the Brazilian scenario, is availability. Tapioca starch products are in use today and perform quite well the depressant role. Tapioca starch products are, however, not available in the required amount throughout the year. Mainly for this reason, very few iron ore flotation plants use tapioca starch products constantly.(10)

Natural polymers, such as starch, regardless of their purity degree, as they are obtained directly from vegetables, have variable properties. These properties can vary from a harvest to another, from a season to another, from a type of grain to another and from the soil type they were planted and the quantity and quality of fertilizers and other additives used for their agriculture. Synthetic polymers, on the other hand, can be produced in a controlled manner and their properties can be guaranteed by the supplier. Several alternatives to starches, some including other natural polymers and others including synthetic reagents have been subject of research in iron ore flotation systems. Table 2 shows a list of reagents already investigated as iron ore depressants in recent years and the stage that their testing has reached (laboratory, pilot plant or industrial application trials).

Table 2 – Alternatives to starch for the depression of iron minerals (Recent investigations in Brazil).

Reagent	Level of testing	References	Qualitative assessment
Carboxymethyl cellulose from supplier A	Laboratory	Viana and Araujo (25)	Only two CMCs showed good results
Carboxymethyl cellulose from supplier B	Laboratory	Viana and Araujo (26)	Negative results
Polysaccharide from supplier A (*)	Pilot plant (column)	Albuquerque and Henriques (27)	Good results
Polysaccharide from supplier C (*)	Pilot plant (column)	Do.	Very negative results
Carboxymethyl cellulose from supplier A	Full industrial test	Castro et al. (28)	Good results
Anionic Polyacrylamide (*)	Laboratory	Turrer (29) and Turrer et al. (30)	Negative results
Non-ionic Polyacrylamide (*)	Laboratory	Do.	Good results
Cationic Polyacrylamide (*)	Laboratory	Do.	Good results
Carboxymethyl cellulose from supplier A	Laboratory	Turrer (31)	One CMC showed good results
Lignin sulfonate	Laboratory	Do.	Negative results
Guar Gum (*)	Laboratory	Do.	Good results
Humic Acids	Laboratory	Do.	Negative results
Humic Acids	Laboratory (micro scale)	Santos (32), Santos and Oliveira (33)	Good results
Carboxymethyl cellulose from supplier A (*)	Laboratory	Mapa (24)	Good results
Non-ionic Polyacrylamide (*)	Laboratory	Do.	Mixed results
Lignin sulfonates	Laboratory	Do.	Negative results
Polyamide (*)	Laboratory	Current work	Good results

(*) Tested in combination with starch.

SOME EXPERIMENTAL RESULTS THAT DEMONSTRATE THE SYNERGIC INTERACTION BETWEEN DEPRESSANTS

Table 3 depicts some of the results recently presented by Albuquerque and Henriques(27) on pilot plant column flotation tests performed at a Brazilian iron ore flotation plant. These results were obtained in a campaign aimed at testing several alternative depressants. An etheramine was used as collector. The starch used should be considered as the base case. It represents a cornstarch derivative (cornmeal or "*fubá*") currently used as depressant. The two other polysaccharide samples, namely PS (1) and PS (2), came from different suppliers and both represent commercially available reagents that are marketed as mining chemicals. The table also shows that a significant synergetic effect takes places when starch is partially replaced by PS (2).

The results in Table 3 clearly demonstrate that by just selecting a single family of reagents for testing can be a serious mistake, especially when it is well know that polysaccharides can vary considerably in polymerization and substitution degrees from one reagent to the other. If only PS (1) were to be tested one would obviously conclude that this type of reagent should never be considered as a potential depressant to replace starch in this flotation system. A 2% increase in iron recovery, associated with a slight decrease in silica grade of the concentrate and an increase in iron content resulted from the combination of the synthetic polysaccharide and cornmeal. Yield decreased by one percentage point in this case.

Table 3 – In-plant column flotation testing of depressants [(27)]

		PS (1)	PS (2)	Starch	Starch+PS (2)
Fe	Feed	52,7	50,3	47,9	46,9
	Concentrate	62,9	67,8	67,3	68,1
	Tailings	38,7	7,4	12,0	9,2
SiO_2	Feed	23,31	26,31	29,35	31,87
	Concentrate	8,49	1,02	1,57	1,34
	Tailings	43,70	88,25	80,93	86,14
Yield (mass% to concentrate)		58	71	65	64
Fe recovery (%)		69	**96**	**91**	**93**
SiO_2 distribution to tailings (%)		79	97	97	97
Selectivity Index		2,9	28,1	18,1	20,7
Dosage (g/t)		858	864	978	898 (521+377)

Table 4 shows results obtained at laboratory scale when pure cornstarch was used in conjunction with a polyamide-polyamine, added as a co-depressant for the flotation of an iron ore sample from Minas Gerais. An etheramine was used as collector. The results clearly demonstrate in this case that even at a reduced total dosage of depressant, starch alone results can be considerably improved by adding polyamide. Further addition of both depressants represented increases of 2% in yield and 8% in iron recovery. The improvement in mass and iron recovery were accompanied by a very significant reduction of silica grade of the final concentrate. In comparison to the change obtained by adding PS(2) to starch, as shown in Table 3, adding polyamide-polyamine to starch made a stronger impact both in iron recovery as well as on selectivity. The overall consumption of depressant was also reduced in the example shown in Table 4.

Table 4 – Laboratory testing of polyamide-polyamine and starch association

		Starch	Starch + Polyamide-Polyamine	
Fe	Feed	46,3	46,6	46,4
	Concentrate	65,1	68,7	68,9
	Tailings	29,6	26,2	24,0
SiO_2	Feed	33,40	33,10	32,7
	Concentrate	6,43	2,49	1,60
	Tailings	57,30	61,50	80,93
Yield (mass% to concentrate)		47	48	50
Fe recovery (%)		66	**71**	**74**
SiO_2 distribution to tailings (%)		91	96	98
Selectivity Index		4,4	8,1	10,7
Dosage (g/t)		750	500 (200+300)	700 (300+400)

Results shown in Tables 3 and 4 can be used to demonstrate that synergy between depressants, through the proper selection of chemicals, can deliver considerable increase in overall iron ore flotation performance.

Synthetic reagents can also bring some advantages regarding their controlled production and constant, reproducible, quality. Although it is very clear that the cationic reverse flotation of iron ore benefits from the use of starches as depressants, nowadays one can demonstrate that there is room for improvement by adding other chemicals to the conventional suite of reagents used in this important application of flotation separation.

One should also take into account that polymers when added to flotation systems perform secondary roles that go beyond than simply serving as depressants. Recent work by Liu and co-workers (34) on model systems involving the polymers dextrin, cornstarch, carboxymethylcellulose and the minerals hematite, apatite and sphalerite has shown that the polymers also play an important role in controlling fine particle entrainment. Some mineral particles in flotation systems, especially those of very fine range, and regardless of their surface conditions (hydrophobic and hydrophilic), tend to follow water flow split, becoming entrained in the froth. For each system investigated by Liu and co-workers, specific polymers were able to reduce particle entrainment and, in this way, enhanced overall flotation performance.

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