FLÁVIA NATALINO OLIVEIRA

EVALUATION OF SUSTAINABLE BIOPOLYMER AS DEPRESSANT FOR IRON ORE CATIONIC REVERSE FLOTATION

Dissertação apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Agroquímica, para obtenção do título *Magister Scientiae*.

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APROVADA: 31 de março de 2014.

Cláudio F. Lima

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Jorge Luiz Colodette
(Orientador)

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SUMÁRIO

RESUMO

OLIVEIRA, Flávia Natalino, M.Sc., Universidade Federal de Viçosa, março de 2014. **Evaluation of sustainable biopolymer as depressant for iron ore cationic reverse flotation.** Orientador: Jorge Luiz Colodette.

A flotação catiônica reversa do minério de ferro é um processo de separação usado na mineralogia para separar compostos de ferro de outros compostos indesejáveis presentes no minério de ferro. Nesse processo, o amido é usado como depressor e amina como coletor. A compreensão do mecanismo de interação existente entre os reagentes usados no processo de flotação e o minério de ferro é de fundamental importância para avanços na tecnologia de enriquecimento de minério de ferro, bem como no desenvolvimento de novos agentes químicos usados no processo para esse fim. Esse trabalho está dividido em dois capítulos: i) O primeiro tem como principal objetivo avaliar algumas características do amido que podem influenciar no processo de flotação, como, tamanho da cadeia polimérica e grupo terminal redutor (GTR) presentes na molécula do depressor e ainda avaliar, por meio de técnicas espectroscópicas os minérios flotados e afundados dos testes de flotação usando dextrina, amido solúvel, amido ceroso e amido de milho industrial como agentes depressores. ii) O segundo capítulo tem como principal objetivo desenvolver um novo depressor (XMC), extraído de resíduo de fibra de milho, para substituir o amido no processo de flotação do minério de ferro. Os estudos do capítulo 1 mostraram que moléculas de amido menores resultam piores desempenhos na flotação e que a presença do GTR começa a ser positivamente influente no desempenho da flotação quando se usa moléculas pequenas, em que esse grupo está em maiores quantidades (DE = 10,6% glicose). Uma análise dos espectros de DRIFT baseada na intensidade da banda da hematita não mostrou nada além de que as amostras de concentrado contém mais hematita que as amostras de flotado, como já era esperado. A análise de espectroscopia Raman não possibilitou a observação de qualquer banda característica dos depressores usados, uma vez que só foi sensível à fase inorgânica. Os estudos do capítulo 2 mostraram o grande potencial da XMC em substituição ao amido no processo de flotação, por excelentes resultados de flotação e por ser uma alternativa sustentável, oferecendo uma destinação nobre a um resíduo industrial. Além da possibilidade em remover o amido parcial ou totalmente do processo industrial, preservando-o para a cadeia alimentar humana e animal.

ABSTRACT

OLIVEIRA, Flávia Natalino, M.Sc., Universidade Federal de Viçosa, march, 2014**. Evaluation of sustainable biopolymer as depressant for iron ore cationic reverse flotation.** Adviser: Jorge Luiz Colodette.

The reverse cationic flotation of iron ore is a separation process used in mineralogy to separate iron compounds from others compounds present in iron ore. In this process, the starch is used as depressant and amine as collector. The knowledge of interaction mechanism between the reagents used in the flotation process and iron ore has a fundamental importance to advance iron ore enrichment technology, as well as to the development of new chemicals used in the process. This work is divided into two chapters: i) The first chapter aims to evaluate some characteristics of starch that can influence the flotation process, such as, size of the polymer chain and reducing end group (REG) present in the depressant molecule. It also aims to evaluate, by spectroscopic techniques, the reject and concentrate minerals from flotation tests using dextrin, soluble starch, waxy starch and industrial corn starch as depressant agents. ii) The second chapter aims to develop a new depressant (XMC), extracted from corn fiber residue (CFR), to replace the starch in iron ore flotation process. The results in Chapter 1 showed that short chain depressant results in worse flotation performance. The amount of REG has no effect on flotation performance up to a dextrose equivalent value of 9.2% glucose. Analysis of the DRIFT spectra based on the intensity of the hematite band only showed the concentrate samples contain more hematite than reject samples, as expected. Using Raman spectroscopy analysis, it was not possible to observe any characteristic band of the depressants used, since the Raman was only sensitive to inorganic phase. The studies in Chapter 2 showed the great potential of XMC replacing starch in flotation process, because of the excellent flotation results and the XMC be a sustainable alternative, offering a prime destination to an industrial waste. Besides, it is possible to remove the starch of industrial process partially or totally, preserving it for human and animal food chain.

INTRODUCTION

Most of the Brazilian reserves of iron ore consist predominantly of iron oxide (mainly hematite) and quartz. Iron ore concentration through flotation represents an important application of reagents in mineral processing. The depletion of deposits of iron ore requires the use of concentration methods to obtain products that meet the specifications for the steel industry, the largest consumer of iron ore concentrate. The final quality of the concentrate is, undoubtedly, the most important parameter in processing of minerals. The production of concentrated iron ore outside the specifications of client can lead to a decline in the sale price, based on the percentage of iron, that in turn, leads to penalties to the producer, in addition the loss of future contracts.

Reverse cationic flotation of iron ore is now receiving more attention by iron ore industry as an efficient beneficiation process. In reverse cationic flotation, quartz is floated after depressing the iron oxide by suitable reagents such as starch.

In the process of separating minerals by flotation, addition of reagents known as depressants, or reagents that makes the surfaces of certain minerals more hydrophilic, have fundamental importance. To understand the selectivity, from a chemical point of view, one needs to understand the interaction between the surface and the mineral reagents. For iron ore, this investigation focuses on the quartz/hematite system using starch as a depressant agent.

Chapter 1 discusses the effects of starch chain length, based on dextrose equivalent quantification (DE), and the presence of reducing end group (REG) in starch during the flotation process. These studies were performed with different starches produced by acid hydrolysis and reduction of REG using sodium borohydride. In addition, spectroscopic studies were performed in order to obtain information about the interaction mechanism between iron ore and the depressant.

There are several studies on the interaction mechanism in the literature and they help to explain this phenomenon. Most studies have shown that the adsorption mechanism of polysaccharides are very complex and involves a number of theories. With this work, it was hoped to be able to evaluate the effect of starch chain length and the presence of REG in starch during flotation process.

The use of other natural or synthetic polymers - carboxymethyl cellulose, lignosulfonate, polyacrylamides, guar gum and humic acid - in mineral industry has been growing in recent years. Several studies have demonstrated the effectiveness of using these reagents for depression in mineral flotation in many systems worldwide. Despite the differences between them, such as in structures and functional groups, all have some common characteristics that suggest similar mechanisms of adsorption, such as: hydrocarbon chain capable of forming hydrophobic interactions, large number of hydroxyl groups capable of ionization and formation of hydrogen bonds, and hydrated polar groups capable of interacting specifically.

Chapter 2 addresses the use a new sustainable potential biopolymer as depressant for iron ore reverse cationic flotation extracted from Corn fiber residue (CFR). Corn fiber residue (CFR) is a byproduct from corn starch processing and constitutes an abundantly available agro-industrial residue, which is about 20% of the milled corn seed. It represents the tough and resistant outer layer of corn core and it has arabinoxylan, cellulose and starch as main constituents. These C-5 and C-6 carbohydrates are potentially substrates for upgrading to be used in several industries for food, fuel, paper and others products. It is estimated that the production of corn fiber residue in Brazil and U.S. in 2013 was 14.5 and 54.8 million tons, respectively, based on maize production in 2012/2013 in these countries (Deagro/FIESP, 2013).

This study aimed to: Evaluate the interaction mechanism between iron ore and depressant to try to clarify this mechanism and develop a new sustainable potential biopolymer as depressant for iron ore reverse cationic flotation that could be more selective than starch.

CHAPTER 1

EFFECT OF CHAIN LENGTH AND PRESENCE OF REDUCING END GROUP OF DEPRESSANT DURING FLOTATION PROCESS

ABSTRACT

Iron ore flotation is a separation process used in mineralogy to separate iron compounds from other components present in the ore. Most of Brazilian mining uses the reverse cationic flotation process as the reference to deal with the variation in iron ore quality and to efficiently remove the main contaminant known as gangue. The main objective of this study was to investigate the effect of starch chain length, based on dextrose equivalent quantification (DE), and the presence of reducing end group (REG) in starch during the flotation process. Waxy starch, dextrin and soluble starch were chemically modified to analyze the chain length (by hydrolysis with HCl) and REG effect (by reduction of this group with sodium borohydride). Results were compared on the basis of: a) iron content in concentrate, b) iron and mass recovery and c) iron loss. In addition, DRIFT and Raman spectroscopy were performed in order to obtain information about interaction mechanism between depressant and iron ore. It was found that the polymeric chain influences the mass and iron recovery, with these parameters tending to be worse with a decrease in molecular weight of the depressant. Reducing end groups also had an effect on the process, when they were present in high amounts (DE = 10.6%). The DRIFT and Raman spectroscopy not showed relevant information about interaction mechanism.

Keywords: Iron ore, reverse cationic flotation, starch, flotation depressant, selective process

1. INTRODUCTION

The method of concentration by flotation is considered the most important method in iron ore separation. For ore with low iron content, it is necessary to perform concentration operations such as flotation, which aim to increase the iron content and minimizing the SiO_2 and Al_2O_3 contents in the flotation concentrate. Most of Brazilian mining uses the reverse cationic flotation process as the reference to deal with the variation in the iron ore quality and to efficiently remove the main contaminant known as gangue. In this process, some of the major standard chemical reagents used include gelatinized starch as depressant and amines as collector (Kar et al, 2013; Abdel-Khalek et al, 2012; Turrer and Peres, 2010; Pavlovic and Brandao, 2003).

Zeta potential measurements show that around pH 5,0 is the condition in which there is the greater difference of charge between the minerals hematite and quartz (Lopes and Lima, 2009). But the differences are not enough for a selective flotation and the differences between charges alone not determined the flotation conditions. For a selective process, corn starch and amines, are used as a depressant for hematite and a collector for quartz respectively. With the addition of these reagents the best separations of minerals occur in pH around 10,5, because of the reagents ionization, chemical interactions and bubbles formation (Kar et al., 2013; Lima et al., 2013; Stapelfeldt and Lima, 2001).

It is reported that starch interacts with both quartz and hematite, but the interaction between starch and hematite is stronger, preferably at slightly alkaline pH (Kar et al., 2013; Lima et al., 2013; Severov et al., 2013; Stapelfeldt and Lima). Moreover, it cannot be disregarded the possibility of interaction between collector and depressant and its synergistic effect on flotation process, for example, the formation of clathrates, where molecules of collector are in inside the helix of amylose molecule (Lima et al., 2013; Khosla et al., 1984).

Starch is a natural polysaccharide comprising two main components, amylose and amylopectin and it can be extracted from several vegetal species, such as corn, manioc, potato, wheat, rice, arrowroot, etc. Normal starches, such as corn, rice, wheat and potato, contain 70 – 80% amylopectin and 20 – 30% amylose. Amylose is a straight chain polymer of α-D-(+)- glucopyranose units linked by C1-C4, whereas amylopectin is branched containing also α-1,4 linkages and α-1,6 linkages of α-D-(+)-glucopyranose units, responsible for branching (Bertolini, 2010; BeMiller & Whistler, 2009). In mineral industries, the corn starch is the most commonly used depressant. The structure of amylose and amylopectin is shown in Figure 1.

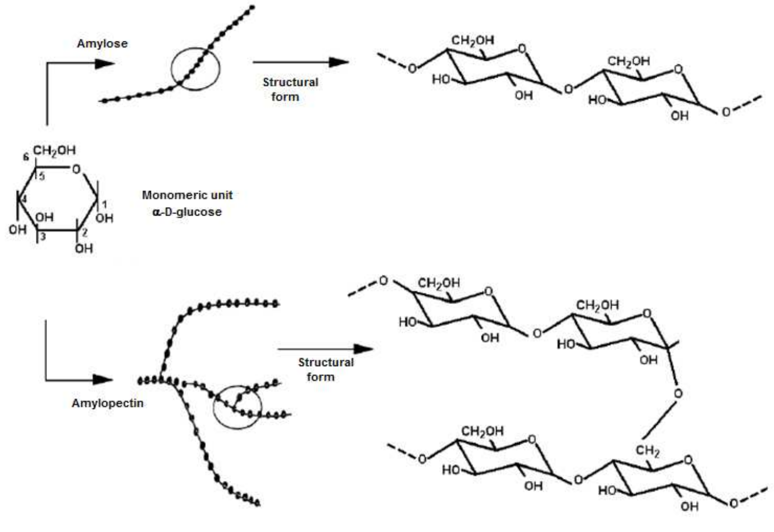

Figure 1. Chemical structure of amylose and amylopectin.

Carbohydrates, in general, have a reducing end group (REG) at the end of molecule chain. Each amylopectin and amylose molecule carries only one REG, which is a hemiacetal group at the end of the polymeric chain that can reduce some substances, like metal ions, and suffer oxidation in aqueous solutions (Figure 2) (Solomons and Fryhle, 2009).

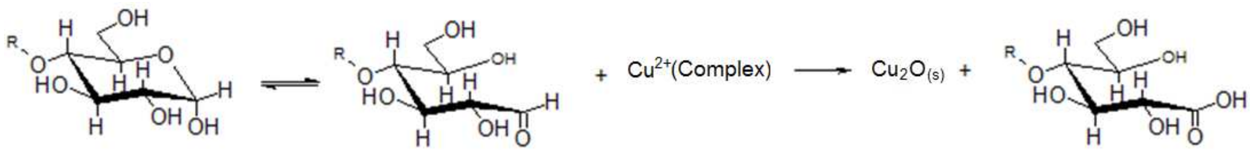

Figure 2. Equilibrium between cyclic and open structure of starch monomeric unity and oxi-reduction reaction of REG with a metal ion.

The arrangement of amylopectin and amylose molecules generates the starch granule and the proportion of amylose and amylopectin and their physical organization are responsible for the physicochemical properties of starch. Under polarizing microscope observation, starch granules show a dark birefringence cross (“Maltese cross”), which is characteristic of a spherulitic macromolecule organization inside each granule. For liberation of amylose and amylopectin in solution, gelatinization is important. Gelatinization corresponds to irreversible disruption of molecular order within the starch granules observed when starch granules are dispersed and heated in water (above 60°C) (Bertolini, 2010; BeMiller & Whistler, 2009).

In the process of separating minerals by flotation, addition of reagents known as depressants, or which make the surfaces of certain minerals more hydrophilic, have fundamental importance. To understand selectivity, from the chemical point of view, one needs to understand the interaction between the surface and the mineral reagents. For iron ore, this investigation focuses on the quartz/hematite system using starch as a depressant agent (Severov et al, 2013; Kar et al, 2013; Pavlovic and Brandao, 2003).

Numerous mechanisms for the adsorption of starch and related polysaccharides onto minerals have been proposed. Because of the presence of a large number of hydroxyl groups on the starch and mineral surfaces, hydrogen bonding between starch and mineral surface has been proposed as a mechanism (Kar et al, 2013; Abdel-Khalek et al, 2012; Liu-yin et al. (2009); Subramanian and Natarajan, 1988; Balajee and Iwasaki, 1969). Other studies propose an electrostatic interaction (Neis and Kiefhaber, 1980; Balajee and Iwasaki, 1969), complexation (Weissenborn et al, 1995; Khosla et al, 1984) and even acid/base interaction as the key association mechanism (Liu et al, 2000).

Abdel-Khalek et al. (2012) investigated several starches (wheat, corn, rice, potato and dextrin) as depressants for hematite evaluating the selectivity of the separation process through zeta potential, adsorption measurements as well as flotation tests. The authors concluded that selectivity of the separation process is strongly affected by the type of starch used, and the best results were obtained with corn starch or wheat starch. The authors proposed that the interaction between corn starch and hematite is an intermolecular interaction since Fourier Transform Infrared Spectroscopy (FTIR) measurements exhibited few differences when compared with the ones of wheat or corn solutions. They concluded that the depressing action of starch occurs due to its strong adsorption to the mineral surface.

In order to investigate the interaction mechanisms between dextrin and mineral surfaces, Liu and Laskowski (1989) studied the floatability, wettability and adsorption tests with modified quartz. The quartz samples were either made hydrophobic by methylation, or lead-coated, or subjected to both forms of surface modifications. They observed that surface hydrophobicity does not contribute significantly to the adsorption of dextrin. But the adsorption depends critically on the presence of metal ionic species on solid surfaces and seems to result from the chemical interaction between dextrin and the surface metal hydroxide groups. Based on this evidence, it was proposed that the lead forms a five-membered ring complex via the oxygen atoms attached to C-2 and C-3 in the starch molecule.

A similar proposition was made by Weissenborn in 1996. According to this author, the complex formation between starch and hematite occurs among hydroxyl groups of C2 and C3 from glucopyranose unit adjacent to the starch molecule, forming an eight-membered ring as depicted in Figure 3.

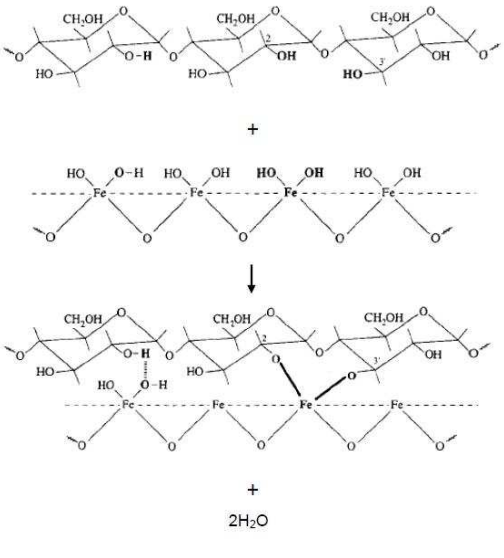

Figure 3. Hydrogen bond interaction and complex formed by eight atoms among starch and hematite according to Weissenborn, 1996.

For the same starch/hematite system, Ravishankar and coworkers in 1995 found that the distance of linkage between oxygen atoms of C1 and C2 (2.85 Å) and the distance of adsorption centers of hematite (2.852 Å) are very similar. They proposed another complex formed by oxygen of reducing end group of C1 and hydroxyl group of C2 from the same glycoside unit of starch and adsorption centers of hematite, forming a six-membered ring (Figure 4).

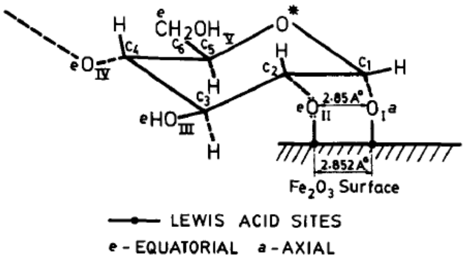

Figure 4. Complex involving the reducing end group of starch and hematite proposed by Ravishankar et al, 1995.

Recently, Kar and coworkers (2013) found a shift of peaks by FTIR spectroscopy in a study of adsorption with hematite and starch, which supported the bonding of hydroxyl oxygens of starch with hematite. The adsorption study indicated better adsorption of all starches at slightly alkaline pH also supported by the zeta-potential measurement. They proposed an interaction involving the hydroxyl groups of C1 and C2 of starch molecules (Figure 5).

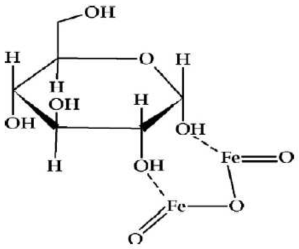

Figure 5. The structure of hematite-starch interaction according to Kar et al, 2013.

Most studies show that the adsorption mechanisms of polysaccharides are very complicated and involve a number of theories. This work was developed in order to evaluate the effect of starch chain length and the presence of REG in starch during the flotation process to add information in investigations and to clarify the mechanism of interaction between the depressant and iron ore.

2. MATERIALS AND METHODS

2.1. Materials

The iron ore used in all experiments of this work was from a mine in the Iron Quadrilateral in Minas Gerais, Brazil. The iron ores were characterized in terms of granulometry and iron, quartz and traces elements content. The granulometry was determined using vibrating sieves with the openings: 1000 µm, 500 µm, 250 µm, 125 µm, 63 µm and 45 µm for 10 min.

Identification of the crystalline phases was determined using the powder method using an X-Ray diffractometer (PANalytical, X'Pert PRO with X'Celerator detector) by comparing the X-Ray Diffraction (XRD) pattern of the sample with the banks of the ICDD data PDF2 - International Centre for Diffraction Data (2003) and PAN ICSD - PANalytical Inorganic Crystal Structure Database (2007). The contents of hematite, quartz and trace elements (Al_2O_3, P, Mn, TiO_2, CaO, MgO) were determined by X-ray fluorescence (XRF) Axios Advanced – Panalytical by quantitative analysis in melted sample with anhydrous lithium tetraborate.

The iron ore density was determined by pycnometer method described in Appendix 1.

Dextrin and waxy starch were obtained from Corn Products Brasil and soluble starch P.A. was purchased from Labsynth Ltda. The industrial starch used was provided by a mining company.

Dextrins are a carbohydrate group of low molecular weight produced from acid hydrolysis of starch. To form dextrin, the starch is submitted to a process of hydrolysis that breaks the large chains of starch. The resultant material is dextrin, a simple carbohydrate with low molecular weight (Huber and BeMiller, 2010)

Waxy starches are extracted from specific genetic varieties of corn and consist of nearly exlusively amylopectin molecules. This kind of starch is called waxy because when the corn kernel is cut, the endosperm appears shiny and waxy, although it contains no actual wax (Schwartz & Whistler, 2009).

Soluble starch is amorphous in nature and highly soluble in water and has a low molecular weight (Kar et al, 2013)

2.2. Biopolymer Chain length

Corn starch is widely used as depressant in reverse cationic flotation system of hematite/quartz (Pearse, 2005). The molar weight of amylose and amylopectin is in order of 10^5 and 10^7, respectively (Bertolini, 2010; BeMiller & Whistler, 2009). Some research shows that amylopectin is a better depressant for hematite than starch (a mixture of amylose and amylopectin) or amylose. Sometimes this result is associated with the great size of amylopectin molecules. However, there are no direct studies demonstrating this causality in the literature (Pavlovic and Brandao, 2003; Weissenborn, 1996; Pinto et al, 1992; Iwasaki and Lai, 1965). Therefore, the size of the polymer chain to be used as depressant in the iron ore flotation process may be an important parameter for the functionality of the polymer. Khraisheh and coworkers (2004) found a systematic increase in talc (mineral with unit structure of $Mg_3(Si_2O_5)_2(OH)_2$) depression when the molecular weight of carboxymethyl cellulose (CMC) was increased in their study of adsorption of CMC onto talc.

With the objective of evaluating the effect of this parameter in the flotation process, a reverse cationic flotation performance test depending on the molecule size was performed. For this, standard corn starches were used as a source of bigger polymers. Polymers with low length were produced by the hydrolysis with concentrated HCl.

The depolymerization was done in order to obtain biopolymers with 4 levels of size (1 standard and 3 hydrolyzed). For this purpose, 25g of biopolymer (dextrin and waxy starch) was swollen in 400mL deionized water at a temperature higher than 90ºC. For waxy starch it was necessary add more 300 mL of water because of the gelatinization and high consistence of suspension. The solutions were cooled to 75ºC and 4mL HCl 36% were added to the reaction mixture. The time of acid hydrolysis was varied between 1h and 5h, depending on the biopolymer, while the temperature was maintained at 75ºC. The hydrolysis was evaluated by power reducing determination, as dextrose equivalent (DE), using titrimetric analysis according to Schoorl Method (1996).

Determination of DE or degree of hydrolysis is, in effect, a determination of average number molecular weight of a hydrolyzed starch. In general, maltodextrins have a DE below 20%, however, for values below 6% the molecular weight becomes independent of this value (Fennema, 1996; Wilson et al, 1995).

2.3. Reducing End Group (REG) Modification

In order to evaluate the REG effect during flotation, the modification of REG were done by REG reduction of dextrin and soluble starch with Sodium borohydride ($NaBH_4$), based on Strumeyer (1967). $NaBH_4$ is a good reducing agent and it is very effective for the reduction of aldehydes and ketones to alcohols (Solomons and Fryhle, 2009) (Figure 6).

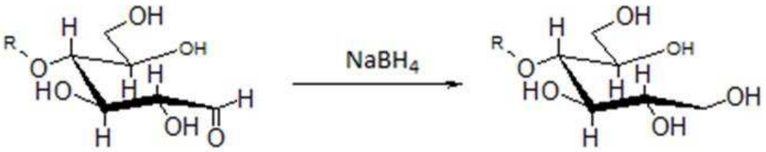

Figure 6. Reduction reaction of REG with Sodium borohydride (Solomons and Fryhle, 2009).

A 1% solution was prepared by gently boiling a suspension of 2.5 g of starch (soluble starch and dextrin) in 50 ml of water until solubilization (~60 sec) and then, the solution was cooled to 80ºC and maintained in agitation for 30 min. The solution was cooled in an ice bath, and then a previously cooled solution of 100 mg of sodium borohydride in 10 ml water was gradually added while magnetically mixing. The reaction mixture was next brought to 25 ºC by equilibrating in a water bath and was then incubated without stirring per one hour, under nitrogen atmosphere. For use, the excess sodium borohydride was destroyed with 0.1% HCl solution and quantitatively transferred to a volumetric flask (250 mL).

For study with reducing of hydrolyzed dextrins, the hydrolysis of this carbohydrate were performed as described in item 2.2. adjusting the final concentration to 5%. Then, the reductions were performed with 50mL of dextrins solutions according to described above in this item.

The reduction in REG was confirmed by power reducing determination or Dextrose Equivalent (DE) using titrimetric analysis according to Schoorl Method (1996).

2.4. Reducing Power Determination

The chemical methods used to determine contents of carbohydrate, such as starch, are based on most of carbohydrates having the power to reduce copper, silver, iron and other substances, producing colored complexes or precipitates that can be quantified. This reducing power is due to the presence of an aldehyde group at the end of carbohydrate chain (Tavares et al, 2010, Solomons and Fryhle, 2009).

The reducing end group (REG) determination was done according to the Schoorl method available from the Corn Refiners Association (Schoorl Method, 1996). The method is based on quantification of copper II ions reduced by the REG present in the starch molecules. Tartrate is used to form a soluble complex with copper and prevent the formation of cupric hydroxide (Figure 7). 20mL Fehling solution (10mL copper sulfate pentahydrate (0.24 mol.L^{-1}) and 10 mL potassium sodium tartrate tetrahydrate (173g tartrate + 50g NaOH in

500mL) are added to an erlenmeyer (250 mL) containing 20 mL of carbohydrate 1% (m/v). Then, 10 mL of deionized water is added and the mixture is heated until boiling point for 3 minutes and the boiling is maintained for 2 minutes. In this step, a red precipitate of Cu_2O is observed. The mixture is rapidly cooled to room temperature. 10mL sulfuric acid solution (28%) and 10 mL of potassium iodide solution (30%) are then added. The iodine formed is titrated immediately with 0.1M sodium thiosulfate standard solution. The difference of titration volumes among blank and sample is registered. A calibration curve was prepared using a 1% glucose solution.

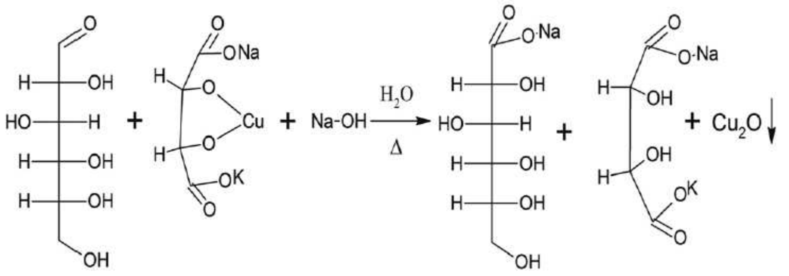

Figure 7. Reaction of the copper complex with potassium sodium tartrate and reducing end group of a carbohydrate (Tavares et al, 2010).

2.5. Flotation tests

Reverse cationic flotation performance tests were done in order to evaluate the performance of modified starches as depressants in the flotation process. All experiments were done in duplicates using a CDC lab scale flotation cell with one sample of iron ore. The homogenization and quartering of the iron ore sample were done and packs contained 790g of iron ore were separated to develop all necessary tests.

For the tests, the solids content of pulp was 50% by mass and Flotigan EDA-C etheramin from Clariant was used as collector. This amin is a mixture of isononyl ether propylamine and isononyl ether propylamine acetate. The flotation tests were performed in laboratory scale with 1200 g/t of depressant (modified starches), 100 g/t SiO_2 of collector (Flotigan EDA C) at pH 10.5. This condition was previously determined as the better condition for flotation varying the industrial starch dosage (from 400 to 1200) and the pH of flotation process (from 8.5 to 10.5) with this iron ore.

The results of iron metallurgical recovery (or iron recovery) and mass recovery in concentrate, iron and gangue content in concentrate and reject were calculated according to the method described in Appendix 1

2.6. Spectroscopic Analysis

The spectroscopic analyzes were performed at Laboratory of Molecular Spectroscopy, Institute of Chemistry – USP, in order to evaluate the interaction mechanism among iron ore components and substances used as depressants in reverse cationic flotation process.

Infrared spectra in diffuse reflectance mode (DRIFT) were obtained on a Bruker – Alpha, with optic of KBr and DTGS detector. All spectra were obtained with a resolution of 4 cm^{-1} and were resulted by the accumulation of 200 consecutive scans. No dilutions with KBr were performed to demonstrate the contribution of the organic phase, present in lower amount as compared to the ore. Spectrum of the raw iron ore also were performed without dilution in KBr to allow the direct comparison with evaluated samples in the region of interest (700 – 900 cm^{-1} e 1300 – 1800 cm^{-1}).

Raman spectra were recorded in a Raman microscope Raman Renishaw inVia Reflex equipped with CCD camera (Renishaw, 600x400 pixels); thermoelectrically cooled; the microscope coupled to the spectrometer is Leica model DM2500 M. The laser line was wavelength 632.8 nm (He-Ne, Renishaw) which was focused on the sample by a objective Leica x50 with long focal length; radiation power was kept below 0.5 mW in the sample in order to avoid thermal degradation.

3. RESULTS AND DISCUSSION

3.1. Iron ore characterization

X-ray diffraction

Figure 8 shows the XRD of raw iron ore. From these results it can be seen that the iron ore used in this work contained mainly hematite (Fe_2O_3) and quartz (SiO_2). Goethite ($Fe_2O_3.H_2O$) was present in trace amounts.

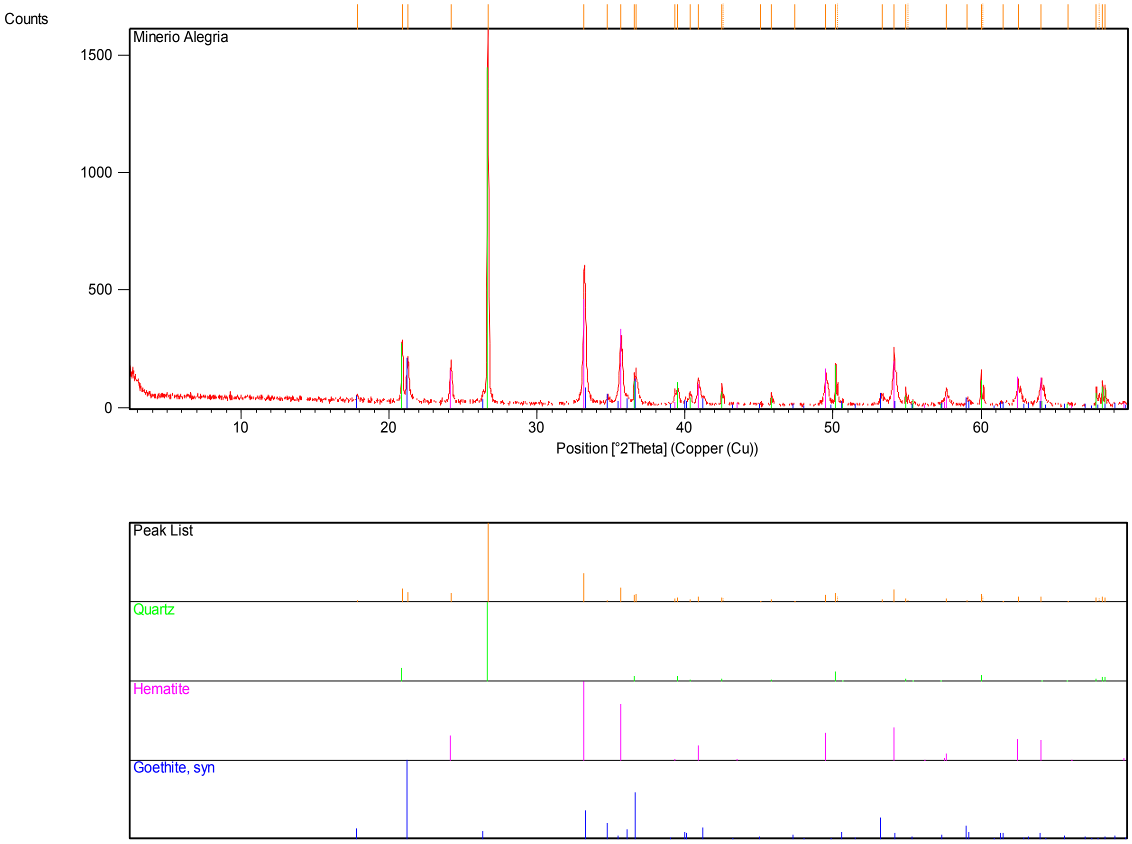

Figure 8. Spectrum of X-ray diffraction of row iron ore.

X-ray fluorescence

The composition of the iron ore was determined using XRF analysis. Table 1 shows the Hematite (represented by iron) and gangue content. It can be observed that most of the gangue content is composed of quartz (SiO_2), the other compounds represent less than 1% of the gangue.

Table 1. Iron ore characterization by XRF.

					Iron Ore					
Substance	Fe_2O_3 (Fe)	SiO_2	Al_2O_3	P	Mn	TiO_2	CaO	MgO	Mass loss at 1000°C	Total
Content (%)	69.64 (48.7)	28.09	0.28	0.05	0.04	0.07	0.01	0.13	1.38	99.69

Iron ore density and particule size

The density of iron ore determined by pycnometer method was 3.95 g.mL^{-1}.

Particle size has as influence on the hydrodynamics of pulp (bubbles dispersion, solids suspension, collision and adhesion between particles and air bubbles) and it is an important parameter in the flotation process (Li and Schneider, 1993). The best range of iron ore particle size for flotation is reported to be between 10 and 300 µm (Lima and Valadão, 2008). Good performance is dependent on flotation conditions such as reagent dosages, pH and pulp concentration. The literature suggests that the best results of the flotation process for iron ore can be achieved using particles smaller than 150 µm (Amorim, 2013; Carvalho e Martins, 2005). Figure 9 shows the iron ore distribution curve of particle size. It can be observed that the entire sample is below 300 µm and most (80%) of the particles are under 125 µm in size, and therefore suitable for flotation.

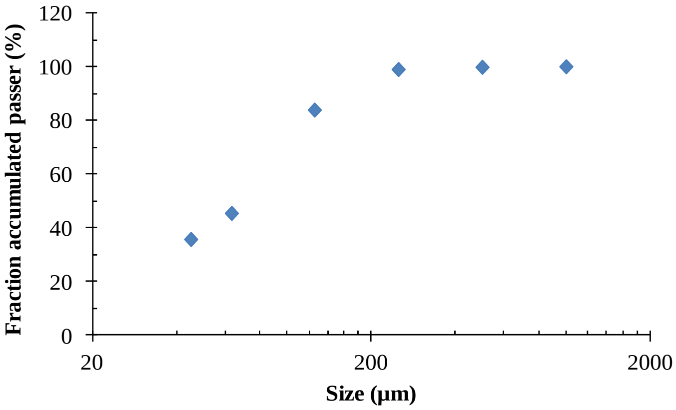

Figure 9: Particle size distribution determined by classificatory sieves.

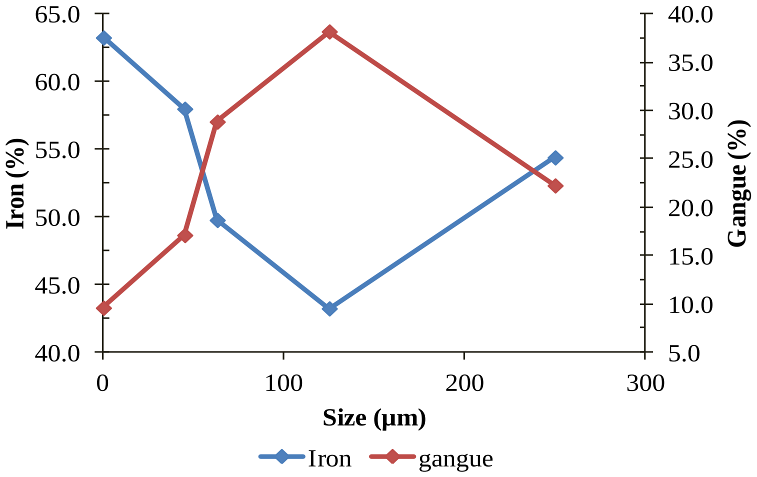

Figure 10. Percentage of iron and gangue content in each fraction of size classification.

Figure 10 shows that most of greater particles (125 µm) are composed by gangue and the most of smaller particles (< 45µm) are composed by hematite. The values above 250 µm were not shown because the amount retained was not enough to perform chemical analysis.

3.2. Evaluation of depressant dosage and pH of flotation test

Although the industrial conditions are 1200 g/t of depressant dosage, 100 g/tSiO_2 of collector dosage at pH 10.5, the flotation test was performed varying the depressant dosage and pH to assure the best conditions in the flotation test. The collector dosage was not evaluated.

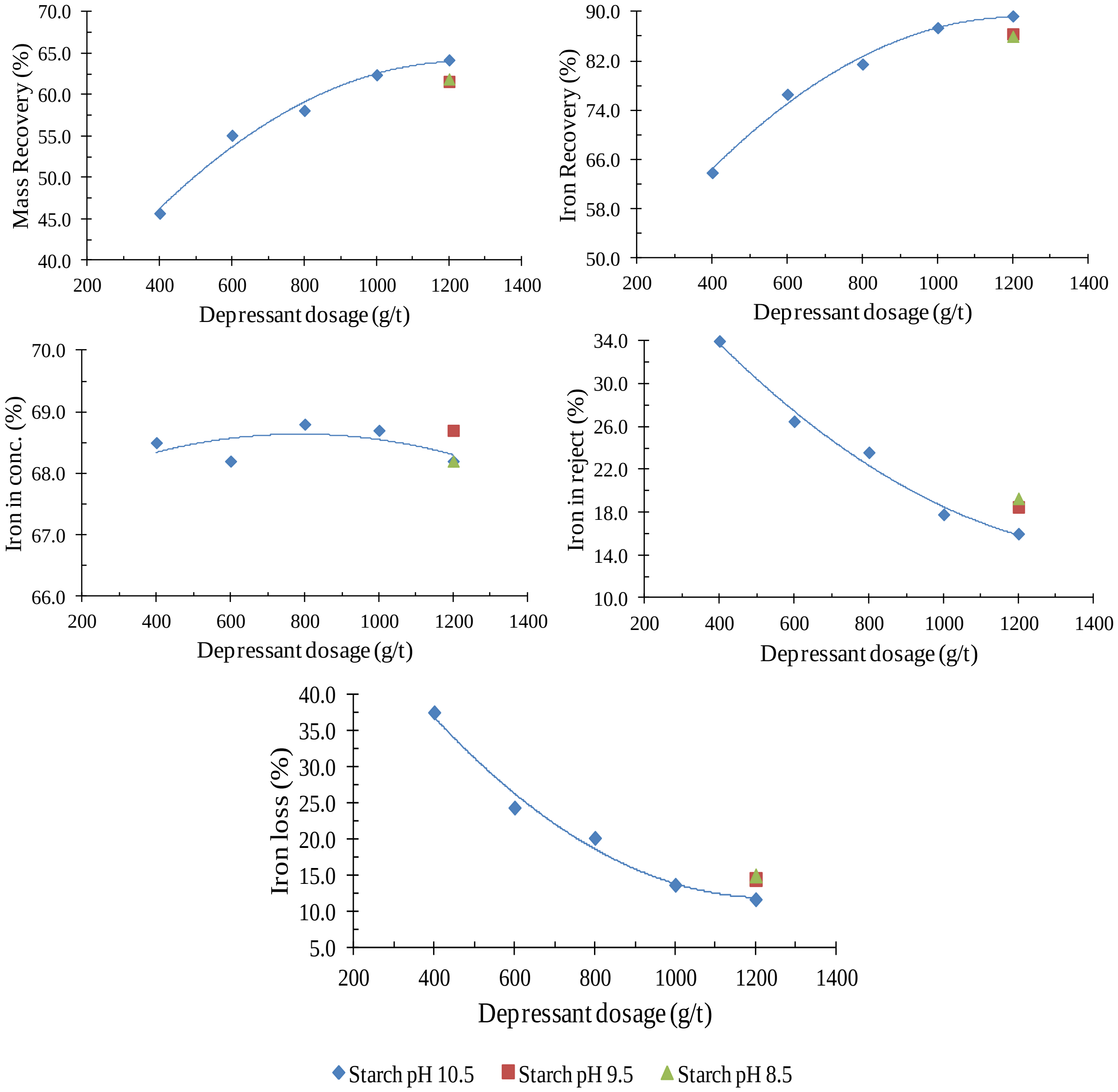

Figure 11. Results of iron and mass recovery, iron content in concentrate and reject and iron loss percentage of flotation test with several depressant dosages and pH values. Flotigan EDA-C it was used as collector (100 g/tSiO_2).

Figure 11 shows the performance of the flotation test with different dosages of industrial starch and different pH in the flotation process. First, a curve with different dosages of starch at pH 10.5 was performed. It can be observed that the iron content in concentrate has few variations with different dosages of depressant, but lower iron loss and better iron and mass recovery were observed with increasing dosage of depressant. So, the best dosage of industrial starch was found to be 1200 g/t.

Then, for 1200 g/t of depressant dosage, pH 8.5 and 9.5 were evaluated for comparison with results of flotation test with pH 10.5. The results showed that iron recovery, mass recovery, iron content in reject as well the iron loss were worse for lower pH values. Although the iron content in concentrate was slightly better at pH 9.5, the other parameters have better results at pH 10.5 and this value was chosen to be the best value for this flotation process, as in the industrial process.

3.3. Reducing Power Determination

For reducing power or reducing end group determination, a calibration curve based on dextrose equivalent was prepared, because the reaction is dependent on the used conditions, such as time and temperature (Tavares et al, 2010).

Figure 12 shows the calibration curve of DE determination volume using a 1% glucose solution and 0.1M sodium thiosulfate solution. The graph is the difference between glucose titer and the average blank titer versus the mass of glucose with good uniformity and a correlation of the data more than 99%.

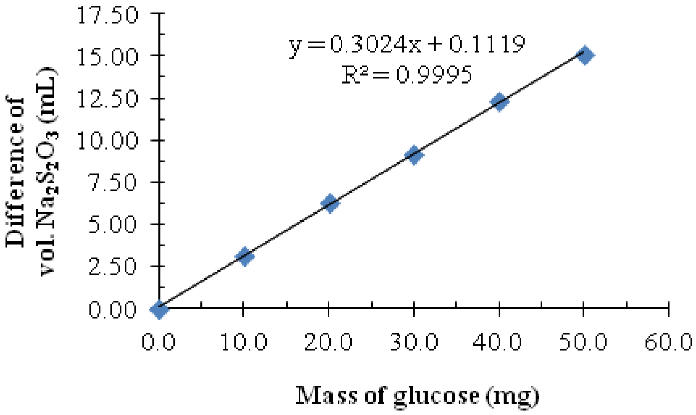

Figure 12. Calibration curve for dextrose equivalent determination.

The mass of glucose can be calculated from the calibration curve and the result of reducing power can be found as Dextrose Equivalent using the equation bellow:

$$\text{DE (\% glucose)} = \frac{\text{mass of glucose (mg)}}{10 \text{ x mass of sample (g)}}$$

3.4. Chain length effect

To evaluate flotation performance as a function of the biopolymer chain length, dextrin and waxy starch were hydrolyzed with hydrochloric acid for different times and the degree of hydrolysis was quantified using REG determination. According to BeMiller and Whistler (2009), the size of the small particle starch varies with the conditions of the acid hydrolysis. The more extensive the acid hydrolysis, the smaller are the particle sizes produced. Figure 13 shows the reduction of molar weight successfully, as the greater number of reducing end groups, smaller is the size of the carbohydrate polymer chain. Both curves showed good uniformity and a correlation of the data more than 97% and 99% for dextrin and waxy starch hydrolysis, respectively.

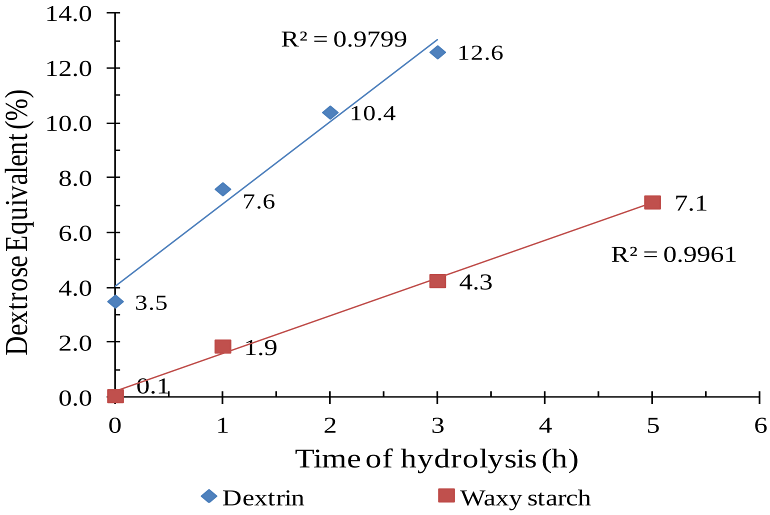

Figure 13. Dextrose Equivalent of hydrolyzed waxy starch and dextrin.

The results of the performance tests with waxy starch and dextrins of various sizes are displayed in Figure 14.

The results showed that for both starches the molecular weight negatively affected the mass recovery. It was observed that for similar values of DE of waxy starch (4.3 and 7.1%) and dextrin (3.5 and 7.6%) the results for mass recovery were different, suggesting that molecular size alone does not explain the flotation performance in mass recovery (Figure 14a).

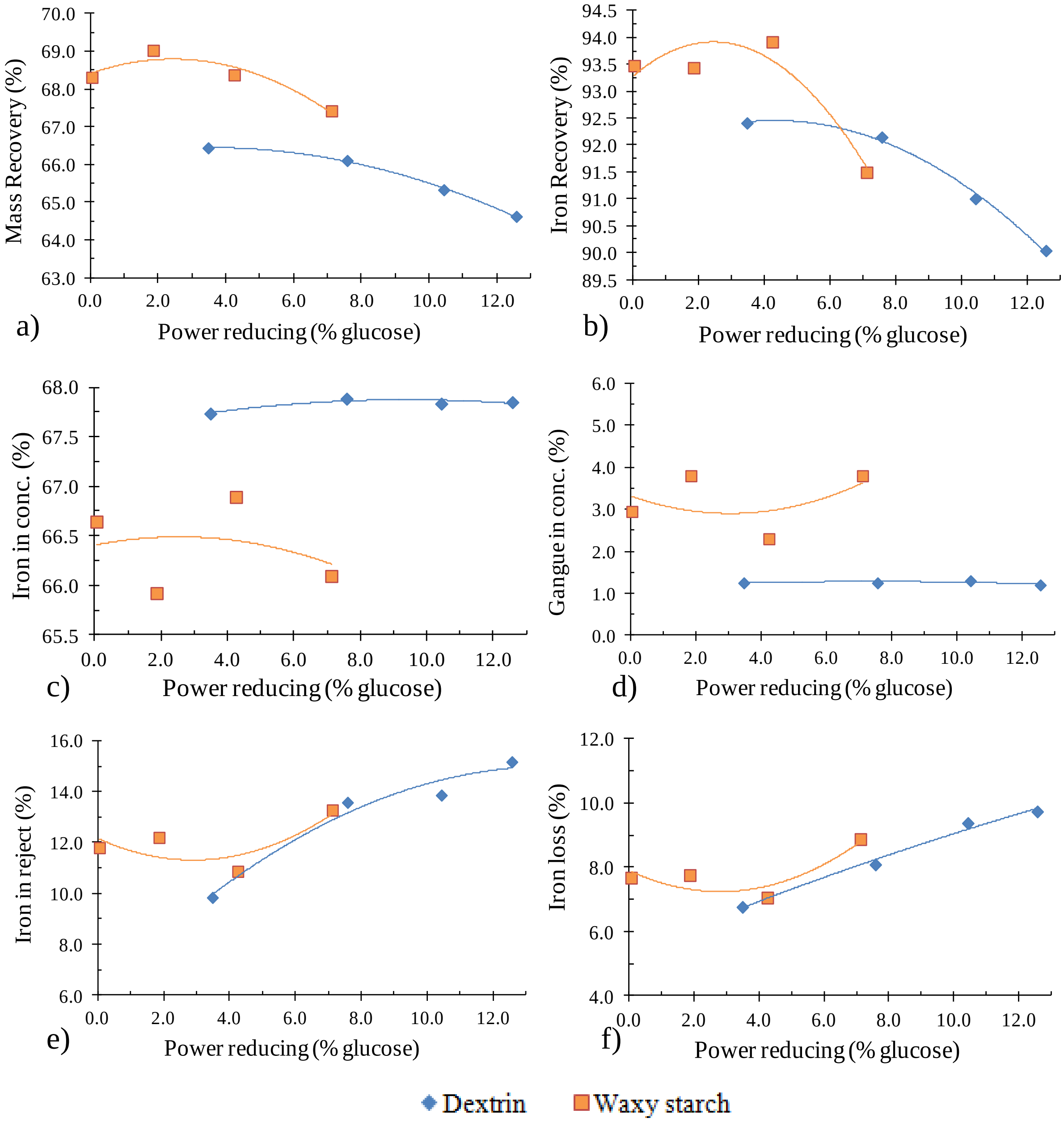

Figure 14. Results of performance flotation with hydrolyzed waxy starch and dextrin. Conditions of flotation: 1200 g/t depressant, 100g/tSiO_2 EDA-C, pH10.5.

Iron recovery is an important parameter to evaluate in a flotation test, as the higher the value of this result, the better it is for the industry, as it demonstrates the mass of iron it is possible to recover. In Figure 14b it can be observed that there is a tendency to improve iron recovery for waxy starch with increase of DE, however, there was a larger drop when DE was 7.1%, giving a similar result to dextrin with DE of 7.6%.

In general, the results show a decrease in the amount of iron recovery with increase of DE, that is, with the decreasing molecular weight (Figure 14b) as observed for mass recovery. Figure 15 shows the good correlation of iron recovery and mass recovery, which is mainly apparent for hydrolyzed dextrin groups that are molecules of smaller size than hydrolyzed waxy starch groups.

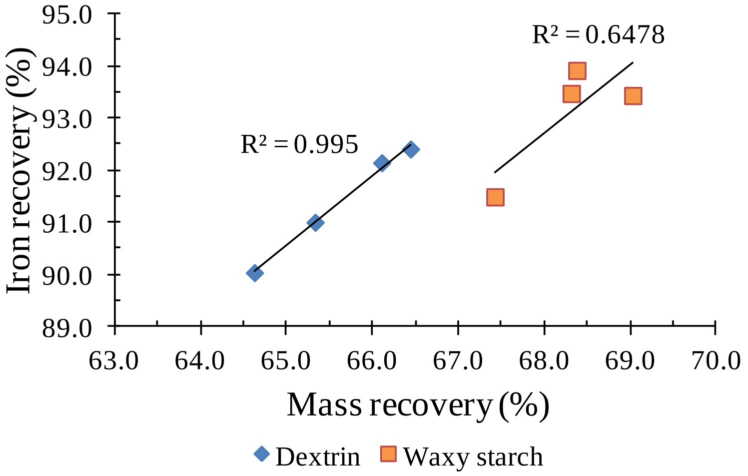

Figure 15. Correlation graph between iron recovery and mass recovery. Conditions of flotation: 1200 g/t depressant, 100g/tSiO_2 EDA-C, pH10.5.

Concerning to iron content in concentrate, the variation of depressant size shows indifferent in this parameter. It can be observed in Figure 14c that the iron content in concentrate maintained relatively constant with DE variation, for both hydrolyzed starches. In addition the results from waxy starch were much dispersed, showing a non correlation among these values. The waxy starch curve had better performance for mass and iron recovery than dextrin, however, dextrin have demonstrated ability to obtain larger amounts of iron in concentrate than waxy starch. The gangue content in concentrate has the same profile that iron in concentrate and it was greater for waxy starch than dextrin. The flotation of iron ore should be able to produce a concentrate for the blast furnace with quartz content lower than 2.0% (DNPM, 2009). For waxy starch, all values of gangue (mainly composed of quartz) in concentrate were greater than 2.0% (Figure 14d).

In addition, the iron content in reject and iron loss increased with decreasing polymer chain size, being this effect more pronounced in dextrin molecules (Figures 14e and 14f). This increase is observed in waxy starch with DE = 7.1 %. Both parameter (Fe_{rej} and Iron loss) have the same profile because the iron loss is calculated from iron content in reject and is directly proportional for this parameter. In general, the iron loss tended to increase with decreasing of molecular weight, including the similar values of DE for waxy starch and dextrin, when iron loss for waxy starch and dextrin were 7.1 and 6.8, respectively, for DE near 4% and, 8.1 and 8.9 for DE near 7% suggesting the great correlation among molecular size and iron loss (Figure 14f).

From studies with hydrolyzed starches showed in Figure 14 the molecular weight is not the unique parameter responsible for good performance in flotation process, as was to be expected, mainly for molecules with DE smaller than 4% approximately. However, the hydrolysis study showed that lower molar mass is worst for flotation process, mainly for molecules with DE greater than 4%, approximately, suggesting the importance of molecule size of depressant in flotation process performance.

3.5. Reducing End Group (REG) Effect

Several hypotheses regarding polysaccharide adsorption mechanism have been proposed, for example, hydrogen bonding, chemical complexation and acid/basic interactions (Kar et al, 2013; Severov et al, 2013; Liu-yin et al. (2009); Pavlovic and Brandao, 2003; Liu et al., 2000; Weissenborn, 1996) Recent studies have suggested the involvement of C1 from starch as being of great importance for the mechanism of interaction depressant/mineral through zeta potential, adsorption measurements and spectroscopic techniques (Kar et al, 2013; Pavlovic and Brandao, 2003; Ravishankar et al. 1995). Although the free C1 in a carbohydrate molecule is the carbon atom present in REG, in literature there is no study involving the REG in mechanism interaction among mineral/depressant.

Therefore, to evaluate the REG effect on flotation process, dextrin and soluble starch were reduced and evaluated by flotation performance test. Table 2 shows the value of REG for these normal and reduced polysaccharides.

Table 2. REG value, in % of glucose, for polysaccharides and reduced one.

Polysaccharide	REG (% glucose)	REG of reduced polysaccharide (% Glucose)
Dextrin	3.5	0.1
Soluble Starch	3.4	0.2

Figure 16 shows the results of flotation tests with carbohydrates and reduced carbohydrates. It can be observed that there is no significant variation in test results with dextrin and soluble starch and reduced ones.

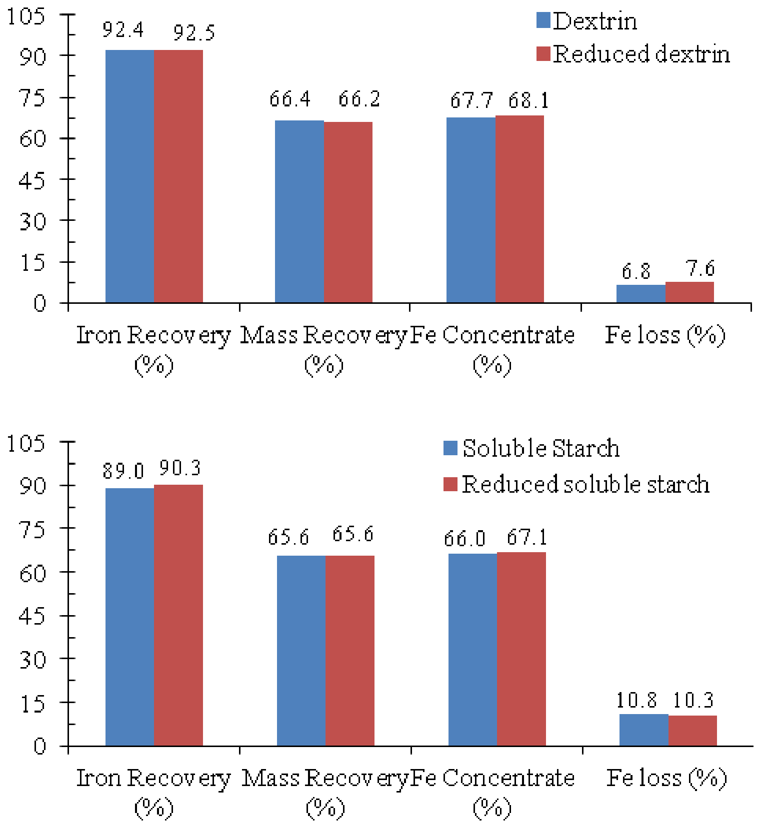

Figure 16. Results of flotation test with dextrin and soluble starch and these carbohydrates reduced. Conditions of flotation: 1200 g/t depressant, 100g/tSiO_2 EDA-C, pH10.5.

To evaluate the REG effect with several REG content, dextrin was hydrolyzed using hydrochloride acid for 1, 2 and 3 hours. After, the hydrolyzed dextrins were reduced with sodium borohydride ($NaBH_4$). Table 3 shows the DE value of dextrin before and after reduction.

Table 3. REG value, in % of glucose, for hydrolyzed dextrin and reduced hydrolyzed dextrin.

Time of hydrolysis of dextrin (h)	REG of hydrolyzed Dextrin (% glucose)	REG of reduced hydrolyzed dextrin (% Glucose)
0	3.5	0.1
1	6.5	0.6
2	9.2	0.6
3	10.6	0.8

Results of flotation test with normal and reduced dextrins are showed in Figure 17. The iron recovery and iron loss results shows the presence of REG effect starts appear when this group is aplenty (Figure 17a and 17c), indicating that the absence of the hemiacetal group can be bad for the flotation process, agreeing with Ravishankar et al (1995) and Kar et al (2013). The results of mass recovery and iron in concentrate (Figure 17b and 17d) showed fewer differences, but also show that REG affects these parameters. Gangue in concentrate tented increase with the reduced dextrin (Figure 17e). For both the reduction was worst for flotation performance.

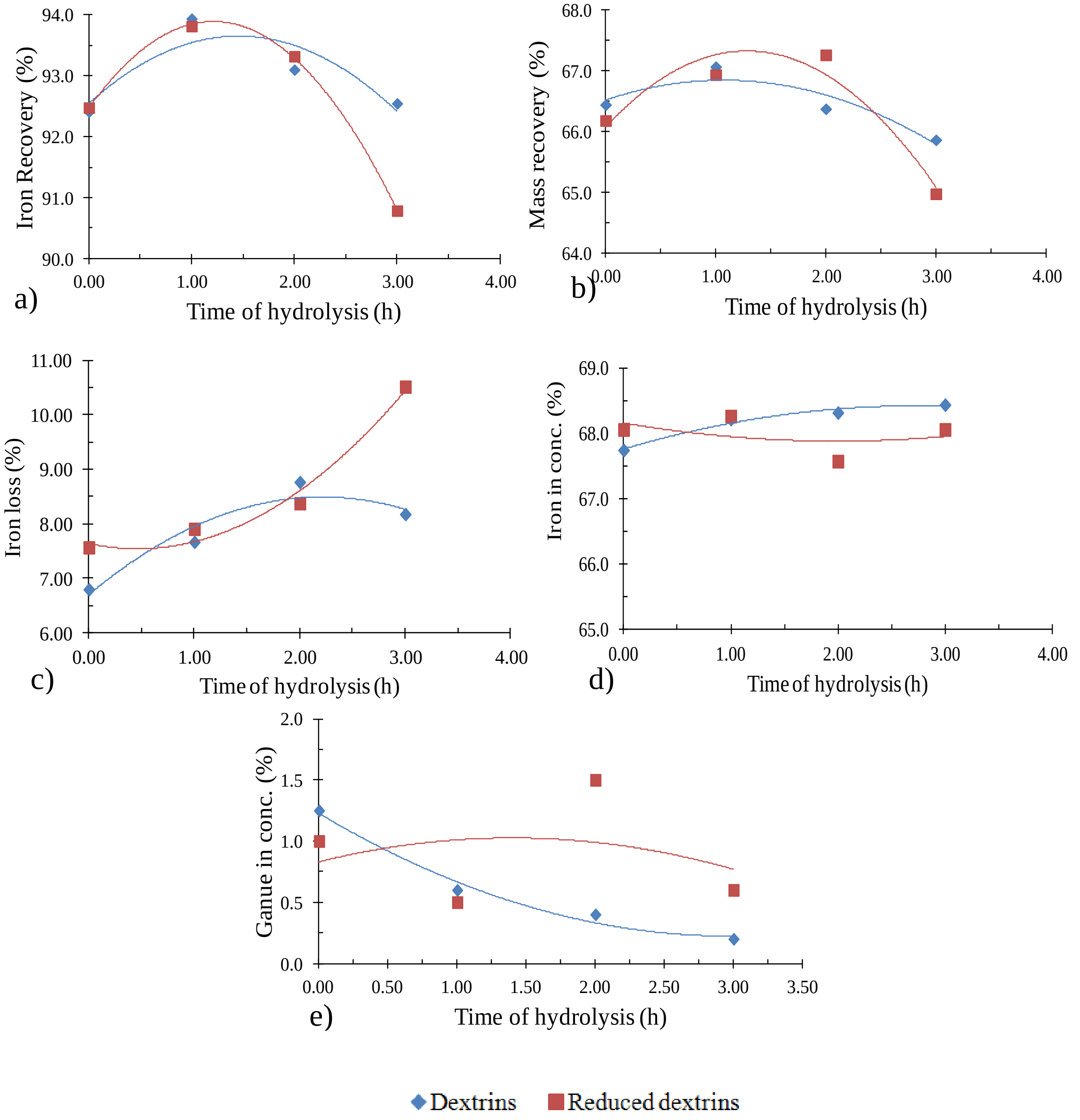

Figure 17. a) Iron recovery, b) Mass recovery, c) Percentage of iron loss, d) iron in concentrate and e) percentage of gangue in concentrate from results of performance flotation with hydrolyzed and reduced dextrin. Conditions of flotation: 1200 g/t depressant, 100g/tSiO_2 EDA-C, pH10.5.

Once the reduction of REG leaves the final glucoside unit in open form, the trend of worse flotation results with reduced dextrins showed in Figure 17 agree with the proposed by Ravishankar et al (1995) and Kar et al (2013) that the linkage among hematite and starch involve the hydroxyl group in α-position of C1 from cyclized unit. However this is just observed for smaller moleculer, where the REG is aplenty, and not with commonly used biopolymers, where DE value is very small.

Based on these results, it can be observed that REG presence in depressant agent has no significant influence on the flotation process, as discussed before, this effect starts appear in smaller molecules (DE=10.6%).

3.6. Spectroscopic Analysis

Flotation tests with industrial corn starch, waxy starch, soluble starch and dextrin as depressant were performed and the reject and concentrate samples were evaluated by spectroscopic analysis.

Table 4 summarizes the flotation test results with several starches (industrial corn starch, waxy starch, soluble starch and dextrin). It can be notated some differences in flotation test parameters varying the depressant. The waxy starch showed better results of iron and mass recovery than other starches agreeing with several authors that found better results of recovery hematite using amylopectin than starch (amylose and amylopectin) (Pavlovic and Brandao, 2003; Weissenborn, 1996; Pinto et al, 1992). However, the iron content in concentrate it was low (66.5%) and gangue in concentrate it was high (2.8%) for this depressant. The best results for these parameters (iron and gangue content in concentrate) are for industrial corn starch used as depressant.

Table 4. Results of flotation test using waxy starch, industrial corn starch, soluble starch and dextrin as depressant.

	Iron recovery (%)	Mass recovery (%)	Iron in concentrate (%)	Iron loss (%)	Iron in reject (%)	Gangue in concentrate (%)
Industrial corn starch	89.3	64.2	68.2	11.7	16.0	0.6
Waxy starch	93.3	68.3	66.5	7.7	11.8	2.8
Soluble starch	89.0	65.6	66.1	10.8	15.3	3.9
Dextrin	92.4	66.4	67.8	6.8	9.8	1.3

Conditions of flotation: 1200 g/t depressant, 100g/tSiO_2 EDA-C, pH10.5.

Infrared Spectroscopy - Diffuse Reflectance Infrared Fourier Transform (DRIFT)

DRIFT spectra of raw iron ore, reject and concentrated samples of flotation tests were carried out and the spectra are shown in Figure 18 through 20. The axis of intensities was reversed for all spectra, so that the reflectance increases from top to bottom in the axis.

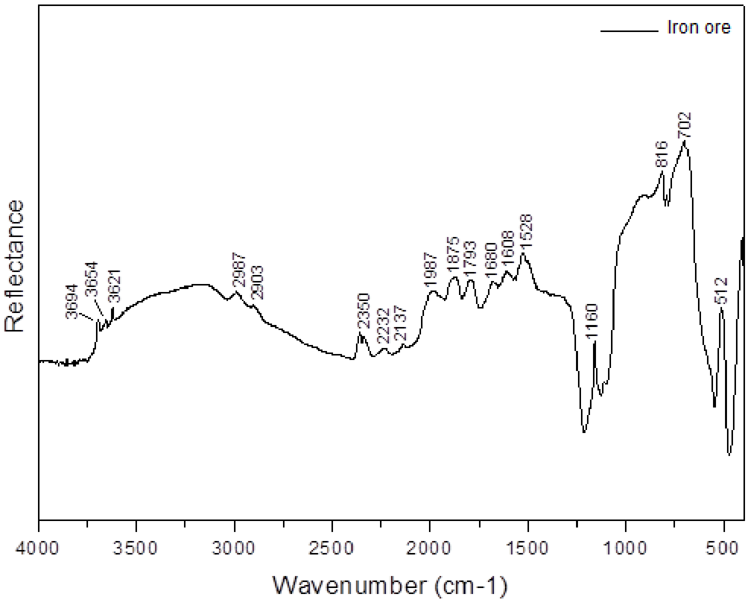

Figure 18. DRIFT spectrum of raw iron ore.

The raw iron ore is a mixture of several compounds, but mostly composed by quartz and hematite. Some characteristic bands of these two minerals can be identified in spectrum of Figure 18. It can be observed that the spectrum of raw iron ore have a similar profile of quartz spectrum in all spectral region obtained by Severov et al (2013). The bands between 950 and 1200 cm^{-1} are similar to bands present in quartz spectrum due several bonds involving Si atom (Henriques, 2012; Panda et al. 2011). But it also is observed a contribution of hematite in 1528 cm^{-1} and in the region between 700 and 1000 cm^{-1}, comparing the Figures 18 and 20.

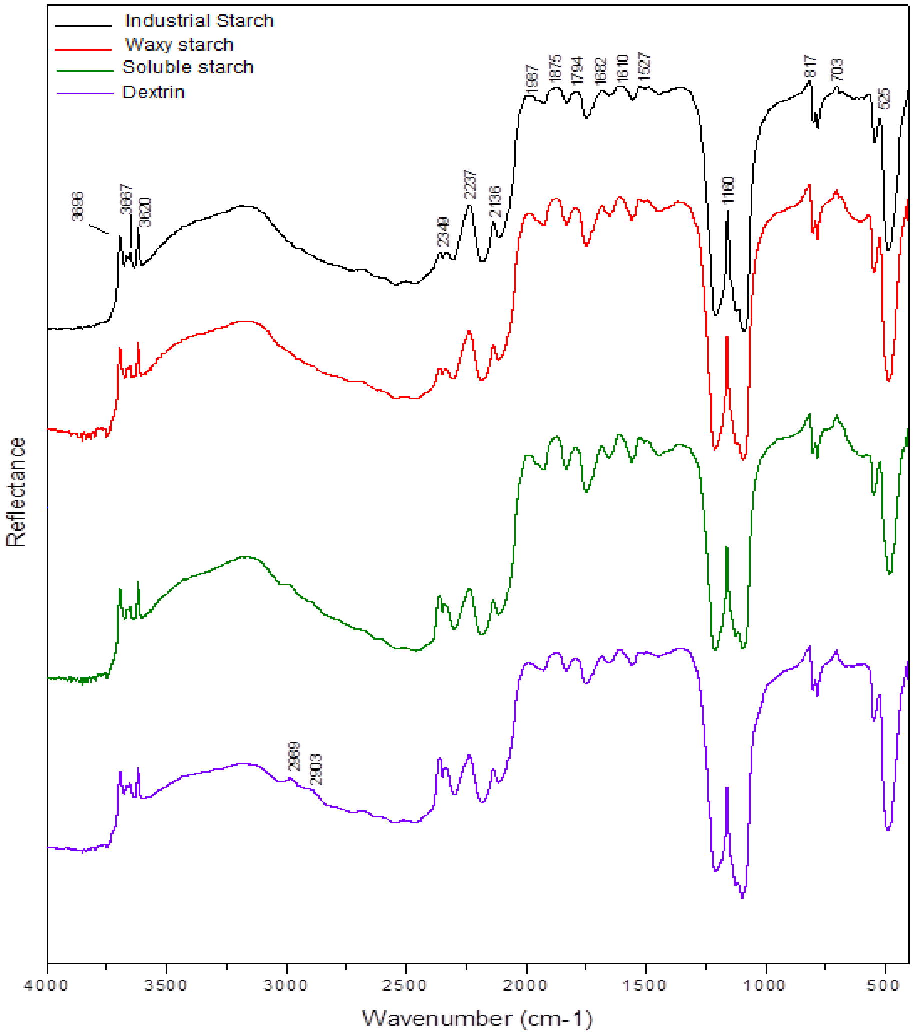

Figure 19. DRIFT spectra of reject samples from flotation tests using industrial starch, waxy starch, soluble starch and dextrin as depressant.

Figure 19 shows the DRIFT spectra of reject samples from flotation tests using industrial starch, waxy starch, soluble starch and dextrin as depressant. For these samples is expected little contribution depressants and great of floating agent. Since the efficiency of iron ore enrichment after flotation is attaches to the selective interaction between depressant and iron ore. Thus, silicates (typified by quartz) have a higher chemical affinity for floating agent which would modify the surface leaving it hydrophobic; so, the gangue could be removed with the aeration of system.

Indeed, the spectral changes reflect the least amount of hematite in the reject, as can be observed by the decrease in intensity of band at 1525 cm^{-1} in the spectra of reject samples which, as will be seen in Figure 20, corresponds to a vibration of hematite (α-Fe_2O_3).

Except for changes in the profile of the broad band between 2500 and 3500 cm^{-1}, consistent with the presence of an amine (even at low concentration) and the change in the amount of iron oxide (the reject is poor in iron oxide such as expected), it was not observed spectral changes that can be unambiguously associated with the interaction between depressant and quartz. Because the amount of depressant is small and the spectral pattern is dominated by the components of the ore.

Figure 20 shows the DRIFT spectra of concentrate samples from flotation tests using industrial starch, waxy starch, soluble starch and dextrin as depressant. The spectrum of pure hematite were recorded for comparison, the characteristic bands of hematite appear around 500 and 700 due Fe-O bonding (Kar et al. 2013).

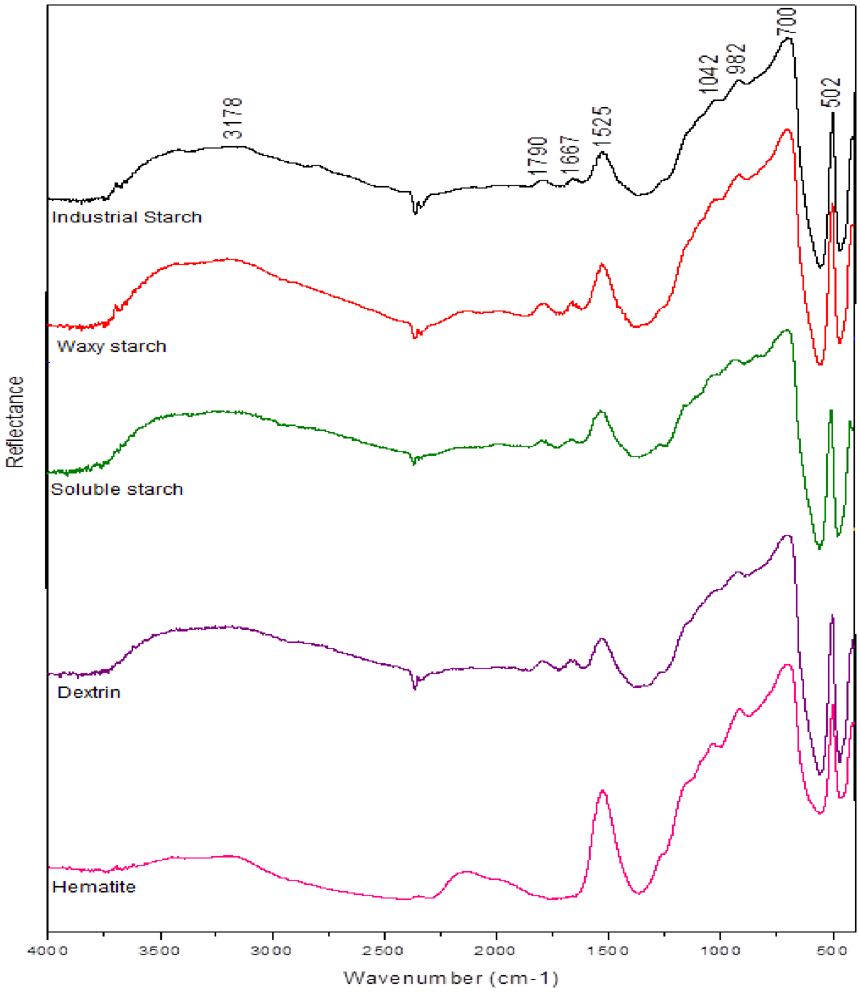

Figure 20. DRIFT spectra of concentrate samples from flotation tests using industrial starch, waxy starch, soluble starch and dextrin as depressant.

The DRIFT spectra of concentrate samples from flotation tests show a different spectral profile from DRIFT of reject samples. But the spectra of concentrate samples are similar to each other. It can be observed bands on 502, 700, 928, 1042, 1525, 1667 and 1790 cm^{-1}, common to all spectra and comparable both in terms of position and intensity. When the spectra are compared with hematite spectrum it is possible to conclude that there was an appreciable increase in the concentration of hematite in concentrate samples (Figure 20).

Whereas it is not pure sample and the small concentration of depressant, it is not possible to obtain information on the nature of the interaction. However, the largest widening of the bands observed in the region of high frequency (2500 - 3500 cm-1), when comparing the spectra of the samples in Figures 19 and 20, confirm a higher hydrophilicity of the surface (from concentrate samples) through hydrogen bonds which may eventually result in a higher amount of adsorbed water (Severov et al., 2013, Kar et al., 2013)

Raman Spectroscopy

Raman spectra of reject and concentrated samples of flotation tests with industrial corn starch, waxy starch, soluble starch and dextrin as depressant were carried out. Due to the heterogeneity of the samples (points of different colors) for each sample several Raman spectra were recorded, in order to explore and investigate the different compositions of the ore and its interactions with the different depressants.

Figure 21 illustrates the heterogeneity observed in the optic microscope for the different samples.

Figure 21. Images of regions with different colors observed for reject sample from flotation test using soluble starch. Named: a) Crystalline; b) Silver; c) Red and d) Black.

The reject samples from flotation test, in general, had predominantly crystalline aspect, with less frequency of black, silver and red points, the opposite observed for concentrate samples from flotation test (table of spectral frequencies in Appendix 3). Although there were differences in aspect of the samples, it was not observed a characteristic Raman spectral profile for the points with particular color. In other words, points with the same color showed different Raman profiles. In addition it was observed that some points with different colors showed the same Raman profile.

The same physical and spectral profile were found for all samples, reject and concentrate. Because of this, the soluble starch was used here for exemplification of results. The spectra results were identified according to Faria et al. (1997), Faria and Lopes (2007) and Faria et al. (2011).

Figures 22, 23, 24 and 25 exemplify the spectral profiles found in different regions of the reject sample from the flotation test using soluble starch as depressant.

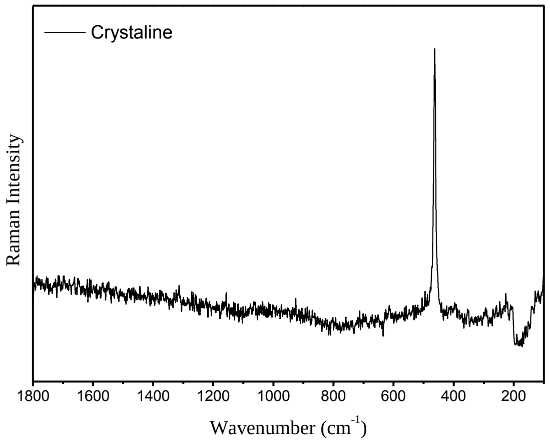

Figure 22. Raman spectrum of crystalline point of reject sample from flotation test using soluble starch as depressant. The spectrum shows the quartz spectral profile (intense band in 467 cm^{-1} due Si-O strech).

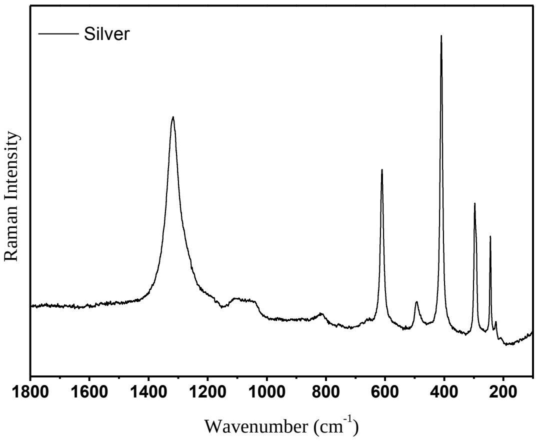

Figure 23. Raman spectrum of silver point of reject sample from flotation test using soluble starch as depressant. The spectrum shows the hematite spectral profile.

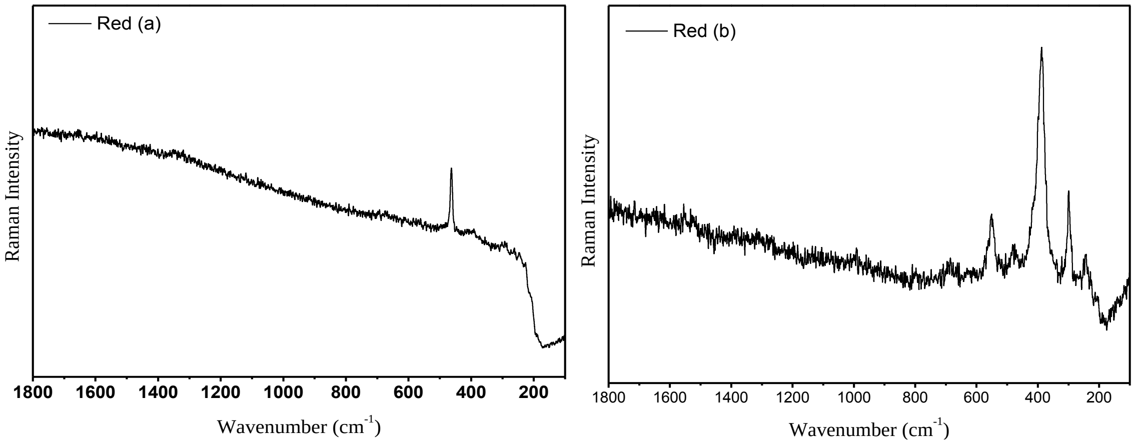

Figure 24. Raman spectra of red points of reject sample from flotation test using soluble starch as depressant. The spectrum (a) shows the quartz spectral profile and the spectrum (b) shows the goethite spectral profile.

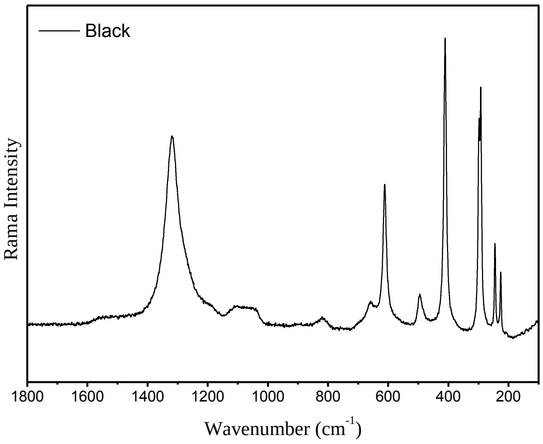

Figure 25. Raman spectrum of black point of reject sample from flotation test using soluble starch as depressant. The spectrum shows the hematite spectral profile.

As can be seen in Figure 22, the crystalline point shows a significant contribution of quartz, whereas red points (Figure 24) showed different spectral profiles with contribution of quartz and goethite. Silver point (Figure 23) showed the same spectral profile observed for black point (Figure 25) corresponding to hematite spectrum.

Figure 26 shows the spectra recorded for concentrate sample from flotation test with soluble starch. It can be observed that concentrate samples showed the same spectral profiles found for reject samples.

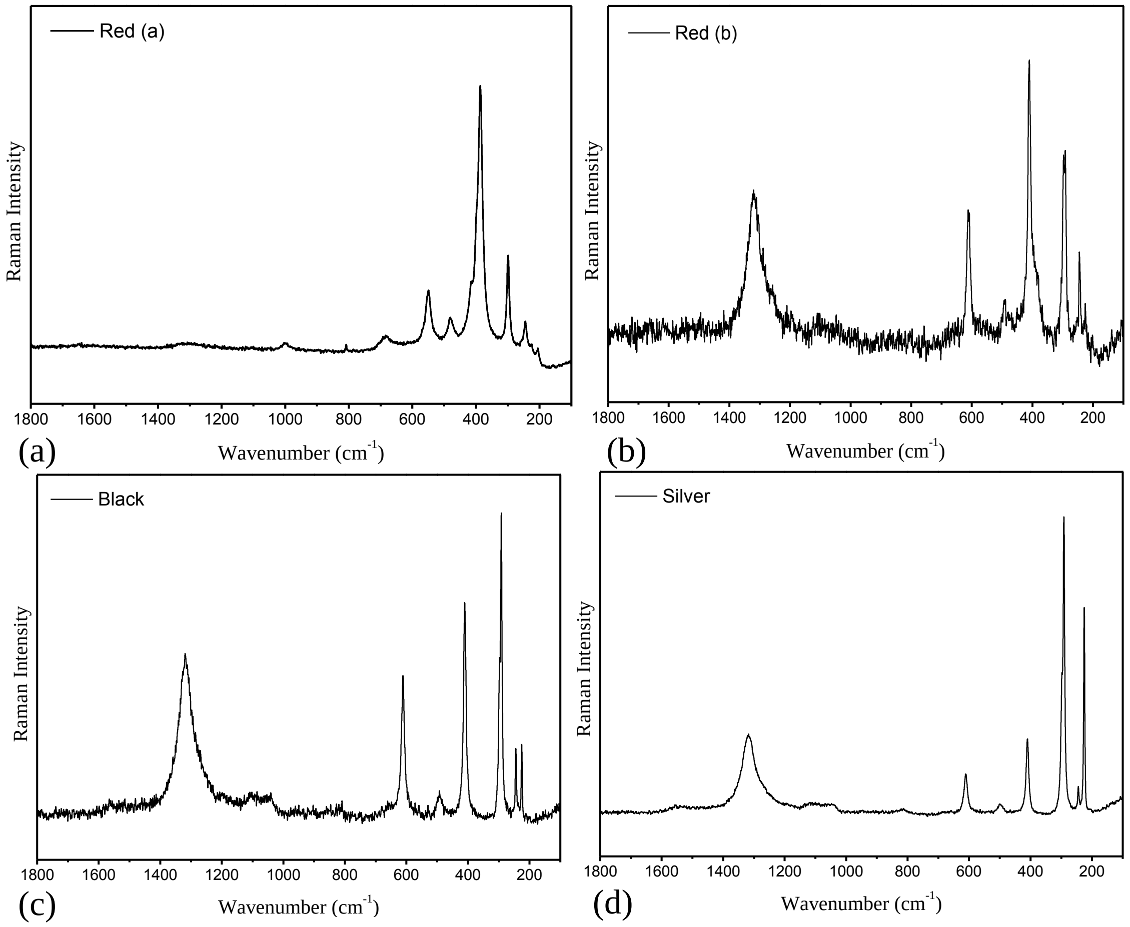

Figure 26. Raman spectra of concentrate sample from flotation test using soluble starch as depressant. Spectral profile observed for the points a) red with goethite profile, b) red with hematite profile, c) black with hematite profile and d) silver with hematite profile.

For the other samples, the same spectral profiles were found. Some variations about the relative intensities of the bands were found, however, without specificity as to the depressant used. The important difference among the results is that the hematite was found with more frequency in concentrate samples than reject samples, as expected.

The spectroscopy Raman not allowed the observation of any band characteristic of organic compounds used as depressant in iron ore flotation. This can be explained because of the low relative concentration of depressant, since the Raman spectroscopy has no sensitivity for the detection of organic species in low concentrations, except for the use of special effects (resonant Raman effect and SERS effect), which are not applicable to this type of problem.

Raman analysis, therefore, not allowed observe significant differences among the samples of reject and concentrate from flotation tests with different depressants, from which it would was possible to extract information about the interaction of these species with the ore.

4. CONCLUSIONS

These studies showed that the molar weight affects the iron and mass recovery and iron loss. These parameters tend be worse with a decrease of molar weight. The iron content in concentrate not changed with the decrease of depressant molar weight.

Although the iron content in concentrate is not affected by chain length neither by REG of depressant, dextrin, a smaller molecule, gave better results for this parameter than waxy starch. This suggests that iron content in concentrate is related to nature of biopolymer, i.e., related to the affinity of biopolymer adsorb in iron ore, maybe because of branching amount. Based on this, the branch effect can be a suggestion for future studies.

Results of hydrolyzed and reduced dextrins show that reducing end group is significant for flotation performance just when it used small molecules (DE~10.6%), where have a greater amount of this group. However, in general, it has no significant gain or loss in flotation performance to reduce the REG of depressants, since this number is not large in depressants commonly used.

Infrared and Raman analyses not allowed the observation of any band characteristic of organic compounds used as depressant in iron ore flotation, maybe because of the low concentration of depressant and real samples. Further studies with infrared can be useful for study the interaction between depressant and iron ore using pure samples as model compounds.

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CHAPTER 2

EVALUATION OF A SUSTAINABLE BIOPOLYMER AS DEPRESSANT IN THE REVERSE CATIONIC FLOTATION PROCESS FOR IRON ORE

ABSTRACT

Iron ore flotation is a separation process used in mineralogy to separate iron compounds from other components present in the iron ore. Most of Brazilian mining uses the reverse cationic flotation process as the standard method to deal with the variation in the iron ore quality and efficiently remove the main contaminant known as gangue. In this process, starch is used as depressant and amines as collector. There are several other natural and synthetic polymers that have been studied for use as depressants in the reverse cationic flotation process for iron ore and other minerals. The goal of this work is to study a biopolymer (XMC) isolated from corn fiber residue (CFR) to be used as depressant, replacing starch, in iron ore concentrating from a mine located in Minas Gerais, considered low in iron content. For this, the best conditions of XMC isolation were evaluated in order to have better results for flotation. Then, the optimization of flotation conditions was performed in order to compare the XMC with industrial starch. Results showed better performance of XMC than starch for all depressant dosages and pH conditions evaluated. High values of iron and mass recovery (91.8 and 65.9 %, respectively) and a low value of iron loss (9.4 %) could be found using XMC, demonstrating the better selectivity of this depressant. Therefore, the substitution of starch by XMC is a sustainable, attractive and promising alternative for the reverse cationic flotation process.

Keywords: Iron ore, reverse cationic flotation, flotation depressant

1. INTRODUCTION

The flotation process is a method for physically separating particles based on differences in the ability of air bubbles to selectively adhere to specific mineral surfaces in a mineral/water slurry. The particles with attached air bubbles are then carried to the surface and removed, while the particles that remain completely wetted stay in the liquid phase. In reverse cationic flotation, the mineral removed by air bubbles is called gangue and the mineral of interest stay in the grounding (Kawatra, 2011).

The flotation system includes many interrelated parameters, for example, chemical components (collectors, frothers, activators, depressants and chemicals for pH control), equipment components (cell design, agitation, air flow, cell bank configuration, cell bank control) and operation components (feed rate, mineralogy, particle size, pulp density, temperature). Because of the interrelationship between these factors, the study of each parameter in isolation is very difficult, since the variation of one component can modify the conditions of the others (Kawatra, 2011; Nagaraj, 2005).

Most of Brazilian mining uses the reverse cationic flotation process as the reference to deal with the variation of the iron ore quality aiming to concentrate the hematite and remove the gangue material from the product. In the flotation process, the addition of reagents called depressants, or compounds that make the surface of particular minerals more hydrophilic, have fundamental importance. Some of the major chemical reagents used include gelatinized starch as depressant and amines as collectors (Kar et al, 2013; Abdel-Khalek et al, 2012; Turrer and Peres, 2010; Pavlovic and Brandao, 2003).

Starch is a natural polysaccharide consisting of two main components, amylose and amylopectin and can be extracted from several vegetal species, such as corn, manioc, potato, wheat, rice, arrowroot, etc. Normal starches, such as corn, rice, wheat and potato, contain 70 – 80% amylopectin and 20 – 30% amylose. Amylose is a straight chain polymer of α-D-(+)-glucopyranose units linked by C1-C4, whereas amylopectin is branched containing also α-1,4 linkages and α-1,6 linkages of α-D-(+)-glucopyranose units, responsible for branching (Bertolini, 2010; BeMiller & Whistler, 2009). The structure of amylose and amylopectin is showed in Figure 1.

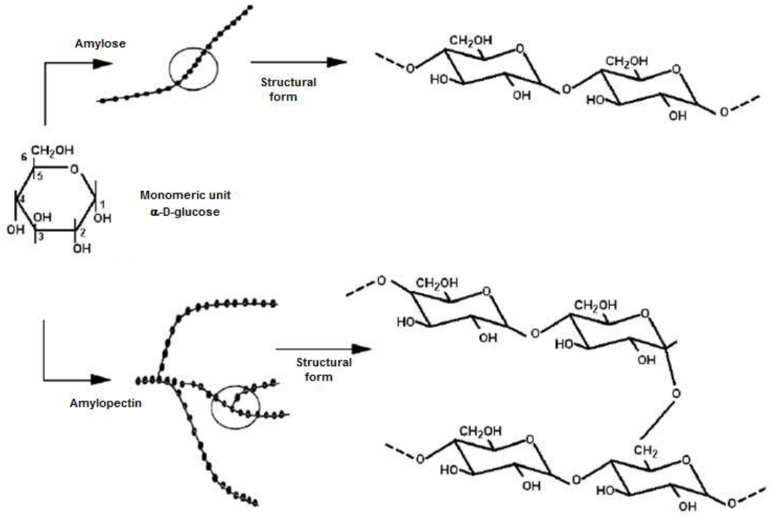

Figure 1. Chemical structure of amylose and amylopectin.

Corn starch is the most used depressant in reverse cationic flotation of iron ores due to its selectivity and availability in large amounts. The production of biopolymers from renewable sources can be an alternative to replace the industrial application of starch, which is also used for human and animal nutrition.

Studies aimed at finding an ideal alternative depressant for use in iron ore flotation have been performed by several authors. Carboxymethylcellulose (CMC) is used as a depressant for many minerals, such as talc, magnesium, quartz, dolomite, and chromite. The substitution of starch by CMC has also been evaluated for iron ore reverse cationic flotation (Turrer, 2007; Liu et al., 2006). The mechanism of humic acid adsorption onto hematite was investigated by Ramos-Tejada et al. (2003) and its use as an iron ore depressant was investigated by Turrer (2007) and Santos (2006).

Santos (2006) evaluated the performance of humic acid as a depressant of hematite based on their physicochemical properties, evaluating the hydrophobicity of quartz and hematite and performing microflotation tests using dodecylamine as a surfactant. In this study, the results showed that after conditioning with humic acid (HA), to low concentrations of dodecylamine (DDA) at pH 10.2, hematite shows values of contact angle lower than quartz and further microflotation tests with the mixture of the two minerals (25% quartz and 75% hematite), resulted in a recovery of 90.75% in hematite concentrate depressed with a content of 86.12% Fe_2O_3.

Turrer (2007) studied 16 polymers (different forms of carboxymethylcellulose, lignosulfonate, humic acid, guar gum and polyacrylamide) as depressants in the iron ore reverse cationic flotation. To evaluate the adsorption and floatability of hematite and quartz, the zeta potential was measured and microflotation was performed. The author found that the partial or total substitution of starch by reagents such as guar gum and DLMAB carboxymethylcellulose resulted in obtaining concentrated iron ore with less than 1.1% Gangue content in concentrate, and maintaining the metallurgical recoveries between 65 to 70%. He further concluded that the essential mechanism of adsorption of these carbohydrates in hematite is not electrostatic, but chemical, so the adsorption continues even above the isoelectric point of hematite.

The microflotation studies of Turrer (2007) showed that none of the carboxymethylcelluloses evaluated had the same effect as starch in the floatability of minerals, however, the DLMAB carboxymethylcellulose could depress the mineral significantly at high dosages; the same was observed for humic acid. The lignosulfonates had little effect on the floatability of the minerals and the use of guar gum had similar effect to starch in the floatability of minerals.

Although the utilization of other natural or synthetic polymers, such as carboxymethylcellulose, lignosulfonates, polyacrylamides, guar gum and humic acid have been evaluated as potential depressant for hematite in iron ore, no depressant comparable to starch both in selectivity as the economic feasibility has been found (Turrer, 2007; Santos, 2006; Monte, 2002).

This work aimed to develop a new sustainable potential biopolymer as depressant for iron ore reverse cationic flotation, called XMC, extracted from Corn Fiber Residue (CFR), that could be more selective than starch.

2. MATERIALS AND METHOD

2.1. Materials

The iron ore used in all experiments of this work came from a mine in the Iron Quadrilateral in Minas Gerais, Brazil. The iron ores were characterized in terms of granulometry and iron, quartz and traces elements content. The granulometry was determined using vibrating sieves with the openings: 1000 µm, 500 µm, 250 µm, 125 µm, 63 µm and 45 µm for 10 min. The identification of the crystalline phases was determined using the powder method using an X-Ray diffractometer (PANalytical, X'Pert PRO with X'Celerator detector) by comparing the X-Ray Diffraction (XRD) pattern of the sample with the banks of the ICDD data PDF2 - International Centre for Diffraction Data (2003) and PAN ICSD - PANalytical Inorganic Crystal Structure Database (2007). The contents of hematite, quartz, e traces elements (Al_2O_3, P, Mn, TiO_2, CaO, MgO) were determined by X-ray fluorescence (XRF) Axios Advanced – Panalytical by quantitative analysis in melted sample with anhydrous lithium tetraborate.

The iron ore density was determined by pycnometer method described in Appendix 1.

XMC was isolated from corn fiber residue and industrial starch was provided by a mining company. The corn residue was obtained from two mills, called here source A and source B, as a byproduct from wet-milling of corn starch.

Corn fiber residue (CFR) is a byproduct of corn starch processing and constitutes an abundantly available agro-industrial residue. It represents the tough and resistant outer layer of corn core and has arabinoxylan, cellulose and starch as its main constituents. These C-5 and C-6 carbohydrates are potentially interesting substrates for upgrading to be used in several industries for food, fuel, paper and others products (Agger and Meyer, 2012; Appeldoorn et al, 2010).

2.2. CFR Characterization

The CFR was characterized as total carbohydrate, soluble and insoluble lignin, ashes, extractives and protein. The Carbohydrate, lignin and ashes were determined according to procedures cited in Table 1. Extractives were determined by extraction with chloroform using soxhlet and protein was determined by Kjeldahl method.

Table 1. Analysis for CFR and respective methodologies

Analysis	Methodology
Total carbohydrates	Wallis et al. (1996b)
Soluble lignin	Gomide & Demuner (1986)
Insoluble lignin	Goldschimid (1971)
Ashes	Tappi T-15

2.3. Production of XMC from CFR

The XMC was produced from corn fiber residue by a treatment developed in the R&D center of Kemira Chemicals Brazil and it is not related here because there is a patent pending for the treatment. The treatment is basically a procedure as shown in Figure 2. The extractives of CFR are removed using a non-polar solvent and then an alkali treatment is performed in order to produce the XMC. The choice of the best conditions to produce XMC was done by evaluating the source of CFR (Source A and Source B), physics aspect (ground and without grinding) and extractor solvent (non-polar solvent and solvent of intermediate polarity) in order to remove the extractives. The milling of CFR was done in a *Wilye mill (Star FT50-Fortinox) and sieved* through a 40 mesh sieve.

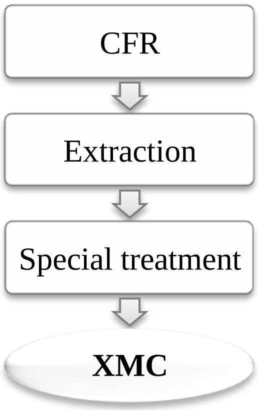

Figure 2. General flowchart of XMC production.

2.4. Flotation tests

For flotation performance, industrial starch (from a mining company) and XMC (biopolymer from CFR isolated in R&D Center of Kemira Chemicals Brazil) were used as depressant (1% solution of depressant) and Flotigan EDA-C etheramin from Clariant was used as collector (1% solution of collector). The starch:NaOH ratio for industrial starch solution was 9:1. The flotation pH was controlled by NaOH 5% (w/v).

The results of iron metallurgical recovery (or iron recovery) and mass recovery in concentrate, iron and gangue content in concentrate and reject were performed according to the method described in Appendix 1 and then compared with standard industrial corn starch to evaluate the performance of XMC. All tables of flotation results can be found in Appendix 4.

3. RESULTS AND DISCUSSION

3.1. Iron ore characterization

X-ray diffraction

Figure 3 shows the XRD of raw iron ore. From these results it was found that the iron ore used in this work contained mainly hematite (Fe_2O_3) and quartz (SiO_2). Goethite ($Fe_2O_3.H_2O$) was present in trace amounts.

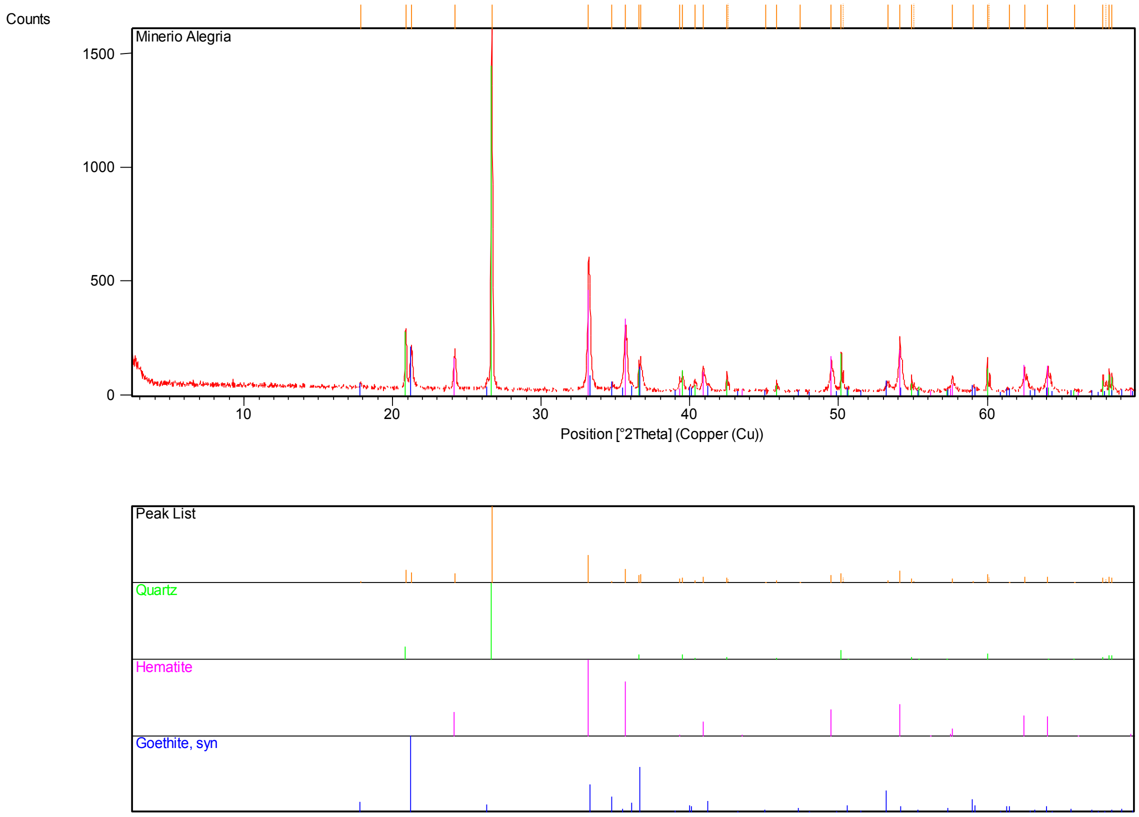

Figure 3. X-ray diffraction spectrum of raw iron ore.

X-ray fluorescence

The composition of the iron ore was determined by XRF analysis. Table 2 shows the iron and gangue content. It can be observed that most of the gangue content is composed of quartz (SiO_2).

Table 2. Iron ore characterization by XRF.

	Iron Ore									
Substance	Fe_2O_3 (Fe)	SiO_2	Al_2O_3	P	Mn	TiO_2	CaO	MgO	Mass loss at 1000ºC	Total
Content (%)	69.64 (48.7)	28.09	0.28	0.05	0.04	0.07	0.01	0.13	1.38	99.69

Iron ore density and particule size

The density of the iron ore determined by pycnometer method was 3.95 g.mL^{-1}.

Good flotation process performance is dependent on flotation conditions such as reagent dosages, pH and pulp concentration. It is reported that better results in the flotation process for iron ore can be achieved using particles smaller than 150 µm (Amorim, 2013; Carvalho e Martins, 2005). Figure 4 shows the iron ore distribution curve of particle size. It can be observed that the entire sample is below 300 µm and most (80%) of the particles are below 125 µm in size and thus suitable for flotation.

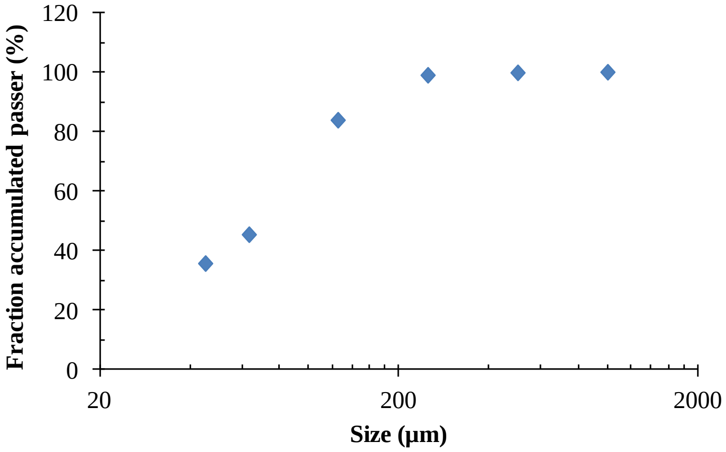

Figure 4. Particle size distribution determined by classificatory sieves.

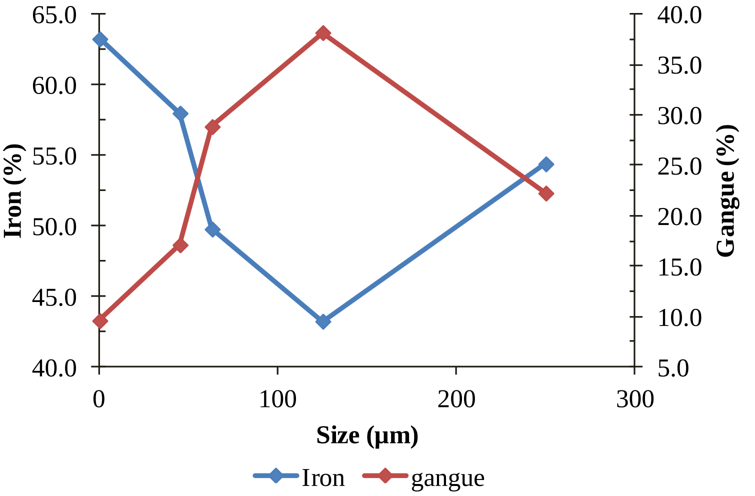

Figure 5. Percentage of iron and gangue content in each fraction of size classification.

Figure 5 shows that most of greater particles (125 µm) are composed by gangue and the most of smaller particles (< 45µm) are composed by hematite. The values above 250 µm were not shown because the amount retained was not enough to perform chemical analysis.

3.2. Corn fiber residue characterization

Table 3 shows the characterization of CFR from source A and source B. Source B contained more lignin, extractives and protein and less carbohydrate than Source A. The carbohydrate, protein and lignin content in CFR was in the same range as that reported by others (Agger and Meyer, 2012).

Table 3. Chemical composition of CFR from source A and source B. Percentage results on *dry* matter *basis*.

	Source A	Source B
Total Carbohydrate (%)	82.3	60.7
Insoluble Lignin (%)	5.9	11.4
Soluble Lignin (%)	0.6	1.1
Ashes (%)	0.3	0.1
Extractives (Cloroform) (%)	2.0	4.0
Protein (%)	7.0	20.5
Total (%)	98.1	97.8

3.3. XMC Production and Flotation tests

In order to choose the best XMC for the flotation process, the source of CFR, physical aspect and extractor solvent were evaluated. To evaluate the effect of using ground and non-ground CFR, XMC production was done with the CFR from both sources A and B, ground and without grinding (Figure 6), and then the XMCs were tested as depressant in iron ore reverse cationic flotation process.

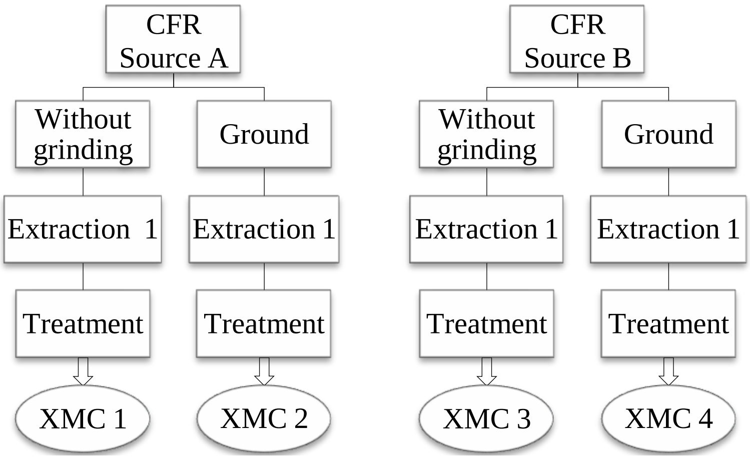

Figure 6. Scheme for XMC production with ground and without grinding CFR.

Table 4. XMC production and flotation results using XMC 1, 2, 3 and 4 as depressant.

Procedure results			Flotation Results					
	Extractives (%)	**Yield (%w/w)**		**Fe (%)**	**Gangue (%)**	**Iron Recovery (%)**	**Mass Recovery (%)**	**Iron loss (%)**
XMC 1	0.9	18.8	CO	63.8	7.0	96.3	74.0	5.2
			RJ	9.8	85.4			
XMC 2	4.0	24.4	CO	67.3	2.0	93.9	68.4	7.4
			RJ	11.4	83.0			
XMC 3	3.8	38.1	CO	68.5	0.3	83.2	59.5	18.5
			RJ	22.4	66.9			
XMC 4	4.2	44.1	CO	68.2	0.7	89.0	64.0	12.4
			RJ	16.7	74.8			

Average results of procedure of XMC production and Flotation test with XMCs 1, 2, 3 and 4 using 100g/t SiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.

Table 4 shows the main results of XMC production from the scheme in Figure 6 and flotation tests performed using the different XMCs. Comparing the results of the flotation test with XMC from source A, the iron content in the final concentrate using XMC 1 as depressant was lower than when using XMC 2 (63.8 and 67.3 % respectively). The better results achieved for iron recovery and iron loss using XMC 1 compared to XMC 2 were attributable to the high mass recovery (74 %). Therefore, the performance of XMC 2 was in general better than that of XMC 1.

For XMC 3 and 4 from corn fiber source B, the iron content in the concentrate was similar (68.5 and 68.2 respectively) and the other parameters were better for XMC 4 than for XMC 3. In addition, the XMC 3 showed high content of iron in reject (22.4 %) and consequently greater iron loss (18.5 %). Therefore, for both sources the performance of XMC from ground CFR were better than from CFR without grinding. A possible explanation is that the greater contact surface and better homogenization of ground CFR can favor the extractives removal and improve the XMC quality.

It can also be observed that the removal of extractives from source A CFR increased significantly with grinding. However, for source B the increase was not as significant. In general, the XMC yield was greater using source B than source A, and with grinding the yield increased approximately 6 percentage points for each source. According to Agger and Meyer (2012), ground corn bran shows better results for enzymatic treatment than corn bran without grinding and they attribute this to the greater contact surface and biomass composition in ground corn bran.

Since XMC from ground CFR had the best flotation results, the source and extractor solvent were evaluated according to the scheme shown in Figure 7. Extraction 1 was performed with a non-polar solvent, the same used initially and Extraction 2 was done with an alternative solvent that is cheaper and of intermediate polarity. The main results of XMC production from the scheme of Figure 7 and flotation test are shown in Table 5.

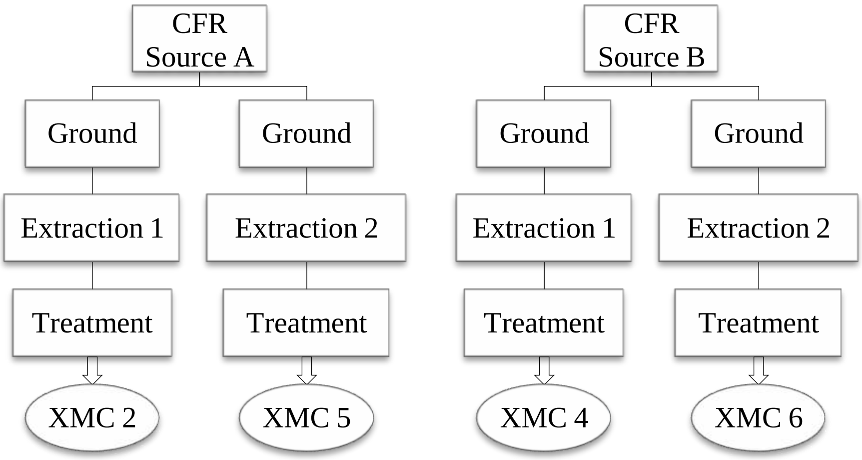

Figure 7. Scheme for XMC production from source A and source B using a non-polar solvent for extraction 1 and a solvent with intermediate polarity for extraction 2.

Table 5. Flotation results using XMCs 2, 5, 4 and 6 as depressant

Procedure Results			**Flotation Results**					
	Extractives (%)	**Yield (%w/w)**		**Fe (%)**	**Gangue (%)**	**Iron Recovery (%)**	**Mass Recovery (%)**	**Iron loss (%)**
XMC 2	4.0	24.4	CO	67.3	2.0	93.9	68.4	7.4
			RJ	11.4	83.0			
XMC 5	9.2	28.6	CO	67.8	1.3	93.3	67.5	7.1
			RJ	10.6	84.0			
XMC 4	4.2	44.1	CO	68.2	0.7	89.0	64.0	12.4
			RJ	16.7	74.8			
XMC 6	18.5	32.3	CO	67.6	1.8	94.0	68.2	7.5
			RJ	11.6	82.8			

Average results for the procedure of XMC production and Flotation test with XMC 2, 5, 4 and 6 using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.

From Table 5 a higher removal of extractives using an intermediate polarity solvent (extraction 2) compared with a non-polar solvent (extraction 1) for both sources can be noted. In addition, the extractives removal was greater for CFR from source B (18.5%) than source A (9.2 %) using this solvent. However, no correlation was observed for yield between the solvents used for extraction, as the XMC yield was higher using the extraction solvent 2 for source A and lower for source B. Despite the differences in extraction and yield, flotation results of XMC 2 and 5 were very similar, showing that solvent extractor did not influence XMC performance in the flotation test. However, for XMCs from source B, the flotation results were different. XMC 6 showed better results than XMC 4, with higher values of iron and mass recovery (94.0 and 68.2 % respectively), less iron loss (7.5 %) and great amount of iron in concentrate (67.6 %), showing that the solvent used in extraction 2 is better than the solvent of extraction 1 for XMC performance from source B. In addition, the solvent of extraction 2 is cheaper than solvent of extraction 1.

Comparing the results between source A and B for the procedure of extraction 2 (XMC 5 and XMC 6), slight differences for iron and mass recovery could be observed, XMC 6 having better results for these parameters than XMC 5. However, the iron content in the concentrate was very similar and iron loss was lower for XMC 5 than XMC 6. The comparison among industrial starch and both XMC are shown in Table 6. It can be observed that both XMCs have greater iron and mass recovery and less iron loss than starch. The iron content in concentrate was similar for XMC and starch.

In order to optimize the XMC flotation performance and compare with industrial starch, the XMC 5 from source A was chosen, because it is from a source more viable economically and displayed better performance than starch.

Table 6. Best results of XMC and industrial starch for comparison.

		Fe (%)	**Gangue (%)**	**Iron Recovery (%)**	**Mass Recovery (%)**	**Iron loss (%)**	**Iron in concentrate (%)**
Industrial corn starch	CO	68.2	0.6	89.3	64.2	11.7	68.2
	RJ	16.0	76.3				
XMC 5	CO	67.8	1.3	93.3	67.5	7.1	67.8
	RJ	10.6	84				
XMC 6	CO	67.6	1.8	94.0	68.2	7.5	67.6
	RJ	11.6	82.8				

3.4. Optimization of flotation conditions

The optimization was performed varying the depressant dosage (starch and XMC 5) at 400, 600, 800, 1000 e 1200 g/t and then, the pH of flotation was evaluated at 8.5, 9.5 and 10.5. The results for iron recovery, mass recovery, iron loss and iron in concentrate from both optimizations are shown in Figure 8 and Figure 10. For a good flotation performance it is desirable to have levels of gangue in concentrate below 1% and iron recovery higher than 90%. For all experiments the values of gangue in concentrate were below 2% and in most of the experiments this parameter was lower than 1%. When this value was not detectable, the value 0 was assumed for the chart plots (Figure 9 and Figure 11).

In Figure 8 it is clear that iron and mass recovery increased and iron loss decreased with an increase in depressant dosage for both depressants – XMC 5 and starch. The iron in concentrate seems constant for different dosages of starch and, for XMC this parameter began to decrease slightly for dosages above 1000 g/t. All results show the good performance of XMC as depressant in iron ore reverse cationic flotation. XMC 5 was better than starch in iron recovery, mass recovery and iron loss results for all dosages. The iron in concentrate was very similar with little change when varying the depressant dosage for both depressants.

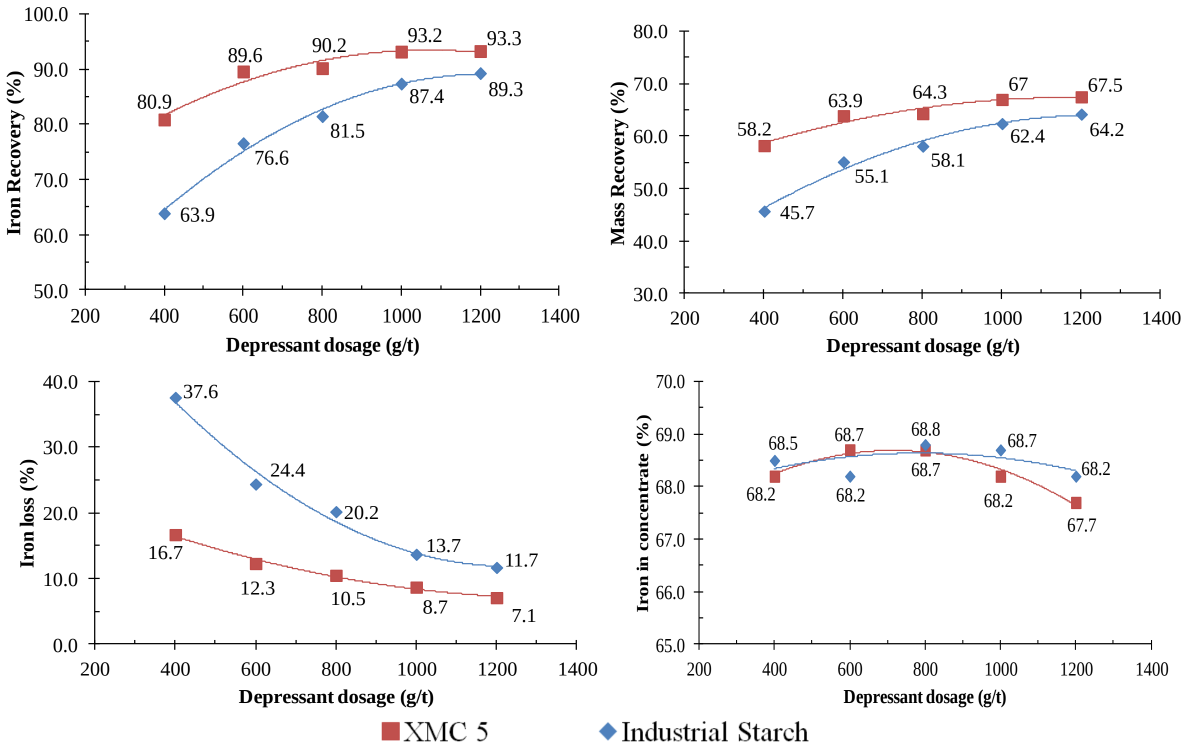

Figure 8. Results of flotation with XMC 5 and Starch as depressant, using different dosages of depressant, 100g EDA-C/tSiO$_2$ and pH 10.5 was used for both depressants.

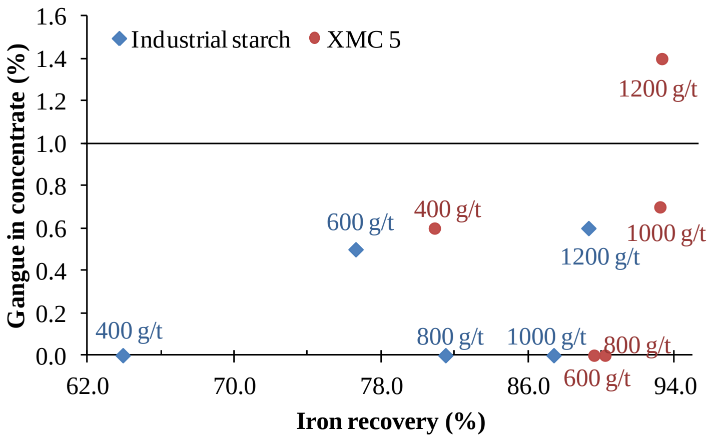

Figure 9. Gangue content in concentrate *versus* iron recovery for flotation with different dosages of depressant.

For XMC 5 it can be observed that 1000 g/t is the best dosage for this depressant, where iron recovery, mass recovery and iron loss tends to stabilize from 1000g/t and the iron content in concentrate starts decrease from this dosage (Figure 8). Additionally, Figure 9 shows that the highest value of iron recovery with gangue content in concentrate below 1% was found for XMC dosage of 1000 g/t. For starch, the best depressant dosage appeared to be 1200 g/t with highest values of iron recovery, mass recovery and iron loss and a good value of iron content in concentrate (Figure 8). The gangue content in concentrate was below 1% for all dosages of starch. I could be seen that increasing XMC increased metal recovery, showing greater selectivity of this depressant for dosage of 1000 g/t, where the largest mass of iron is retained in the concentrate and most of the gangue is rejected (Figure 9).

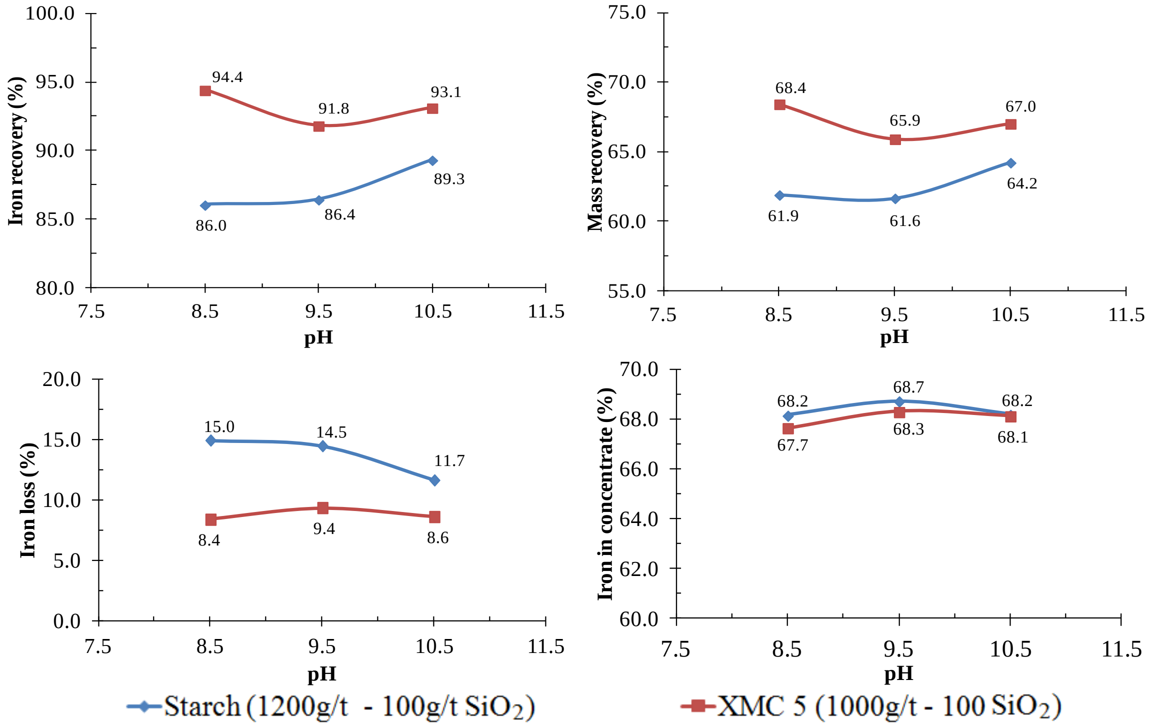

Figure 10. Results of flotation with XMC 5 and Starch as depressant, using 1000g/t of XMC 5, 1200g/t of starch, 100g EDA-C/tSiO_2 for both depressants and varying pH.

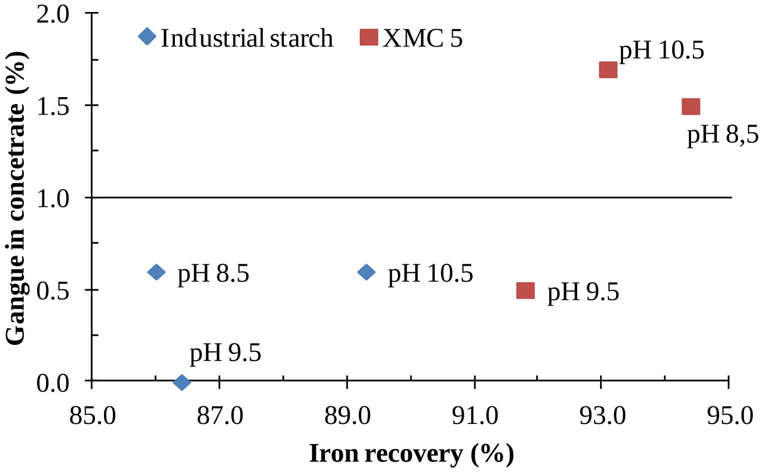

Figure 11. Gangue content in concentrate *versus* Iron recovery for flotation with different pH.

Figure 10 shows the flotation results at different pH. For starch, the flotation results of iron recovery, mass recovery and iron loss improve with an increase in pH. For XMC these values decrease at pH 9.5 and increase again at pH 10.5 having the best values using pH 8.5. The changes in iron content in concentrate from variations in pH were not significant for either depressant. However, Figure 11 shows that the gangue content in concentrate was greater than 1% for XMC in pH 8.5 (1.5 %) and 10.5 (1.7 %). Because of this, the best pH for flotation using XMC seems to be 9.5. Table 7 summarizes the best results using XMC compared with starch. Using 1000g/t of XMC at pH 9.5 it is possible achieve good results with iron recovery greater than 90%, gangue in concentrate lower than 1%, high iron content in concentrate (68.3%) and low iron loss (9.4 %).

Table 7. Best conditions and flotation results found for XMC as depressant.

Depressant	Depressant dosage (g/t)	pH	Iron in conc. (%)	Gangue in conc. (%)	Iron recovery (%)	Mass recovery (%)	Iron loss (%)
XMC	1000	9.5	68.3	0.5	91.8	65.9	9.4
Starch	1200	10.5	68.2	0.6	89.3	64.2	11.7

Flotation tests using 100g/t SiO_2 of Flotigan EDA-C as collector.

From this work it can be observed that XMC exhibited great advantages over the starch as depressant in iron ore reverse cationic flotation process, proving to be a very competitive alternative for starch in all ranges of dosage and pH of flotation evaluated. Besides, the XMC has the possibility to be used in smaller dosages and the flotation to be run at lower pH than using starch.

The only parameters still to be improved are iron and gangue content in concentrate where good results were achieved, but only equal to or slightly worse than starch. Optimization studies are therefore suggested including the effect of collector dosage.

4. CONCLUSIONS

The results indicate the technical feasibility for the implementation of XMC replacing starch in iron ore reverse cationic flotation. Safety aspects regarding the use of a less NaOH (starch gelatinization not required) should be considered an added benefit of this novel depressant.

Results from the XMC performance test were better than those for starch at all dosages and pH conditions tested, with the best conditions being 1000g/t of XMC, 100g/tSiO_2 of collector and pH 9.5, achieving 91.8 % of iron recovery, 0.5% of gangue in concentrate, 68.3 % of iron content in concentrate and 9.4 % of iron loss (9.4 %). XMC therefore has the possibility to be used in smaller dosages and the flotation to be run at lower pH than using starch.

Therefore, replacement of starch by XMC is an attractive and sustainable alternative offering a prime destination for industrial waste and removing starch from the industrial process partial or totally, preserving it for the food and feed chain.

As a negative factor for this substitution, the current costs of acquisition of XMC should be highlighted, being higher than for starch, and the feasibility of partial or total substitution of starch should be separately verified. However, it should also be considered that the increased use of this new reagent might result in lower cost in the long term.

The project aimed to use an industrial residue to replace starch, a polysaccharide present in the human and animal food chain, characterizing this work as a promising biorefinery project in Brazil.

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OVERALL CONCLUSIONS

In the first part of this study, which evaluated the effect of some the characteristics of starch molecules, it was showed the importance on size of depressant for flotation performance test, concluding that performance of flotation worsens with a decrease in the molecule chain length. It seems that smaller sizes of molecules are associated with the ability to keep the iron in the concentrate, shown by higher levels of iron in the concentrate to dextrin than waxy starch. The reduction of REG with sodium borohydride showed that the presence of the REG, or even free carbon C1 present in this group in cyclic form, does not affect the flotation performance as it has been suggested by other authors. The spectroscopic analyzes did not seem to study the interaction mechanism for real samples. It is likely that a study with model compounds can show some useful information for this purpose.

In the second part of this work, it is described the preliminary studies on a sustainable alternative to substitute the starch on the flotation process. The XMC from CFR showed an excellent profile as depressant agent in the process of enrichment of iron ore by flotation. High values of mass and iron recovery could be found with low iron loss during the process. The better selectivity of XMC compared with starch can have influence of interaction between depressant and collector. Further studies about interaction of XMC with amine and others collectors can be an interesting propose. With these results, the XMC project is a promising and big biorefinery project in Brazil.

APPENDIX 1

Procedures of Chapter 1 and Chapter 2

Procedure for iron ore density determination

The density of iron ore was determined from measurements of mass and volume using a pycnometer. The iron ore is placed in a pycnometer filled with water (liquid of known density), the volume of the water that overflows is equal to the solid volume. The mass of the liquid which will overflow is determined as the difference between the sum of the mass of the pycnometer filled with water plus the mass of the solid and the mass of pycnometer filled with water after the solid has been placed inside. The volume occupied by this mass is determined from the water density.

Procedure for iron recovery, mass recovery, iron and gangue content in concentrate and iron loss determination used in chapter 1 and chapter 2

Iron content determination

For iron content determination it was used the technique of titration after iron ore reduction by tin(II) chloride ($SnCl_2$).

About 0.100 g sample of iron ore were weighed on an analytical balance and transferred to a 250 mL beaker. In laminar flow chapel, 10 mL of concentrated hydrochloric acid (HCl) and 3 mL solution 0.25 M $SnCl_2$ were added in the beaker, which was heated to boiling for complete elimination of yellow coloration (reduction of Fe^{3+} to Fe^{2+}). To ensure the complete reduction of iron, about three drops of 0.25 M $SnCl_2$ solution were added, waiting for the solution cooling. Then, 10 mL of a solution of mercuric chloride ($HgCl_2$) were added 0.18M, leaving a white precipitate (hydrated quartz). After the time interval 2 to 3 min, 25 mL of solution were added Zimmermannn Reinhardt, by supplementing it with distilled water until the 250 mL mark. The procedure was a titration with potassium permanganate solution (0.02 M) under constant stirring, recording the volume required. The calculations can be carried out accompanied by the following equation:

$$\% \, Fe = Vg \times M \times Fc \times me \times 100/w \qquad \text{Equation 1}$$

Where: Vg = volume spent of $KMnO_4$; Fc = correction factor of $KMnO_4$; me = milliequivalents iron 0.05585; w = weight of the sample; M = molarity of the $KMnO_4$

The solution Zimmermannn Reinhardt was prepared by adding 70 g $MnSO_4.4H_2O$ in 500 mL of distilled water and 125 mL of concentrated sulfuric acid, 125 mL of concentrated phosphoric acid and diluting the mixture to 1000 mL with distilled water.

Iron metallurgical recovery

Iron recovery (IR) of a concentration process is an important parameter to determinate the level of iron utilization in the process. Thus, if the product is of interest in the concentrate that has (Turrer, 2007):

$$IR=\frac{C_{conc}*M_{conc}}{C_{feed}*M_{feed}} \qquad \text{Equation 2}$$

Where: C_{conc} = Iron content (%); $M_{conc.}$ = Mass of concentrate; C_{feed}: Iron content in iron ore (%); M_{Feed} = Mass of iron ore.

Mass recovery

The mass recovery (MR) is the fraction of one component in the chain of interest

$$MR=\frac{m_{conc}}{m_{feed}} \times 100 \qquad \text{Equation 3}$$

Where: $m_{conc.}$= mass of concentrate; m_{feed} = mass of iron ore

Iron Loss

The process of iron ore concentration must be done with proper planning so without loss of final product quality, reducing the volume of material discarded, that can produce enviromental problems with high cost (Turrer, 2007). The Fe loss is calculated according the equation below:

$$Fe_{loss(\%)}= \frac{m_{rej}\times Fe_{rej} \text{ x } 100}{m_{feed} \text{ x } Fe_{feed}} \qquad \text{Equation 4}$$

Were: m_{rej} = mass of reject; Fe_{rej} = Iron content in reject; m_{feed} = mass of iron ore; Fe_{feed} = iron content in iron ore

Gangue determination

Once the value of hematite or iron is known, the gangue is determined from subtraction of content hematite and organic material of 100. The organic material was determined gravimetrically by calcination of sample (1g) ina mufle (1000 ºC) for at least 1h.

APPENDIX 2

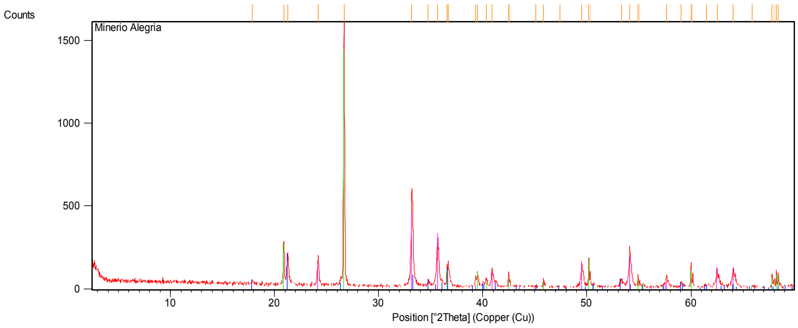
Results of characterization of iron ore used in chapter 1 and chapter 2.

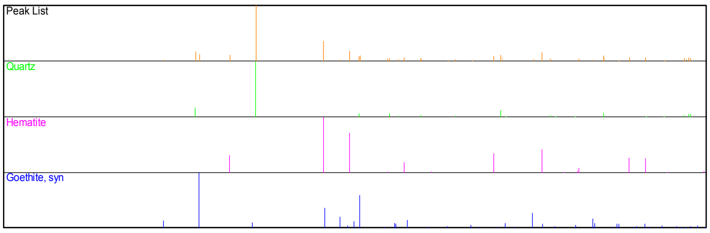
Granulometry

Sieve size (mesh)	Sieve size (µm)	Simple frequency (%)	Retained cumulative frequency (%)	Passer cumulative frequency (%)
18	1000	0,06	0,07	99,93
35	500	0,22	0,29	99,71
60	250	2,34	2,64	97,36
120	125	18,77	21,41	78,59
230	63	42,18	63,59	36,41
325	45	11,49	75,08	24,92
background	0	24,92	100,00	0,00
	Total	100,00	100,00	

Sieve size (µm)	Iron (%)	Gangue (%)
250	54,41	22,27
125	43,24	38,22
63	49,78	28,88
45	58,01	17,13
0	63,28	9,60

Results from XRD of iron ore sample.





Name and formula

Reference code: 01-085-0794

Mineral name: Quartz

ICSD name: Silicon Oxide

Empirical formula: O_2Si

Chemical formula: SiO_2

Crystallographic parameters

Crystal system: Hexagonal

Space group: P3221

Space group number: 154

a (Å): 4,9100

b (Å): 4,9100

c (Å): 5,4000

Alpha (°): 90,0000

Beta (°): 90,0000

Gamma (°): 120,0000

Calculated density (g/cm^3): 2,65

Volume of cell (10^6 pm^3): 112,74

Z: 3,00

RIR: 3,11

Subfiles and Quality

Subfiles: Inorganic

Mineral

Alloy, metal or intermetalic

Corrosion

Pharmaceutical

ICSD Pattern

Quality: Calculated (C)

Comments

Additional pattern: See PDF 78-2315 and PDF 33-1161.

ICSD collection code: 027826

Test from ICSD: No R value given.

At least one TF missing.

References

Primary reference: *Calculated from ICSD using POWD-12++*

Structure: Machatschki, F., *Fortschr. Mineral.*, **20**, 45, (1936)

Peak list

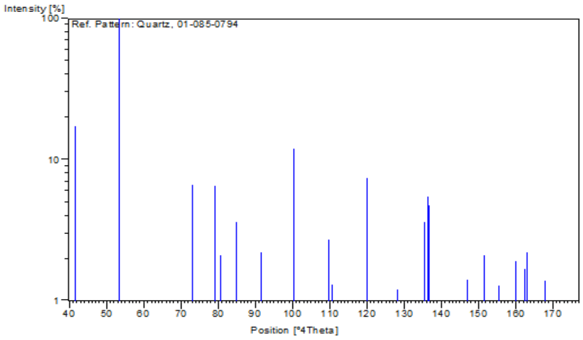
No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	0	0	4,25218	20,874	17,2
2	0	1	1	3,34077	26,662	100,0
3	1	1	0	2,45500	36,573	6,7
4	1	0	2	2,27933	39,504	6,5
5	1	1	1	2,23488	40,324	2,1
6	2	0	0	2,12609	42,484	3,6
7	2	0	1	1,97828	45,832	2,2
8	1	1	2	1,81640	50,185	11,9
9	0	0	3	1,80000	50,674	0,3
10	0	2	2	1,67038	54,923	2,7
11	0	1	3	1,65760	55,383	1,3
12	2	1	0	1,60717	57,278	0,3
13	1	2	1	1,54040	60,009	7,4
14	1	1	3	1,45162	64,099	1,2
15	3	0	0	1,41739	65,839	0,4
16	1	2	2	1,38103	67,804	3,6
17	2	0	3	1,37378	68,211	5,5
18	0	3	1	1,37095	68,371	4,8
19	1	0	4	1,28671	73,548	1,4
20	3	0	2	1,25498	75,729	2,1
21	2	2	0	1,22750	77,737	1,3
22	2	1	3	1,19884	79,963	1,9
23	2	2	1	1,19696	80,114	0,9
24	1	1	4	1,18294	81,260	1,7
25	3	1	0	1,17934	81,561	2,2
26	1	3	1	1,15219	83,911	1,4

27	2	0	4	1,13966	85,049	0,2
28	2	2	2	1,11744	87,156	0,1
29	3	0	3	1,11359	87,534	0,2

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,40300	0,15000	0,12233	0,5000	1,0000	6c
2	SI1	Si	0,53100	0,00000	0,33333	0,5000	1,0000	3a

Stick Pattern



Name and formula

Reference code: 01-079-0007

Mineral name: Hematite

ICSD name: Iron Oxide

Empirical formula: Fe_2O_3

Chemical formula: Fe_2O_3

Crystallographic parameters

Crystal system: Rhombohedral

Space group: R-3c

Space group number: 167

a (Å): 5,0285

b (Å): 5,0285

c (Å): 13,7360

Alpha (°): 90,0000

Beta (°): 90,0000

Gamma (°): 120,0000

Calculated density (g/cm^3): 5,29

Volume of cell (10^6 pm^3): 300,79

Z: 6,00

RIR: 3,29

Subfiles and Quality

Subfiles: Inorganic
Mineral
Alloy, metal or intermetalic
Corrosion
Pharmaceutical
ICSD Pattern

Quality: Calculated (C)

Comments

Additional pattern: See PDF 33-664.

Temperature: Pattern taken at 153 K.

ICSD collection code: 064599

Test from ICSD: At least one TF implausible.

References

Primary reference: *Calculated from ICSD using POWD-12++*, (1997)

Structure: Tsirel'son, V.G., Antipin, M.Y., Strel'tsov, R.P., Ozerov, R.P., Struchkov, Y.T., *Dokl. Akad. Nauk SSSR*, **298**, 1137, (1988)

Peak list

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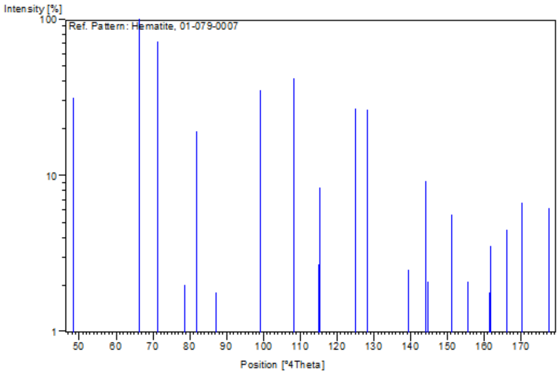
3	1	1	0	2,51425	35,682	71,7
4	0	0	6	2,28933	39,324	2,0
5	1	1	3	2,20384	40,917	19,2
6	2	0	2	2,07559	43,570	1,8
7	0	2	4	1,83890	49,529	34,9
8	1	1	6	1,69275	54,137	42,0
9	2	1	1	1,63427	56,243	0,5
10	1	2	2	1,60064	57,533	2,7
11	0	1	8	1,59733	57,664	8,5
12	2	1	4	1,48427	62,527	26,9
13	3	0	0	1,45160	64,100	26,2
14	1	2	5	1,41194	66,126	0,2
15	2	0	8	1,34825	69,686	2,5
16	1	0	10	1,30998	72,034	9,2
17	1	1	9	1,30466	72,374	2,1
18	2	1	7	1,26107	75,299	0,3
19	2	2	0	1,25712	75,577	5,7
20	0	3	6	1,22593	77,855	2,1
21	2	2	3	1,21226	78,903	0,9

22	1	3	1	1,20316	79,618	0,1
23	3	1	2	1,18955	80,715	1,8
24	1	2	8	1,18819	80,827	3,6
25	0	2	10	1,16175	83,066	4,5
26	0	0	12	1,14467	84,590	0,2
27	1	3	4	1,13939	85,074	6,7
28	2	2	6	1,10192	88,702	6,2

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,30582	0,00000	0,25000	0,5000	1,0000	18e
2	FE1	Fe	0,00000	0,00000	0,14480	0,5000	1,0000	12c

Stick Pattern



Name and formula

Reference code: 01-081-0463

Mineral name: Goethite, syn

ICSD name: Iron Oxide Hydroxide

Empirical formula: $FeHO_2$

Chemical formula: FeO (OH)

Crystallographic parameters

Crystal system: Orthorhombic

Space group: Pbnm

Space group number: 62

a (Å): 4,6158

b (Å): 9,9545

c (Å): 3,0233

Alpha (°): 90,0000

Beta (°): 90,0000

Gamma (°): 90,0000

Calculated density (g/cm^3): 4,25

Volume of cell (10^6 pm^3): 138,91

Z: 4,00

RIR: 2,79

Subfiles and Quality

Subfiles: Inorganic
Mineral
Corrosion
ICSD Pattern

Quality: Calculated (C)

Comments

ICSD collection code: 071809

Test from ICSD: At least one TF missing.

References

Primary reference: *Calculated from ICSD using POWD-12++*, (1997)

Structure: Hazemann, J.L., Berar, J.F., Manceau, A., *Materials Science Forum*, **79**, 821, (1991)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	0	2	0	4,97725	17,806	13,1
2	1	1	0	4,18752	21,200	100,0
3	1	2	0	3,38444	26,312	10,3
4	1	3	0	2,69425	33,226	36,4
5	0	2	1	2,58396	34,688	20,4
6	1	0	1	2,52908	35,465	4,4
7	0	4	0	2,48862	36,062	12,5
8	1	1	1	2,45121	36,631	58,2
9	2	0	0	2,30790	38,995	2,4
10	1	2	1	2,25470	39,954	9,1
11	2	1	0	2,24827	40,073	7,1
12	1	4	0	2,19053	41,177	13,9
13	2	2	0	2,09376	43,173	1,0
14	1	3	1	2,01143	45,034	2,8
15	0	4	1	1,92140	47,270	4,7
16	2	3	0	1,89467	47,978	0,4
17	1	5	0	1,82810	49,842	0,7
18	2	1	1	1,80410	50,551	8,6
19	1	4	1	1,77386	51,475	2,0
20	2	2	1	1,72129	53,168	26,8
21	2	4	0	1,69222	54,156	7,6

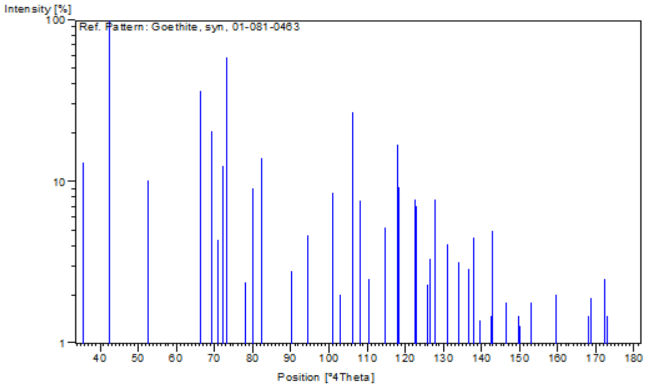
22	0	6	0	1,65908	55,329	2,5
23	2	3	1	1,60546	57,345	5,2
24	1	5	1	1,56435	58,998	16,9
25	1	6	0	1,56129	59,125	9,2
26	3	1	0	1,52054	60,875	0,5
27	0	0	2	1,51165	61,271	7,7
28	2	5	0	1,50750	61,458	7,1
29	2	4	1	1,47664	62,887	2,3
30	3	2	0	1,46997	63,205	3,3
31	0	6	1	1,45447	63,958	7,7
32	0	2	2	1,44641	64,357	0,6
33	1	1	2	1,42184	65,607	4,1
34	3	3	0	1,39584	66,989	3,2
35	1	6	1	1,38723	67,460	0,1
36	1	2	2	1,38023	67,848	0,8
37	3	0	1	1,37124	68,354	2,9
38	1	7	0	1,35903	69,055	4,5
39	2	6	0	1,34712	69,753	1,4
40	3	2	1	1,32199	71,279	1,5
41	1	3	2	1,31832	71,508	5,0
42	3	4	0	1,30868	72,117	0,1
43	0	4	2	1,29198	73,199	1,8
44	3	3	1	1,26729	74,866	1,5
45	2	0	2	1,26454	75,057	1,3
46	2	1	2	1,25446	75,766	0,5
47	0	8	0	1,24416	76,506	1,8
48	2	6	1	1,23050	77,512	0,3
49	2	2	2	1,22561	77,880	0,2
50	3	5	0	1,21742	78,504	0,1
51	2	7	0	1,21069	79,025	0,1
52	1	8	0	1,20099	79,791	2,0
53	2	3	2	1,18164	81,369	0,1
54	1	5	2	1,16496	82,787	0,1
55	4	0	0	1,15395	83,754	0,3
56	0	8	1	1,15067	84,047	1,5
57	4	1	0	1,14627	84,444	1,9
58	3	5	1	1,12930	86,017	0,8
59	2	4	2	1,12735	86,202	2,5
60	4	2	0	1,12392	86,529	1,5
61	0	6	2	1,11739	87,161	0,8

62	2	8	0	1,09526	89,385	0,8
63	4	3	0	1,08992	89,942	0,3

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,05270	0,25000	0,30300	0,5000	1,0000	4c
2	O2	O	0,19880	0,25000	0,79200	0,5000	1,0000	4c
3	FE1	Fe	0,35420	0,25000	0,04790	0,5000	1,0000	4c

Stick Pattern



APPENDIX 3

Tables with all results of flotation tests from Chapter 1.

REG quantification			
Mass of glucose (mg)	Vol $Na_2S_2O_3$ titred (mL)	Average vol. (mL)	Difference of volumes (mL)
0.00	27.30 27.10	27.20	0.00
10.00	24.10 24.05	24.08	3.13
20.00	20.85 20.90	20.88	6.33
30.00	18.00 18.05	18.03	9.18
40.00	14.85 14.90	14.88	12.33
50.00	12.15 12.10	12.13	15.08

Tables of flotation tests

		Industrial Starch – Optimization					
Depressant dosage (g/t)		**Fe (%)**	**Gangue (%)**	**LI (%)**	**Iron Recovery (%)**	**Mass Recovery (%)**	**Iron loss (%)**
400	CO	68.5	ND	2.2	63.9	45.7	37.6
	RJ	34	50.7	0.7			
600	CO	68.2	0.5	2	76.6	55.1	24.4
	RJ	26.5	61.5	0.7			
800	CO	68.8	ND	2	81.5	58.1	20.2
	RJ	23.6	65.5	0.8			
1000	CO	68.7	ND	1.9	87.4	62.4	13.7
	RJ	17.8	73.8	0.7			
1200	CO	68.2	0.6	1.9	89.3	64.2	11.7
	RJ	16	76.3	0.9			

Average results of flotation with Industrial Starch, using 100g/tSiO_2 of EDA-C as collector, pH 10.5.
LI = Loss on ignition.

Evaluation of pH in flotation process

	pH		Fe	Gangue	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)
Starch (1200g/t - 100g/t SiO_2)	10.5	CO	68.2	0.6	1.9	89.3	64.2	11.7
		RJ	16.0	76.3	0.9			
	9.5	CO	68.7	ND	1.8	86.4	61.6	14.5
		RJ	18.5	72.3	1.2			
	8.5	CO	68.2	0.6	2.0	86.0	61.9	15.0
		RJ	19.3	71.4	1.1			

LI = Loss on ignition

Flotation results for hydrolyzed dextrin

Time of hydrolysis (h)		Fe (%)	Gangue (%)	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)	REG (% gluc.)
0	CO	67.7	1.3	2.0	92.4	66.4	6.8	3.5
	RJ	9.8	85.3	1.1				
1	CO	67.9	1.3	1.7	92.1	66.1	8.1	7.6
	RJ	11.6	82.8	1.2				
2	CO	67.8	1.3	1.8	91.0	65.3	9.4	10.4
	RJ	13.1	80.6	1.2				
3	CO	67.9	1.2	1.8	90.0	64.6	9.7	12.6
	RJ	13.2	80.5	1.2				

Results of flotation with hydrolyzed dextrins, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5. LI = Loss on ignition.

Flotation results for hydrolyzed Waxy starch

Time of hydrolysis (h)		Fe (%)	Gangue (%)	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)	REG (% glucose)
0	CO	66.6	2.8	1.9	93.5	68.3	7.7	0.1
	RJ	11.8	82.6	0.6				
1	CO	65.9	3.8	2.0	93.4	69.0	7.8	1.9
	RJ	12.2	81.6	1.0				
3	CO	66.9	2.0	2.0	93.9	68.4	7.1	4.3
	RJ	10.9	84.1	0.6				
5	CO	66.1	3.8	1.7	91.5	67.4	8.9	7.1
	RJ	13.3	80.2	0.8				

Results of flotation with hydrolyzed Waxy starch, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.
LI = Loss on ignition

Flotation results for hydrolyzed dextrin and reduced hydrolized dextrins

Time of hydrolysis (h)		Fe (%)	Gangue (%)	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)	REG (% gluc.)
0	CO	67.7	1.3	2.0	92.4	66.4	6.8	3.5
	RJ	9.9	85.3	0.7				
1	CO	68.2	0.6	1.9	93.9	67.1	7.7	6.5
	RJ	11.3	83.2	1.0				
2	CO	68.3	0.4	2.0	93.1	66.4	8.8	9.2
	RJ	12.7	81.0	0.9				
3	CO	68.4	0.2	2.0	92.5	65.9	8.2	10.6
	RJ	11.7	82.3	1.0				
0h reduced	CO	68.1	1.0	1.7	92.5	66.2	7.6	0.1
	RJ	10.9	83.2	0.5				
1h reduced	CO	68.3	0.5	1.9	93.8	66.9	7.9	0.6
	RJ	11.6	81.8	2.0				
2h reduced	CO	67.6	1.5	1.9	93.3	67.3	8.4	0.6
	RJ	12.4	81.5	0.8				
3h reduced	CO	68.1	0.6	2.1	90.8	65.0	10.5	0.8
	RJ	14.6	78.2	0.9				

Results of flotation with hydrolyzed dextrins and reduced hydrolized dextrins, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.
LI = Loss on ignition

Flotation results for starch and reduced starches

		Fe (%)	Gangue (%)	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)	REG (% gluc.)
Dextrin	CO	67.7	1.3	2.0	92.4	66.4	6.8	3.5
	RJ	9.9	85.3	0.7				
Reduced Dextrin	CO	68.1	1.0	1.7	92.5	66.2	7.6	0.1
	RJ	10.9	83.2	0.5				
Soluble Starch	CO	66.0	3.9	1.8	89.0	65.6	10.8	3.4
	RJ	15.3	77.4	0.8				
Reduced Soluble starch	CO	67.1	3.1	1.7	90.3	65.6	10.3	0.2
	RJ	14.5	78.9	0.7				

Results of flotation with hydrolysed dextrins, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.
LI = Loss on ignition

Flotation results for different starches used in spectroscopic analysis

		Fe (%)	Gangue (%)	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)	REG (% glucose)
Dextrin	CO	67.7	1.3	2.0	92.4	66.4	6.8	3.5
	RJ	9.9	85.3	0.7				
Soluble Starch	CO	66.0	3.9	1.8	89.0	65.6	10.8	3.4
	RJ	15.3	77.4	0.8				
Waxy starch	CO	66.6	2.8	1.9	93.5	68.3	7.7	0.1
	RJ	11.8	82.6	0.6				
Industrial starch	CO	68.2	0.6	1.9	89.3	64.2	11.7	1.1
	RJ	16.0	76.3	0.9				

Results of flotation with different starches, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5. LI = Loss on ignition

Number of Raman spectra recorded in the points: Red, Black, Silver and Crystalline.

	Red				**Black**				**Silver**				**Crystalline**			
	H	*G*	*Q*	*Um*	*H*	*G*	*Q*	*Un*	*H*	*G*	*Q*	*Un*	*H*	*G*	*Q*	*Un*
Dextrin (C)	0	3	0	0	3	0	0	0	3	0	0	0	-	-	-	-
Dextrin (F)	0	2	0	1	3	0	0	0	-	-	-	-	0	0	2	1
Soluble Starch (C)	1	2	0	0	3	0	0	0	3	0	0	0	-	-	-	-
Soluble Starch (F)	1	1	1	0	2	0	0	0	0	0	2	1	0	0	2	1
Waxy starch (C)	1	2	0	0	3	0	0	0	2	1	0	0	-	-	-	-
Waxy starch (F)	1	2	0	0	2	0	0	0	2	0	1	0	0	0	3	0
Industrial starch (C)	1	2	0	0	3	0	0	0	3	0	0	0	-	-	-	-
Industrial starch (F)	0	3	0	0	3	0	0	0	2	0	1	0	0	0	1	2

*H = Hematite; G = Goethite; Q = Quartz e Un = Spectrum with unknown profile. The sign (-) indicates that non-crystalline points were found in the respective samples. (C) = concentrate samples and (F) reject samples.

APPENDIX 4

Tables with all results of flotation tests from Chapter 2.

Flotation results for XMC 1 as depressant

		Fe	Gangue	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)
A	CO	63.3	7.8	1.8	95.8	74.2	5.0
	RJ	9.4	85.8	0.7			
B	CO	64.4	6.3	1.7	96.8	73.8	5.4
	RJ	10.1	84.9	0.6			
Average	CO	63.8	7	1.8	96.3	74	5.2
	RJ	9.8	85.4	0.7			

Results of flotation with XMC 1, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.

XMC 1 = XMC from CFR source A, without grinding and extraction 1.
LI = Loss on ignition

Flotation results for XMC 2 as depressant

		Fe	Gangue	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)
	CO	67.7	1.5	1.7			
A	RJ	12.1	82	0.8	93.4	67.7	8.0
	CO	66.9	2.5	1.8			
B	RJ	10.8	83.9	0.7	94.5	69.2	6.8
	CO	67.3	2	1.8			
Average	RJ	11.4	83	0.7	93.9	68.4	7.4

Results of flotation with XMC 2, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.
XMC 2 = XMC from CFR source A, ground and extraction 1.
LI = Loss on ignition

Flotation results for XMC 3 as depressant

		Fe	Gangue	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)
A	CO	68.4	0.3	1.8	83.7	59.9	18.3
	RJ	22.4	67	0.9			
B	CO	68.6	0.04	1.9	82.8	59.1	18.8
	RJ	22.5	66.8	1.0			
Average	CO	68.5	0.2	1.8	83.2	59.5	18.5
	RJ	22.4	66.9	0.9			

Results of flotation with XMC 3, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.

XMC 3 = XMC from CFR source B, without grinding and extraction 1.
LI = Loss on ignition

Flotation results for XMC 4 as depressant

		Fe	Gangue	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)
A	CO	68.2	0.7	1.8	85.5	61.5	15.3
	RJ	19.5	71	1.2			
B	CO	68.2	0.7	1.7	92.4	66.4	9.6
	RJ	14	78.7	1.3			
Average	CO	68.2	0.7	1.8	89.0	64.0	12.4
	RJ	16.7	74.8	1.2			

Results of flotation with XMC 4, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.

XMC 4 = XMC from CFR source B, ground and extraction 1.
LI = Loss on ignition

Flotation results for XMC 5 as depressant							
		Fe	**Gangue**	**LI**	**Iron Recovery (%)**	**Mass Recovery (%)**	**Iron loss (%)**
A	CO	67.8	1.2	1.8	93.6	67.6	7.0
	RJ	10.5	84.1	0.8			
B	CO	67.7	1.4	1.7	93.1	67.4	7.1
	RJ	10.7	83.9	0.8			
Average	CO	67.8	1.3	1.8	93.3	67.5	7.1
	RJ	10.6	84	0.8			

Results of flotation with XMC 5, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.

XMC 5 = XMC from CFR source A, ground and extraction 2.
LI = Loss on ignition

Flotation results for XMC 6 as depressant							
		Fe	**Gangue**	**LI**	**Iron Recovery (%)**	**Mass Recovery (%)**	**Iron loss (%)**
A	CO	67.4	1.9	1.6	95.5	69.4	6.3
	RJ	10.1	85.3	0.3			
B	CO	67.7	1.6	1.6	92.6	67.1	8.8
	RJ	13	80.3	1.1			
Average	CO	67.6	1.8	1.6	94	68.2	7.5
	RJ	11.6	82.8	0.7			

Results of flotation with XMC 6, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.

XMC 6 = XMC from CFR source B, ground and extraction 2.
LI = Loss on ignition

Main results of XMC production

	Extractives (%)	Average (%)	Yield (%)	Average (%)
XMC 1	1.0 0.8	0.9	18.8 18.8	18.8
XMC 2	3.9 4.0	4.0	23.9 24.9	24.4
XMC 3	3.6 4.0	3.8	37.2 39.0	38.1
XMC 4	4.2 4.1	4.2	44.1 44.1	44.1
XMC 5	9.2 9.2	9.2	29.1 28.0	28.6
XMC 6	18.5 18.5	18.5	36.5 28.2	32.3

Extractives after stage of extraction and yield in percentage dry basis.

Flotation results for Industrial Starch as depressant

		Fe	Gangue	LI	Iron Recovery (%)	Mass Recovery (%)	Iron loss (%)
A	CO	68.1	0.5	1.9	89.9	64.1	11.5
	RJ	15.5	76.7	0.8			
B	CO	68.2	0.6	1.8	89.8	64.2	11.9
	RJ	16.0	75.9	0.9			
Average	CO	68.2	0.6	1.9	89.9	64.2	11.7
	RJ	16.0	76.3	0.9			

Results of flotation with industrial starch, using 100g/tSiO_2 of EDA-C as collector, 1200g/t of depressant, pH 10.5.
LI = Loss on ignition

Industrial Starch - Optimization								
Depressant dosage (g/t)		**Fe**	**Gangue**	**LI**	**Iron Recovery (%)**	**Mass Recovery (%)**	**Iron loss (%)**
400	CO	68.5	ND	2.2	63.9	45.7	37.6
	RJ	34	50.7	0.7			
600	CO	68.2	0.5	2	76.6	55.1	24.4
	RJ	26.5	61.5	0.7			
800	CO	68.8	ND	2	81.5	58.1	20.2
	RJ	23.6	65.5	0.8			
1000	CO	68.7	ND	1.9	87.4	62.4	13.7
	RJ	17.8	73.8	0.7			
1200	CO	68.2	0.6	1.9	89.3	64.2	11.7
	RJ	16	76.3	0.9			

Average results of flotation with Industrial Starch, using 100g/tSiO_2 of EDA-C as collector, pH 10.5.
LI = Loss on ignition

XMC 5 – Optimization							
Depressant dosage (g/t)		**Fe**	**Gangue**	**LI**	**Iron Recovery (%)**	**Mass Recovery (%)**	**Iron loss (%)**
400	CO	68.2	0.6	1.9	80.9	58.2	16.7
	RJ	19.6	71.1	0.8			
600	CO	68.7	ND	1.8	89.6	63.9	12.3
	RJ	16.8	75	1			
800	CO	68.7	ND	1.8	90.2	64.3	10.5
	RJ	14.5	78.3	0.9			
1000	CO	68.2	0.7	1.8	93.2	67	8.7
	RJ	13	80.5	0.9			
1200	CO	67.7	1.4	1.7	93.3	67.5	7.1
	RJ	10.7	83.9	0.9			

Average results of flotation with XMC 5, using 100g/tSiO_2 of EDA-C as collector, pH 10.5.
LI = Loss on ignition

	Evaluation of pH in flotation process							
	pH		**Fe**	**Gangue**	**LI**	**Iron Recovery (%)**	**Mass Recovery (%)**	**Iron loss (%)**
Starch (1200g/t - 100g/t SiO_2)	10.5	CO	68.2	0.6	1.9	89.3	64.2	11.7
		RJ	16.0	76.3	0.9			
	9.5	CO	68.7	ND	1.8	86.4	61.6	14.5
		RJ	18.5	72.3	1.2			
	8.5	CO	68.2	0.6	2.0	86.0	61.9	15.0
		RJ	19.3	71.4	1.1			
XMC 5 (1000g/t - 100 SiO_2)	10.5	CO	68.1	1.7	0.9	93.1	67	8.6
		RJ	12.8	81.3	0.4			
	9.5	CO	68.3	0.5	1.8	91.8	65.9	9.4
		RJ	13.5	79.9	0.8			
	8.5	CO	67.7	1.5	1.7	94.4	68.4	8.4
		RJ	13.0	80.4	1.0			

Average results of flotation with Industrial Starch and XMC, using 100g/tSiO_2 of EDA-C as collector.

LI = Loss on ignition