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SPECIFICALLY ADSORBED IONS IN HEMATITE FLOTATION

By

Natalia Parra Alvarez

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Chemical Engineering

MICHIGAN TECHNOLOGICAL UNIVERSITY

2021

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This thesis has been approved in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE in Chemical Engineering.

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Abstract

Specifically adsorbed ions, such as calcium and magnesium in iron ore flotation, are ions that can chemically bind with the mineral surfaces and alter the surface properties. Calcium and magnesium are unavoidable in process water and their concentrations are increasing due to water recirculation and reagent additions. These ions are detrimental to the flotation process. Calcium has always been the main focus in research, yet we found that magnesium is more detrimental in flotation due to its smaller atomic size. Starch adsorption in iron ore flotation is key for the effective depression of hematite. It has been determined by flotation, zeta potential, and settling tests, that increasing calcium concentrations promote starch adsorption and reduce entrainment of hematite, whereas increasing magnesium concentrations greatly reduce the selectivity overall by promoting the adsorption of starch to everything in the slurry and resulting in lower selectivity.

1 Introduction

1.1 Ions Classification in Iron Ore Flotation

1.1.1 Electrical Double Layer and Zeta Potential

When a solid surface is immersed in water, it interacts with the charged ions and dipoles in the water. Even though solids are considered electrically neutral, at a microscopic level they do not behave as such. When immersed in water they form electrically active layers around them known as the electrical double layer which is composed of two layers of ions from solution that neutralize the surface charge (Carlson and Kawatra, 2013). Figure 1.1 shows an example of these electrically active layers around a small hematite particle in water.

As observed in Figure 1.1, at alkaline pH levels the surface of the hematite is negatively charged. The first layer of ions that are directly adsorbed to the surface is the stern layer. This layer is usually considered to be one layer of ions thick and composed of ions with an opposing charge to the surface, in this case positively charged (Carlson and Kawatra, 2013). The next layer is called the diffuse layer. Some of the ions in the diffuse later will tend to move with the particle as the surface moves, and some will follow the bulk liquid. The shear plane is defined as the point at which the ions begin to move with the bulk liquid and not with the surface (Carlson and Kawatra, 2013). The zeta potential is the effective surface charge at the shear plane. Further away from the surface the ion concentrations go back to equilibrium, which marks the end of the electrical double layer.

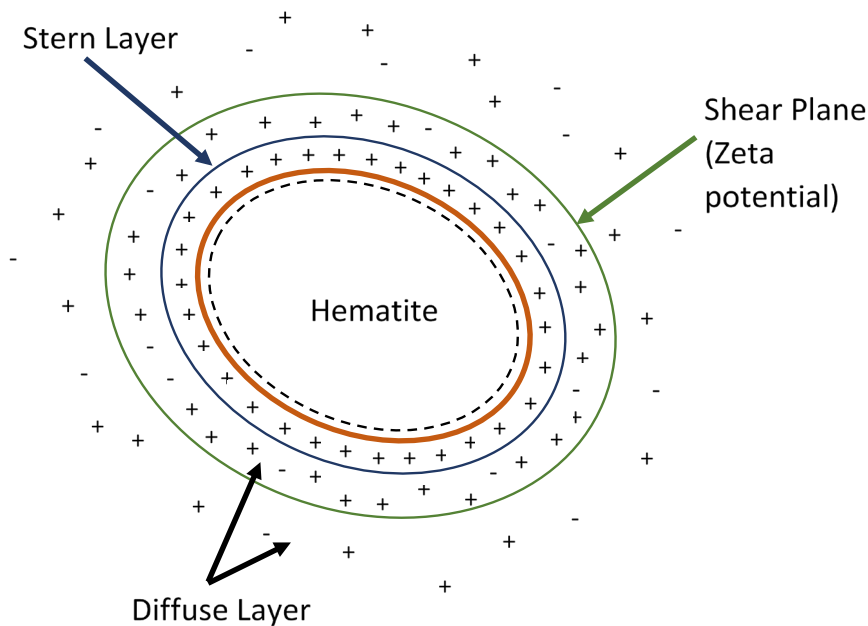


Figure 1.1: Representation of the electrical behavior of a hematite particle in water at alkaline pH levels.

1.1.2 Potential-Determining Ions, Indifferent Ions, and Specifically Adsorbed Ions

Ions can be classified in many ways. The distinction between potential-determining ions, indifferent ions, and specifically adsorbed ions is particularly important. The concentration of potential-determining ions in the aqueous phase determines both the sign and magnitude of the zeta potential. In oxide minerals, H^+ and OH^- are the potential-determining ions (Leja and Rao, 2004). This means that by changing the pH of the solution, the surface charge can be controlled. For instance, the quartz surface has a positive charge when the pH is less than 2.65 and a negative charge when the pH is greater than 2.65 (Zhang et al., 2019). Iron ore flotation is commonly performed at basic pH conditions where silica and hematite have negative surface charges.

Indifferent ions can only adsorb by Coulombic forces. They are attracted to surfaces with opposite charges, repelled to surfaces with like charges, and do not adsorb to uncharged surfaces (Delgado et al., 2007). These ions are mainly monovalent ions that are not potential-determining, such as sodium (Na^+), potassium (K^+), and chloride (Cl^-) for silica and hematite surfaces. On the contrary, specifically adsorbed ions can form chemical bonds with the surface regardless of the electrostatic charge (Delgado et al., 2007). Multivalent ions that are specifically adsorbed can reduce the magnitude of the zeta potential as well as change its sign. In iron ore flotation, calcium (Ca^{+2}) and magnesium (Mg^{+2}) are the principal specifically adsorbed ions. These ions are found within the stern layer (Delgado et al., 2007).

When ions are attracted to the surface they can form inner-sphere or outer-sphere complexes at the surface. As shown in Figure 1.2, specifically adsorbed ions such as calcium (Ca^{+2}) and magnesium (Mg^{+2}) can form inner-sphere complexes at the stern layer as they can bind to the surface by single covalent bonds. On the contrary, indifferent ions such as sodium (Na^+), potassium (K^+), and chloride (Cl^-) can only form outer-sphere complexes at the diffuse layer as they are only attracted by electrostatic forces and cannot bind chemically (Stumm et al., 1992). The point at which electrostatic forces can no longer hold outer-sphere complexes to the surface is defined as the shear plane. The surface charge at this location is known as the zeta potential (Carlson and Kawatra, 2013).

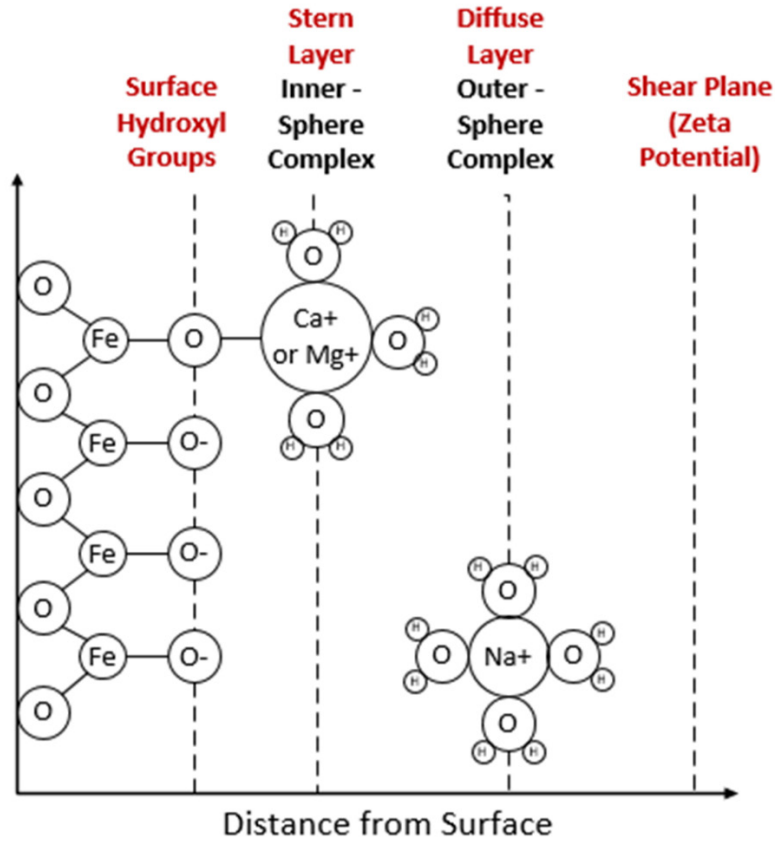


Figure 1.2: Schematic of the electrical double layer of a hematite surface as it interacts with the solution. Calcium and Magnesium (specifically adsorbed ions) create inner-sphere complexes located at the stern layer and can chemically bind with the hematite surface. Sodium (non-specifically adsorbed ion) can only create outer-sphere complexes at the diffuse layer due to electrostatic forces. (Based on Haselhuhn, 2012a)

1.2 Background on Iron ore Flotation

1.2.1 Iron Ore Beneficiation Process Overview

As high-grade iron ores become less available in the United States, the mining industry has had to create new technologies to concentrate low-grade iron ores. Magnetite (Fe_3O_4) and hematite (Fe_2O_3) are the main iron ore bodies concentrated in the United States (Haselhuhn and Kawatra, 2015). Unlike magnetite, the process of beneficiating the non-magnetic hematite ore is very complex, especially as it is mainly available at very low grades ($<40\%$ Fe) and at a very fine liberation size ($\sim 25 \mu\text{m}$ at 80% passing) (Haselhuhn and Kawatra, 2015). The only economical method available for concentrating such an ore consists of selective flocculation and dispersion (desliming) followed by reverse cationic flotation (Mariani and Nelson, 1993; Keranen, 1986). Figure 1.3 shows a summarized flowsheet of this process.

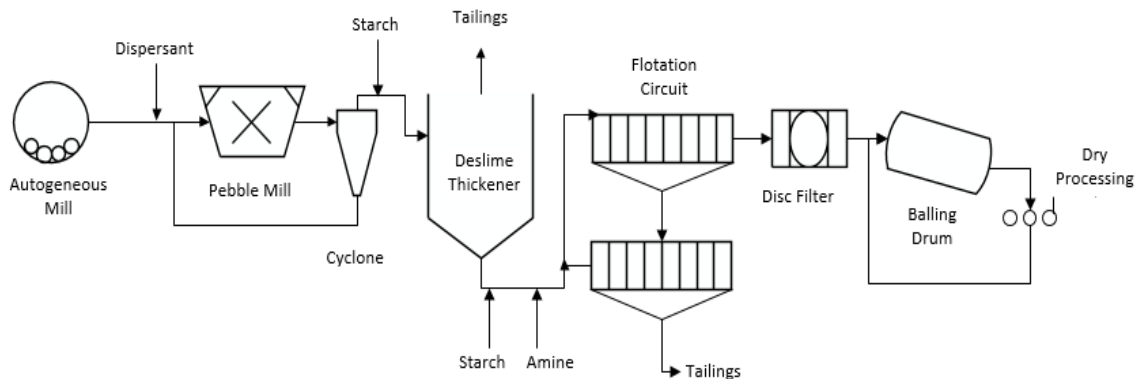


Figure 1.3: Fine and low-grade hematite ore beneficiation process flowsheet (Mariani and Nelson, 1993; Keranen, 1986; Haselhuhn and Kawatra, 2015).

Initially, the ore is treated with sodium hydroxide (NaOH) and ground in a ball mill (semi autogenous) and pebble mill (autogenous) until the liberation size is reached ($\sim 25 \mu\text{m}$ at 80% passing). The coarse material is separated from the fine material with a cyclone. While the coarse material returns to the grinding step, the fine material is sent to the selective or deslime thickeners where the ore is initially concentrated to $\sim 40\text{-}50\%$ Fe. The thickener's overflow, mainly composed of very fine particles or slimes are sent to the tailings pile, whereas the thickener's underflow is sent to flotation. The flotation circuit is composed of 10 rougher cells followed by 4 scavengers where the tailings are floated to improve recovery (Mariani and Nelson, 1993). The concentrates from the 4 scavenging steps are combined and redirected to the rougher's feed, while the froth is sent to the tailings pile. The final concentrate coming from the rougher cells continues to filtration, and pelletization stages. From there the pellets are sent for dry processing to a smelting plant.

1.2.2 Reverse Cationic Flotation of Hematite

Froth flotation is a widely used process in mineral processing to concentrate ores. In flotation, air bubbles are used to selectively separate hydrophobic (non-polar) compounds from hydrophilic (polar) compounds. Air will selectively attach itself to the hydrophobic surfaces, while the hydrophilic surfaces will remain primarily in the aqueous phase. Due to the buoyancy of the air bubbles, the hydrophobic particles are forced upwards into the froth phase, achieving separation. (Kawatra, 2009)

The most common method for concentrating iron ore is the reverse cationic flotation process (Lelis et al., 2019). Contrary to direct flotation, in reverse flotation the gangue material is floated and recovered in the froth product. In reverse flotation of hematite, the gangue silica particles are floated to the surface while the hematite is depressed and recovered in the “sinks” product (see Figure 1.4). The word “cationic” is included in the method’s name to specify the charge of the collector. In iron ore flotation the main collector used is ether amine which is a cationic collector that will only adsorb to negatively charged surfaces.

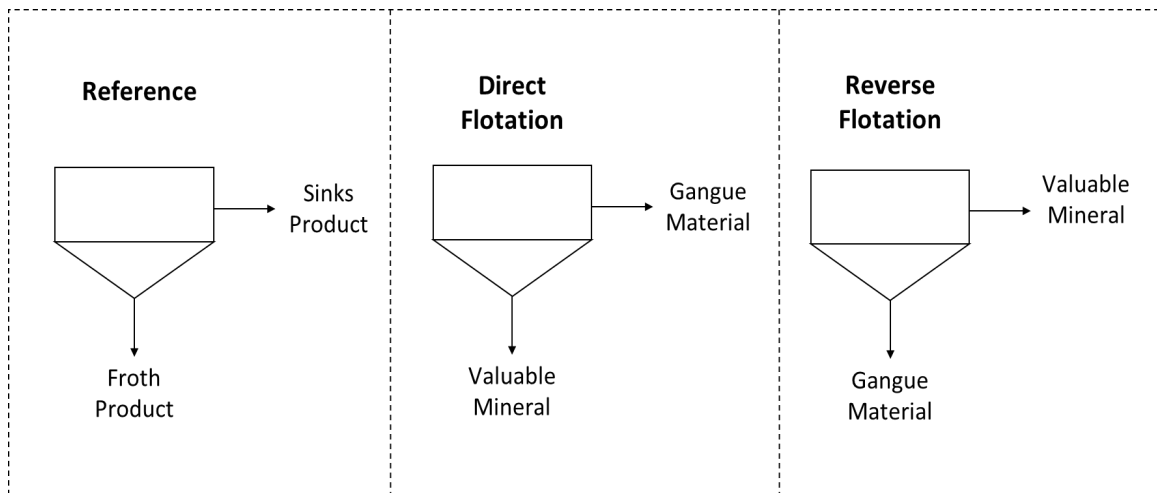


Figure 1.4: Contrary to direct flotation, in reverse flotation the gangue material is floated and recovered in the froth product.

Selective flocculation and dispersion, also called desliming, is a very important step in the beneficiation of low-grade and fine hematite ores. Very fine particles or slimes (<25 μm) need to be removed from the slurry prior to flotation otherwise the performance of the process is affected. Clemmer (1947) discovered the importance of desliming prior to the reverse cationic flotation process, since a high content of fine particles lowers selectivity and increases the cationic collector dosage required to obtain desired results (Filippov et al., 2014).

As the slimes are removed from the slurry there is always the chance of losing hematite. The key to the process is to remove as much slimes with the lowest iron loss possible. Selective flocculation of hematite is generally achieved with the help of a flocculant. Corn starch is the most common reagent used for this purpose as it is very effective creating hematite flocs or larger molecules that settle faster. Additionally, for the desliming process to be effective, the fine particles need to be highly dispersed.

Generally, the level of dispersion is achieved by maintaining alkaline levels of pH with the addition of sodium hydroxide (NaOH). Haselhuhn and Kawatra (2015) discovered that the optimal pH for the process is at 10.5. At this pH dispersion is favored and the maximum starch adsorption is achieved. Although the alkaline levels assist with dispersion, chemical reagents known as dispersants (sodium silicates, tripolyphosphates, among others) are needed to increase and maintain a high dispersion (Filippov et al., 2014; Colombo and Frommer, 1976; Colombo, 1980).

1.2.3 Reagents in Iron Ore Flotation

Reagents in flotation can be divided in three types which are depicted in the “triangle of flotation reagents” as described by Nagaraj and Ravishankar (2007). As shown in Figure 1.5 there are collectors, frothers, and modifiers.

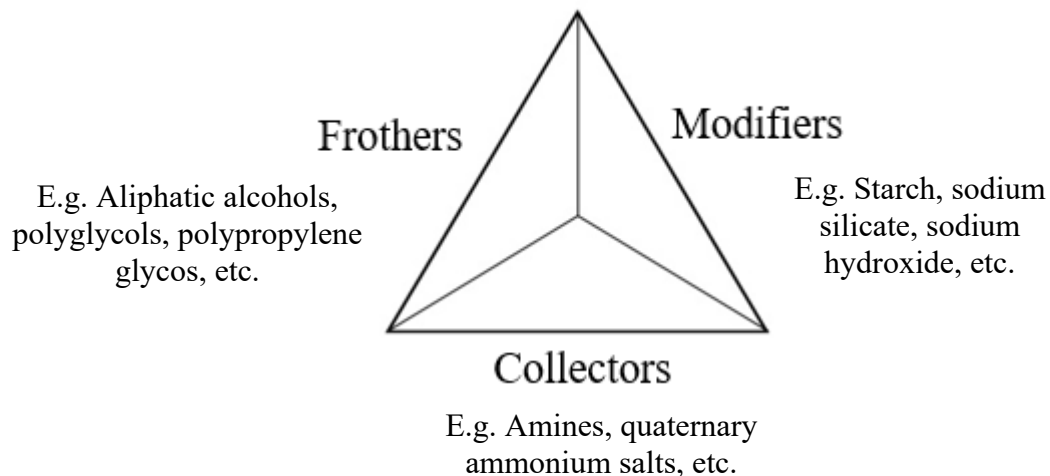


Figure 1.5: Triangle of flotation reagents: collectors, frothers, and modifiers.

The main purpose of iron ore flotation is to remove silicates and in some cases alumina or phosphorus containing minerals to improve the grade of the iron concentrate. The degree to which a mineral is hydrophobic can be influenced by the solution pH and the addition

of collectors. Collectors generally function by influencing the surface chemistry of the mineral in question. (Nakhaei and Irannajad, 2018)

Frothers are an essential part of flotation. Air bubbles are the main way of transporting the hydrophobic silica to the surface of the flotation cell and forming the froth phase, however, without the help of reagents, air bubbles will never be able to make it to the surface without collapsing. Frothers are reagents that help control bubble formation, size, and strength, as well as regulate froth stability and mobility (Bulatovic, 2007).

Modifiers constitute a very broad selection of reagents. Basically, every reagent used in flotation that does not classify as a collector or frother is known as a modifier (Nagaraj and Ravishankar, 2007). This includes pH modifiers, activators, depressants, dispersants, flocculants, coagulants, among others. As mentioned in the previous section, dispersants and flocculants are used for the selective flocculation and dispersion process. In the cationic reverse flotation process, only depressants and pH modifiers are used.

In iron ore flotation ether amine acts as both collector and frother, corn starch is used as a depressant, and sodium hydroxide (NaOH) is used as the pH modifier. The background and function of these three reagents in iron ore flotation is described below.

1.2.3.1 Ether Amine (collector and frother)

In the reverse flotation of hematite, amine collectors are used to make the silica particles hydrophobic so they can be rejected in the froth product. Amines are considered cationic collectors, which means that they are positively charged in an aqueous solution and can react with minerals with a negative surface charge (Nakhaei and Irannajad, 2018; Zhang et al., 2019).

Fatty amines, such as dodecylamine, were the first amine collectors used in the cationic flotation process established by the U.S. Bureau of Mines (Ma, 2012). Later on, the use of fatty amines in iron ore flotation became less popular due to their low collection power at low temperatures, poor selectivity, and cohesive bubble formation (Zhang et al., 2019). Nowadays, more soluble amines, mainly ether amines, are used in iron ore flotation despite of poor selectivity (Nakhaei and Irannajad, 2018).

There are records that state the use of specific frothers in iron ore flotation such as polypropylene glycols and alcohols, but in the United States the use of frothers is not common in the case of the reverse cationic flotation of hematite (Houot, 1983; Nakhaei and Irannajad, 2018). At the pH range that this process is performed (~10.5), the ether amine collector also acts as a frother. The fact that one reagent is used as both collector and frother makes it difficult to identify the individual impact of either function (Zhang et al., 2019). Hence, there is continuous research on partially substituting the ether amine with a frother so that by separating these effects, recovery and grade may be further optimized (Zhang et al., 2019).

1.2.3.2 Sodium Hydroxide (pH modifier)

Sodium Hydroxide (NaOH) is the most common pH modifier used in hematite flotation. It is generally used to adjust the pH to alkaline conditions. Based on Keranen (1986), at the Tilden Plant in Michigan, caustic soda is added as a 25% solution to control the pH and the selectivity of the process. This reagent is added to the primary grinding mill and to the dilution spray water in two different points of the flotation circuit. The pH of the slurry is one of the factors that determines the zeta potential of minerals.

1.2.3.3 Corn Starch (depressant)

The depressant plays a very important role in reverse flotation. Depressants are used to either prevent the collector attachment, or to decrease the hydrophobicity of a mineral so it is less likely to appear in the froth product (Zhang et al. 2019). Since in iron ore flotation the focus is on floating the silica, the hematite needs to be depressed. The most common depressants in iron ore include starch, guar, carboxymethylcellulose, and dextrin (Nakhaei and Irannajad, 2018). In the reverse cationic flotation of hematite corn starch is the most widely used depressant due to its high availability, low cost, and good performance (Nakhaei and Irannajad, 2018).

Starch is a natural polymer produced by green plants for the purpose of energy storage over long periods of time (Perez and Bertoft, 2010). Starches can be produced from various sources such as corn, rice, cassava, potato and others (Perez and Bertoft, 2010). Most starches used in industry contain 20-30% amylose, 70-80% amylopectin, and <1% lipids and proteins (Nakhaei and Irannajad, 2018). Amylose consists of a straight chain of glucose monomers while amylopectin is a branched polymer made up of amylose chains (Figure 1.6 and 1.7). In the starch molecules, both amylose and amylopectin are linked to each other by hydrogen bonds. These bonds form 3-100 μm starch granules which are insoluble in cold water.

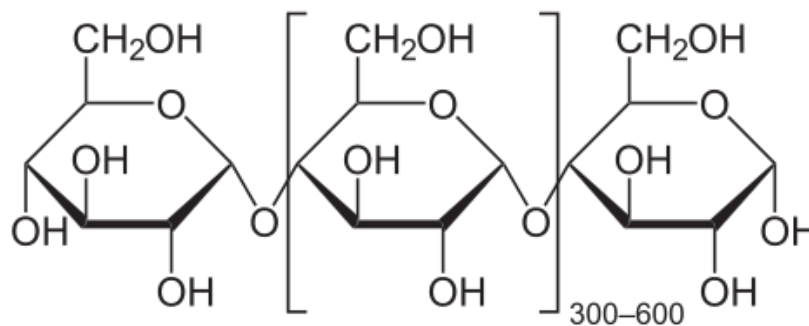


Figure 1.6: Amylose structure. Amylose consists of a straight chain of glucose monomers.

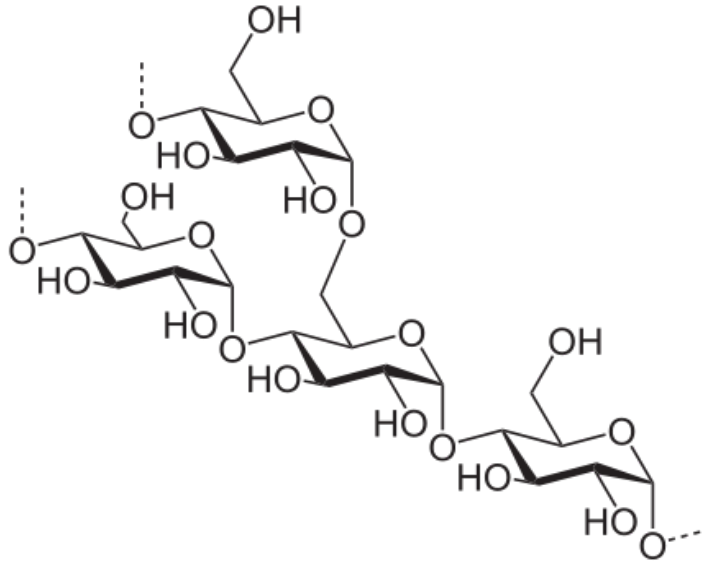


Figure 1.7: Amylopectin structure. Amylopectin is a branched polymer made up of amylose chains.

In order for starch dissolution to occur a “cooking process” named gelatinization needs to take place. This process can be divided in three stages (Yang et al., 2017):

1. Swelling: There is an increase in the diameter of the starch granules due to a raise in temperature up to 50°C. The water molecules bond to the hydroxyl groups of the amylose and amylopectin molecules that are exposed.
2. Rupture: As soon as critical temperatures are reached, the starch molecules rupture and ultimately deconstruct.
3. Starch molecules/ghosts: Once the rupture occurs the starch molecules inside the granule dissolve, leaving the empty shells (ghosts) intact. The starch ghosts do not have a significant impact in flotation.

There are four critical factors involved in gelatinization. These are described in Table 1.1.

Table 1.1: Critical factors that affect gelatinization (Based on Yang et al., 2017).

Critical Factors Involved in Gelatinization	Description
Mass ratio (amylopectin: amylose)	Amylopectin is harder to dissolve than amylose in basic solutions (>7pH), but amylose is harder dissolve at high temperatures.
Temperature	After the solution is cooled down, the dispersed starch molecules start a

	<p>reassociation process known as retrogradation.</p> <p>This process causes opalescence, turbidity, lower viscosity and precipitation.</p> <p>While amylopectin retrogrades very slowly, amylose retrogrades within a few hours.</p> <p>This is the reason why starch solutions are not stored for long periods of time.</p>
pH of the pulp	<p>In acidic conditions starches experience hydrolysis and turn into simpler sugars. However, the progress of starch gelatinization is accelerated at alkaline conditions.</p>
Size of the starch granules	<p>The size determines the duration of the gelatinization process as larger granules take longer. Typically, 30 minutes is enough for this process.</p>

1.2.4 Mechanisms of Solids Recovery in the Froth

In reverse flotation, only silica particles are expected to be recovered in the froth, however, some hematite is always lost in the tailings by being transferred to the froth phase. To reduce the hematite loss in the tailings, it is important to understand the different mechanisms by which silica and hematite are recovered in the froth. There are three mechanisms of solids recovery in the froth (Figure 1.8):

1. True flotation
2. Entrapment
3. Entrainment

True flotation corresponds to the selective attachment of hydrophobic particles to air bubbles, which are then recovered in the froth product, entrainment is where particles are trapped in between bubbles and recovered in the froth, and entrapment occurs when particles are trapped in between other particles and recovered in the froth (Nykänen et al., 2020; Melo and Laskowski, 2005).

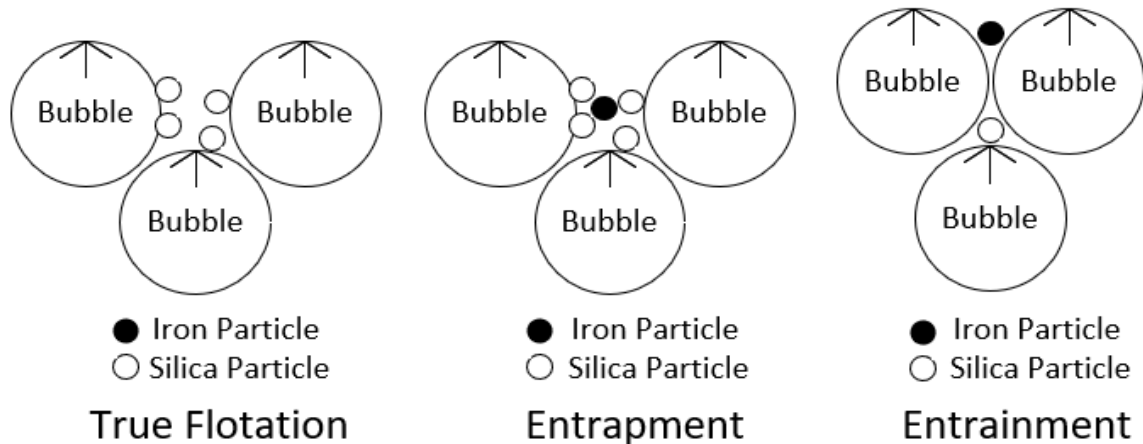


Figure 1.8: Mechanisms of solid recovery in the froth. True flotation: hydrophobic particles attach to air bubbles. Entrapment: particles are trapped in between other particles. Entrainment: particles are trapped in between air bubbles.

In general, silica is expected to be recovered in the froth by true flotation with the assistance of the collector. Hematite is not expected to be recovered in the froth at all, however, no system is ideal and some iron loss in the froth is always a possibility. Normally, the hematite that is recovered in the froth is recovered via entrainment. If the hematite appears to be recovering by true flotation, it typically means that the collector is adsorbing non-selectively to the silica and the hematite due to depression failure (Nykänen et al., 2020).

Entrainment is one of the main causes of low performance in flotation as it is a non-selective mechanism, which means that if it is not controlled, either the grade or recovery of the final product would be affected. In iron ore flotation, entrainment occurs when hematite and silica particles are trapped by bubbles and recovered in the froth phase. This mechanism can be divided into two key steps (Wang et al., 2015):

- Both silica and hematite particles are suspended in water and then transferred from the pulp phase to the froth phase.
- These entrained particles are transferred from the froth phase to the tailings product.

There are three main theories that explain the mechanism by which particles are transferred from the pulp phase to the froth phase by entrainment. Wang et al., (2015)

describes these theories and concludes that all three mechanisms contribute to entrainment with the third theory being the dominant mechanism.

1. The boundary layer theory: proposes that particles are transferred from one phase through the other in the bubble lamellae, which is the thin liquid film surrounding the bubbles. (Gaudin, 1975; Moys, 1978; Hemmings, 1981; Bascur and Herbst, 1982)
2. Bubble wake theory: suggests that particles suspended in water are transferred to the froth due to the water being forced upwards by the wake of a bubble that is ascending. (Smith, 1984; Yianatos et al., 1988)
3. Bubble swarm theory: as bubbles raise to the surface, they start accumulating in the region right below the froth/pulp interface. While some water and suspended particles drain back to the pulp, the rest is forced upwards due to bubbles buoyancy. The more particles are accumulating in the interface, the more water and suspended particles are entrained. (Smith and Warren, 1989)

Based on these mechanisms it is clear that the more hematite particles accumulate right below the froth/pulp interface, the higher the chances of hematite being recovered in the froth via entrainment. There are many factors that affect the level of entrainment such as water recovery, percent solids, particle size and density, froth height, froth structure, depressant activity, among others (Wang et al., 2015). In this thesis the focus is on one of the most important factors which is the efficiency and selectivity of the starch depressant. If the starch does not depress the hematite properly, the hematite will disperse in the solution. Dispersed hematite is more easily suspended in the aqueous phase, likely leading to a higher degree of entrainment.

In this research it has been found that calcium and magnesium affect the starch adsorption onto the hematite differently, thus, they have a different impact on the entrainment of hematite. The purpose of this project is to determine the differing effect of calcium and magnesium in starch adsorption in hematite flotation so that by knowing this, measures can be taken to promote flotation efficiency and reduce the entrainment of hematite.

2 Importance of Calcium and Magnesium in Flotation

2.1 Calcium and Magnesium Characterization

Table 2.1: Facts and Properties of Magnesium and Calcium.

Chemical Characteristic	Magnesium (Mg)	Calcium (Ca)	Reference
Element Category	Alkaline earth metal	Alkaline earth metal	Jahnen-Dechent and Ketteler, 2012
Atomic number	12	20	Enghah, 2004
Atomic Weight	24.30 g/mol	40.08 g/mol	Jahnen-Dechent and Ketteler, 2012
Ground State Electron Configuration	$[Ne]3s^2$	$[Ar]4s^2$	Enghah, 2004
Valence	2	2	Jahnen-Dechent and Ketteler, 2012
Crystal Structure	Hexagonal	Faced-centered cubic	Jahnen-Dechent and Ketteler, 2012
Occurrence			
Most important minerals	Magnesite ($MgCO_3$), Dolomite ($CaMg(CO_3)_2$), Carnallite ($KMgCl_3 \cdot 6H_2O$), Kieserite ($MgSO_4 \cdot 4H_2O$),	Calcite ($CaCO_3$), Dolomite ($CaMg(CO_3)_2$), Gypsum ($CaSO_4 \cdot 2H_2O$), Apatite ($Ca_5[(F,Cl,OH)(PO_4)_3]$)	Enghah, 2004

	Olivine ((Mg, Fe) ₂ SiO ₄)		
Abundance in the earth's crust	7 th most abundant element	5 th most abundant element	Enghah, 2004
Mean content in earth's crust	23,300 ppm	4.15 x 10 ⁴ ppm	Enghah, 2004
Mean content in oceans	1,290 ppm	412 ppm	Enghah, 2004
Chemical Characterization			
Atomic radius	150 pm	180 pm	Enghah, 2004
Covalent radius	130 pm	174 pm	Enghah, 2004

2.2 Calcium and Magnesium in Flotation Process Water

2.2.1 Calcium and Magnesium Variations in Feed Water at Processing Plants

Because calcium and magnesium are two of the most abundant elements in the earth's crust, they are unavoidable in process water. The term water hardness refers to the presence of multivalent metallic cations such as manganese, iron, calcium and magnesium, with the last two being the primary contributors to water hardness (Sepehr et al., 2013). There are many ways to classify water hardness but a common way is to express the concentration of calcium and magnesium ions as equivalent of calcium carbonate (CaCO₃) denominated "total water hardness" (Hammer, 1986). In general, waters with 0-50 mg/L of CaCO₃ are considered soft, with 50-150 mg/L of CaCO₃ are considered moderately hard, with 150-300 mg/L of CaCO₃ are considered hard, and over 300 mg/L of CaCO₃ are considered very hard (Hammer, 1986).

Nowadays there has been an increase in government and corporations demands for the mining industry to reduce freshwater extraction. Some of the motives for these demands include water resources becoming scarce, freshwater availability becoming more limited, water discharge triggering environmental pollution, competition for water resources by multiple industries, corporate policies for sustainability, and local community concerns regarding water safety and other cultural and spiritual concerns about water (Liu et al., 2013; Peters and Meybeck, 2000; Ridoutt and Pfister, 2010; Carlson et al., 2002; Johnson

et al., 2002; Boulay et al., 2011; Rijsberman, 2006; Jenkins and Yokovleva, 2006; Kapelus, 2002; Amezaga et al., 2010; Moran, 2006).

Flotation plants are starting to take measures to optimize the use of freshwater. Some of these measures include recirculating water and accessing multiple water sources which can cause great variations in water hardness and compromise flotation performance (Liu et al., 2013). Processing plants prefer more consistent water hardness ranges in the process because they are able to set standard reagent dosages and operation procedures (Liu et al., 2013). However, there are many factors that cause significant variations in water chemistry that require attention. Liu et al., (2013) classified these factors as internal and external.

Internal factors include ore oxidation and dissolution, which might not be significant at first but as the water is reused, substances such as calcium and magnesium that dissolve in the water can build up and eventually be detrimental to the process (Liu et al., 2013; Johnson, 2003). Reagent addition can bring other undesirable substances. For instance, lime is added as a pH modifier in the flotation of molybdenite-copper ore, but aside of adjusting alkalinity it releases calcium ions into the solution (Liu et al., 2013; Raghavan and Hsu, 1984). Substances introduced by reagent addition can also accumulate as the water is recycled and impact flotation (Liu et al., 2013; Slatter et al., 2009).

External factors include the use of multiple sources of raw water such as sea water which contains high levels of calcium, magnesium and iron salts (Levay et al., 2001), ground water, defined as water that is entrained in the minerals that are processed, surface water which includes rainfall reservoirs, rivers, and lakes, among other sources that all together cause a huge impact on the water chemistry that is later introduced in the flotation process (Liu et al., 2013). Another factor that is considered external is the use of water extracted from tailing ponds. The quality of this water varies significantly not only by the tailing's composition but by the local climate as day/night temperature changes or seasonal changes can alter the concentration of the dissolved substances due to evaporation and variations in solubility (Liu et al., 2013; Levay et al., 2001).

2.2.2 Calcium and Magnesium Variations during the Iron Ore Flotation Process

In iron ore flotation plants, the processes heavily rely on water chemistry and chemical reagents. In addition, the water chemistry of the iron ore flotation process is directly affected by the addition of reagents and removal of tailings in desliming. Table 2.2 shows the variation in the concentration of important ionic species at three different locations of an iron ore concentration plant in the USA.

Haselhuhn et al. (2012) determined that some of the most important ions present in the iron ore concentration plant in the USA are calcium, magnesium, sodium, potassium, chloride, and insoluble iron. The concentrations of sodium, potassium, and chloride are higher than those reached by calcium and magnesium in the three locations shown in Table 2.2. However, the magnesium and calcium concentrations are much more critical

to the process due to their divalent nature. Since they can chemically bind to the iron surface (specifically adsorbed), they have a much greater impact on the flotation process. As observed in Table 2.2, calcium concentrations are usually higher than magnesium, but as will be discussed later in Section 2.3 it is found that magnesium is far more detrimental to the flotation process.

Table 2.2: Concentrations of important ionic species in process water at different locations in an iron ore concentration plant (Haselhuhn et al., 2012)

	Screen Underflow (before dispersant)	Flotation Feed (after starch, before amine)	Flotation Rougher Concentrate	Discussion
pH	10.59	10.67	10.59	Maintained above 10.5 where dispersion of silica and hematite is critical.
Calcium (mg/L)	4.47	9.2	4.36	Divalent cations adsorb to negative surfaces and disrupt the sign and magnitude of the surface charge, affecting the surface properties of minerals and reagents.
Magnesium (mg/L)	2.67	8.49	0.23	
Sodium (mg/L)	455	448	433	Monovalent ionic species are less likely to cause harmful effects in the process. These ions only affect the magnitude of the zeta potential. Their effects in flotation are self-limiting because they cannot cause sign reversals.
Potassium (mg/L)	11.4	11.9	10.9	
Chloride (mg/L)	110	110	100	

2.3 Why do Calcium and Magnesium have Different Impacts in Flotation?

Both calcium and magnesium can alter the surface properties of minerals and reagents as they are specifically adsorbed ions. However, magnesium is more detrimental in the flotation process than calcium. The reason why magnesium results in a stronger interaction than calcium in flotation can be attributed to atomic size differences. Even though they have the same charge (+2), magnesium has a covalent diameter of 278 pm and calcium has a covalent diameter of 342 pm (Pyykkö and Atsumi, 2009).

The smaller atomic size of magnesium allows it to penetrate the electric double layer faster than calcium. Site spacing and surface charge density are the main arguments used to validate this statement. Site spacing is defined as the distance between sites available for adsorption. To confirm that calcium and magnesium behave differently in flotation due to site spacing, strontium and barium were selected for comparison (Haselhuhn, 2012a). Although strontium and barium are not commonly present in iron ore flotation in the USA, they were selected as they have the same charge as calcium and magnesium (+2) and have greater covalent diameters (370pm for strontium and 392pm for barium) (Pyykkö and Atsumi, 2009).

As shown in Figure 2.1, the average distance between the hydroxyl groups in the [100] plane of hematite is 285 pm (Pradip, 1994). Because the covalent diameter of magnesium (278 pm) is smaller than the hydroxyl group spacing in the hematite, magnesium can form complexes at every hydroxyl group (Haselhuhn, 2012a). Meanwhile, the covalent diameter of calcium (342 pm), strontium (370 pm), and barium (392 pm) is greater than the hydroxyl group spacing in the hematite so these ions can only form at every other hydroxyl group (Haselhuhn, 2012a).

Figure 2.2 shows that between the four ions, magnesium has the strongest impact in the zeta potential of hematite as it inverts the sign from negative to positive at very low concentrations. A much larger concentration of calcium, barium and strontium were required to invert the zeta potential from a negative to a positive charge. Based on site spacing, the maximum extent of adsorption appears to be the same for calcium, barium and strontium, but zeta potential results show that strontium and barium are much less impactful on the zeta potential than calcium. This means that site spacing is not the only reason why magnesium has a stronger interaction than calcium on flotation.

Surface charge density is defined as the amount of electric charge at the surface of a particle per unit length, surface area, or volume (Lucas et al. 2007). Magnesium and calcium have the same charge but due to atomic size differences magnesium has a greater surface charge density than calcium. Similarly, calcium has a greater surface charge density than strontium and barium, hence the different impact in the zeta potential of hematite. Therefore, magnesium can penetrate the electric double layer faster than calcium due to its greater surface charge density and site spacing.

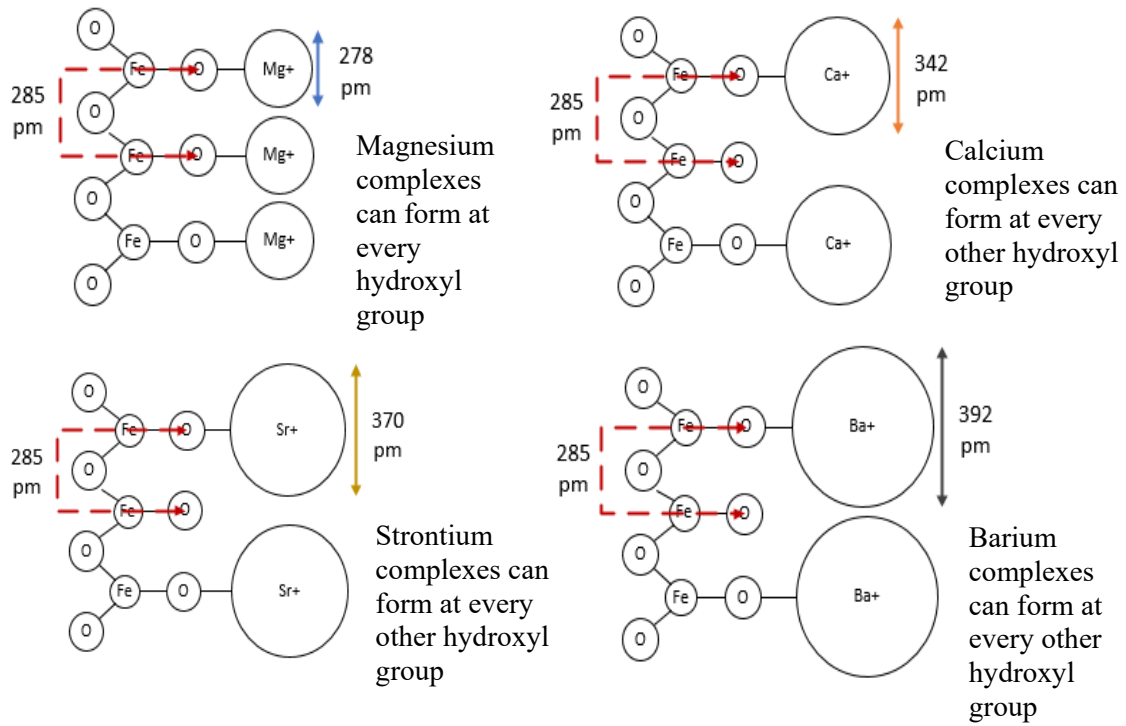


Figure 2.1: Magnesium, Calcium, Strontium and Barium complexes with the hydroxyl groups in the [100] plane of hematite. (Based on Haselhuhn, 2012a)

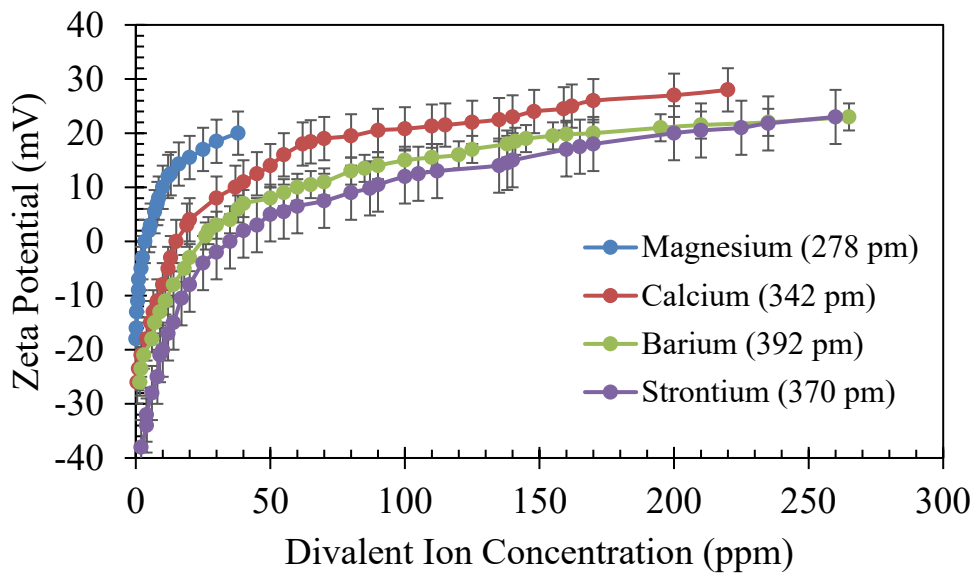


Figure 2.2: Zeta Potential of a concentrated hematite ore at various concentrations of Magnesium, Calcium, Barium, and Strontium (Based on Haselhuhn, 2012a)

2.4 Literature Review on the Effect of Calcium and Magnesium in Flotation

It is complicated to generalize the effect of cations in flotation since their effect depends on the characteristics of the ore, the type of reagents used in the process, the valence level and concentration of cations, among other factors (Tang and Wen, 2018). Research has shown that in iron ore flotation cations such as calcium and magnesium can promote flotation in some cases yet they can be detrimental to the process in other instances (Tang and Wen, 2018). Calcium and magnesium are beneficial primarily in the anionic reverse flotation of iron ore as they help activate the silica for the anionic collector adsorption (Cao et al., 2013; Ruan et al., 2018; Fuerstenau and Palmer, 1976). On the contrary, at high concentrations, calcium and magnesium are known to bring disadvantages in the reverse cationic flotation of iron ore.

The effect of calcium and magnesium in the reverse cationic flotation of hematite is not fully understood. Fuerstenau and Palmer (1976) found that high concentrations of calcium and magnesium make the sign of the zeta potential of the silica reverse from negative to positive, preventing the adsorption of the cationic collector onto the silica. Similar findings by Lelis et al. (2019) and Lelis et al. (2020) show that silica recovery in the froth is decreased as calcium chloride and magnesium chloride concentrations increase over 10 mg/L, because Ca^{+2} and Mg^{+2} ions are attracted to the negatively charged silica, competing with the amine collector. This is a major problem because most cationic collectors (alkyl ether amines and dodecylamines) adsorb onto the surface of the silica by electrostatic interactions (Rao, 2004; Ren et al., 2018).

Other researchers have found that divalent cations not only affect collector adsorption but can cause problems in the depression activity. Haselhuhn (2012a) mentions that at ion concentrations greater than 15 ppm, calcium and magnesium cause hetero-flocculation of silica and hematite in the selective flocculation and dispersion process, yielding low iron grades in the concentrate product. On a similar note, Ruan et al. (2018) also observed a depression effect in dolomite flotation attributed to the reaction of these cations with the fatty acid collector causing precipitation and lower concentrations of collector available for adsorption onto the surface of the dolomite. Shortridge et al. (1999) found that calcium and magnesium promote the depressive activity of long chain polysaccharide depressants such as carboxymethylcellulose (CMC) used in talc flotation.

Recently, researchers have discovered that calcium and magnesium behave differently in flotation. Haselhuhn (2012b) determined that magnesium is more detrimental than calcium in the selective flocculation and dispersion process because of site spacing as mentioned in Section 2.3. Lelis et al. (2020) observed a stronger depression effect in the presence of magnesium attributed to the $\text{Mg}(\text{OH})_2$ species in solution precipitating on the particle and creating a slime coating around the surface. A similar conclusion was reached by Li et al. (2018) in chalcopyrite flotation, where magnesium lowered the chalcopyrite recovery more than calcium due to the precipitation of $\text{Mg}(\text{OH})_2$ at a pH of 10. This precipitate adsorbed onto the surface of the chalcopyrite and lowered its hydrophobicity. Laskowski and Castro (2012) found similar results in the flotation of

molybdenite at pH levels greater than 10, where the $\text{MgOH}^+(\text{aq})$ adsorbs onto the surface of molybdenite and then the precipitation of $\text{Mg}(\text{OH})_2(\text{s})$ forms a hydrophilic coating around the molybdenite and lowers its floatability.

The objective of the present study is to understand more in depth the differing effects of calcium and magnesium in the reverse cationic flotation of iron ore. We have found that these ions, especially magnesium, are affecting the adsorption of starch onto the hematite causing low iron grades and recoveries. By understanding the mechanisms by which calcium and magnesium affect iron ore flotation, we can develop new strategies to control water quality in the process and improve process efficiency.

2.5 Methods to Control Water Hardness in a Flotation Plant

We have mentioned that in the iron ore industry the selective flocculation and dispersion process and the flotation process heavily rely on water chemistry. Because high concentrations of calcium and magnesium affect the efficiency of the process, different strategies are necessary to manage the water quality at processing plants. In general, flotation problems originated from water chemistry changes are dealt directly in the flotation process (Liu et al., 2013). The most common method followed in iron ore concentration plants is the addition of chemical reagents.

Sequestering ions such as calcium and magnesium using chemical reagents is one of the most common methods used in industry. Examples of ion-sequestering chemicals include chelating agents like EDTA (ethylenediaminetetraacetic acid) and a variety of dispersants such as PAA (polyacrylic acid), SHMP (sodium hexametaphosphate), among others (Lelis et al., 2019; Lelis et al., 2020; Li et al., 2018; Rebolledo et al., 2017). All these reagents are very large compounds that can form complexes with ions such as calcium and magnesium so that they cannot adsorb to mineral surfaces or other reagents. Figure 2.3 shows the Calcium-EDTA complexation as an example. Similar complexes are formed by the reagents mentioned above with both calcium and magnesium ions present in solution.

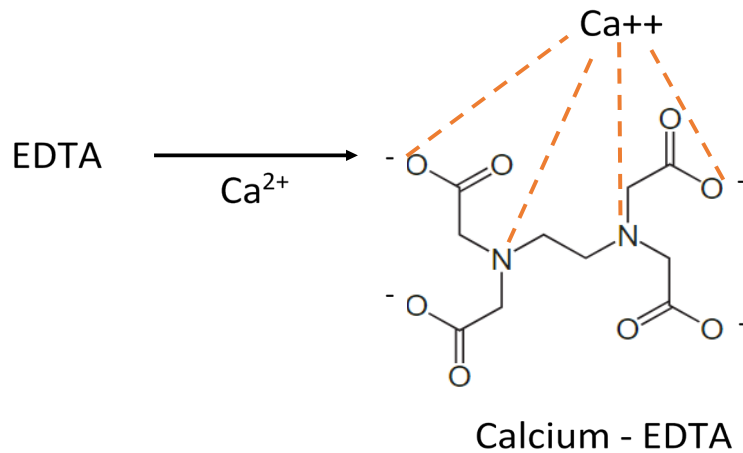


Figure 2.3: Calcium – EDTA (ethylenediaminetetraacetic acid) complexation (Based on Wu et al., 2015)

In iron ore flotation, adjusting dispersant dosages is usually enough to control the calcium and magnesium concentrations in flotation, however this solution is time consuming and the labor involved is considerable. Selecting and controlling dispersant addition depends in a lot of factors, especially since aside of reducing water hardness the dispersant needs to disperse the silica properly for process efficiency.

Another common method used to reduce water hardness in flotation is the ion exchange process (Williams and Phelan, 1985). In this process, calcium and magnesium dissolved in water are exchanged for sodium ions. As depicted in Figure 2.4, hard water passes over ion exchange resin beads which are negatively charged. At the base state the resin beads hold positively charged sodium ions. As calcium and magnesium contact the resin beads, they displace the sodium ions from the exchange sites (Millar et al., 2014). After the ion exchange takes place, the displaced sodium ions leave through the softener outlet, thus delivering “soft water” or water with low water hardness levels. The main drawbacks from this method are the high power consumption and the need of regular saturated resins regeneration (Sepehr et al., 2013).

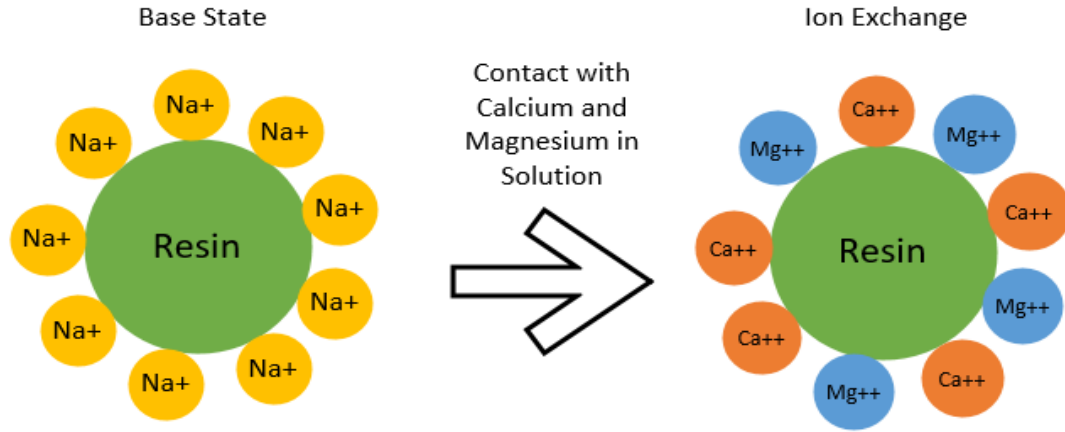
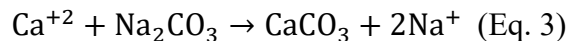


Figure 2.4: Depiction of the Ion Exchange Process. As the calcium and magnesium come in contact with the resin beads, they displace the sodium ions from the exchange sites.

Water hardness removal is also commonly performed by chemical precipitation by treatment with lime (calcium hydroxide, $\text{Ca}(\text{OH})_2$) and soda ash (sodium carbonate, Na_2CO_3). In this process the pH of the water is raised to exceed the solubility products of calcium carbonate (CaCO_3) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) (Mercer et al., 2005). The traditional soda-ash treatment can be divided in three stages shown in Equations 1-3 (Mohammadesmaeili et al., 2010).



As shown in Equations 1-3, calcium hardness precipitates as calcium carbonate (CaCO_3) and magnesium hardness precipitates as magnesium hydroxides ($\text{Mg}(\text{OH})_2$). These precipitates are removed in a later step by various processes such as filtration, coagulation, flocculation, or sedimentation (Mercer et al., 2005). The main disadvantage of this technique is that it will change the pH of the solution. Because iron ore flotation relies so much in the pH of the solution, this method is not very popular. Additional drawbacks from this process include the liquid sludge waste and the need for re-carbonation of the soft water (Sepehr et al., 2013).

Other methods reported in literature to control water hardness include the electrodeionization, electromembrane, and capacitive deionization processes, as well as the membrane and fluidized pellet reactor (Sepehr et al., 2013; Fu and Wang, 2009; Park et al., 2007; Seo et al., 2010; Li et al, 2005). Most current techniques to manage water hardness levels in flotation do not individually control the levels of calcium and magnesium in solution. In this research we find that magnesium is more detrimental than calcium in the flotation process, however, further research is necessary to control these concentrations independently.

3 Experimental Work at Michigan Tech

3.1 Research Objective

Most of the hematite ore reserves found in the USA are low grade (~30% Fe) and very fine (25-37 μm at 80% passing) in comparison with hematite ore reserves found in Brazil, India, Australia, and other countries (Zhang et al., 2019). These characteristics make this ore very difficult to process. The only feasible method to concentrate this kind of ore is by selective flocculation and dispersion followed by reverse cationic flotation which heavily rely on water chemistry and chemical reagents (Haselhuhn and Kawatra, 2015).

Calcium and magnesium are unavoidable in process water and because they are specifically adsorbed ions, they will affect the surface properties of minerals and reagents and cause problems in flotation. Previously, calcium had always been the main focus in research, but magnesium is far more detrimental in iron ore flotation. The objective of this project is to determine the differing effect of calcium and magnesium in the starch adsorption onto the hematite. We have discovered that in hematite flotation, magnesium affects the starch adsorption on the hematite much more than calcium, causing low iron grades and recoveries in the final product.

3.2 Initial Tasks

3.2.1 Sample Collection and Characterization

The hematite ore used in these tests was sampled from an iron ore concentration facility in the Upper Peninsula of Michigan. As shown in Figure 3.1, the samples have been collected at two different locations in the processing plant. The first time that samples were collected was in Location #1 which is in the deslime thickener underflow right before the starch addition. Collecting the samples at this location was recommended by plant engineers since it is right before flotation which is the focus of this study. However, surface active reagents such as dispersants and flocculants have already been added at this point which can change the surface properties of the minerals and make it difficult to analyze flotation results accurately. Ever since, the samples have been collected in location #2 at the autogenous mill screen underflow right before dispersant addition.

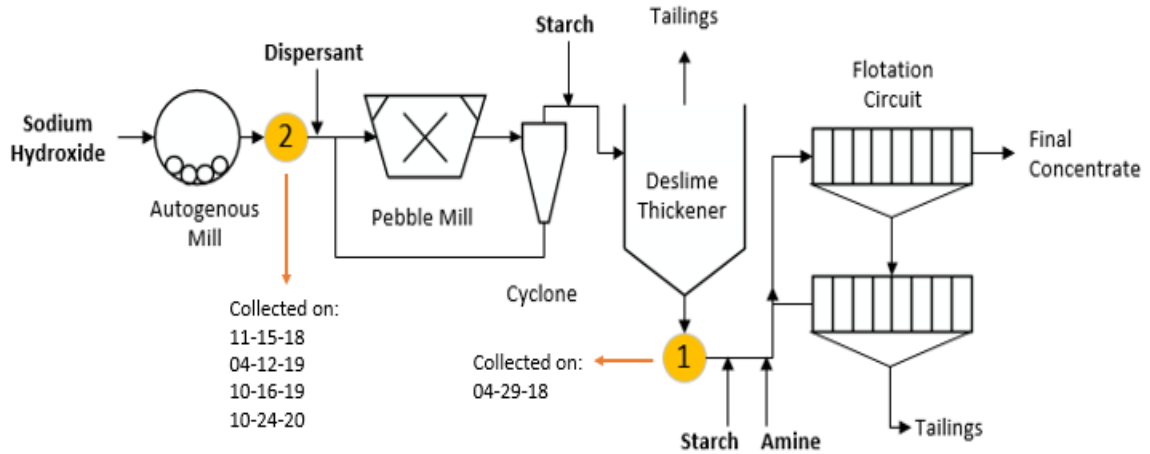


Figure 3.1: Sampling locations at the iron ore concentrator plant. Location #1: Deslime thickener underflow, right before starch addition. Samples at this location had a $40.95 \pm 0.6\%$ grade and a particle size of $12.09 \mu\text{m}$ at 80% passing. Location #2: Autogenous mill screen underflow, right before dispersant addition. Samples at this location had a $32.32 \pm 0.7\%$ grade and a particle size of 0.8 mm at 80% passing. Collection dates included.

The samples used in this investigation were collected in location #2 after primary grinding and right before dispersant addition. As Haselhuhn and Kawatra (2015) stated, this sample collection location is ideal since at this point surface active reagents have not been added to the slurry. Also, by sampling before secondary comminution, fresh surface sites can be achieved after grinding the ore in the lab prior to any experiments (Haselhuhn and Kawatra, 2015). The reason why samples were not collected earlier in the process is because before the ore goes thru primary comminution it is very difficult to obtain a representative sample (Haselhuhn and Kawatra, 2015). Figure 3.2 shows an X-Ray Diffraction (XRD) of the ore used. Results showed a composition of 65.15% quartz, 21.45% hematite, 7.7% magnesioferrite, and 5.7% goethite.

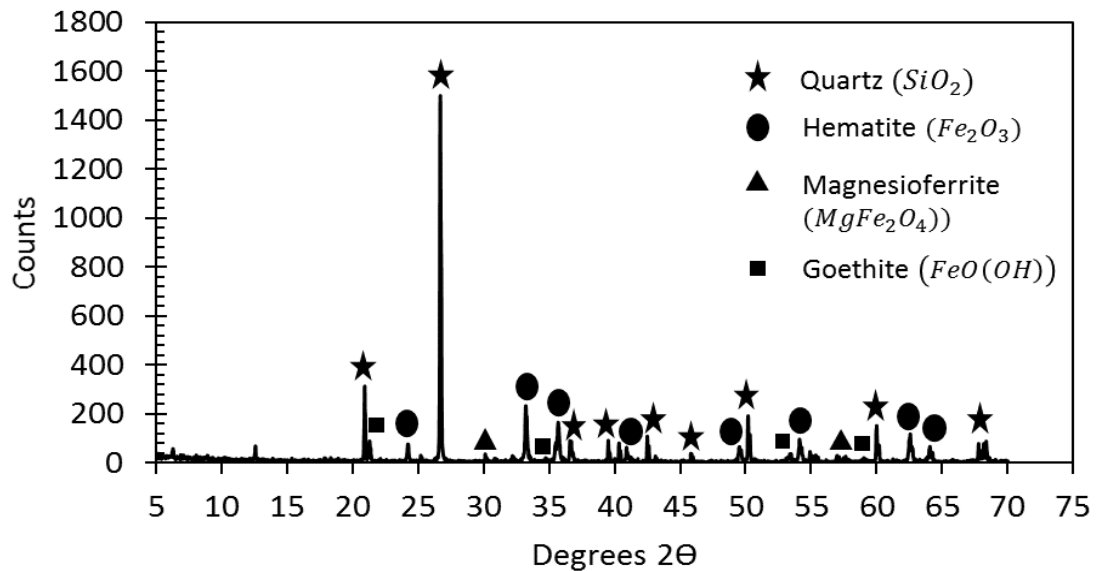


Figure 3.2: X-Ray diffraction results for the hematite ore used in this investigation. Quartz: 65.15%, Hematite: 21.45%, Magnesioferrite: 7.7%, Goethite: 5.7%

3.2.2 Recreation of the Iron Ore Concentration Process in the Laboratory

The focus of this research is flotation, but as the samples were collected so early in the process (Location #2 – Figure 3.1), it is necessary to recreate the iron ore concentration process in the laboratory, starting from secondary grinding up until flotation. As this process relies so much on water chemistry, it is important to recreate the process using feed water with similar water chemistry than the process water at the plant.

Feed water used:

To use similar water chemistry to the plant, ICP test were performed with the help of the Forestry Department at Michigan Tech to determine the calcium and magnesium concentrations in a sample of the city water available at MTU’s lab and in a sample of the flotation water at the plant. Similarly, titration tests were performed with both samples to compare their total water hardness (CaCO_3 concentration). As shown in Table 3.1 the calcium and magnesium concentrations and the total water hardness for the city water sample is much greater than the concentrations at the flotation plant. Because the water chemistry can vary between days, this table cannot be used for direct comparison. Though it is useful to conclude that the city water available at MTU’s lab needs to be softened for use in flotation.

The water used for the laboratory experiments consisted of a mixture of city water with deionized water to achieve lower calcium and magnesium concentrations comparable to the plant. The mixing ratio was determined every time a new batch of water was prepared

by performing titration tests on the city water sample to be used and using a simple dilution equation to reach a total water hardness concentration of approximately 16-18 mg/L of CaCO₃. Once the mixing was performed ICP test confirmed the exact calcium and magnesium concentrations that would be in the feed water added in grinding, desliming, and flotation.

Table 3.1: Water chemistry comparison between Houghton’s city water, flotation process water at the plant, and the feed water used for recreating the flotation process at MTU.

	Houghton’s City Water (03-06-19)	Plant’s Flotation Water (04-25-19)	Feed Water used in MTU Lab (01-27-21)
Calcium (mg/L)	63.4	3.2	7.5
Magnesium (mg/L)	13.4	1.4	1.5
Total Water Hardness (mg/L of CaCO ₃)	298.9±5	18.7±0.02	16.6±0.0

Grinding process:

For the grinding process, 500 g samples of hematite ore were conditioned with feed water, sodium hydroxide (NaOH), and Cyquest 3223 antiprecipitant - anionic polyacrylamide dispersant (for desliming), to prepare a hematite slurry of 60% solids at a pH of 10.5. The grinding process was repeated at various grinding times to determine in how long the ore reaches approximately 25 µm at 80% passing which is the liberation size of this ore (Haselhuhn and Kawatra, 2015). Results showed that grinding for 50 minutes in the lab rod mill produced a particle size distribution of 25.57 ± 0.3 µm at 80% passing. From this point on, prior to flotation, the ore is ground for 50 minutes.

Selective flocculation and dispersion (desliming) process:

As observed in Figure 3.3, the next step after grinding is selective flocculation and dispersion (also called desliming). To recreate this process in the laboratory a ten-liter transparent cell was used as shown in Figure 4.3. During this process the ground ore is added to the cell and conditioned with feed water (7% solids), sodium hydroxide (NaOH) to maintain the pH at 10.5, and causticized corn starch (0.3% solution) to flocculate the hematite. Once the solution was conditioned and let to settle for 30 seconds the ultra-fine silica particles (tailings) were siphoned out, while the settled hematite concentrate was filtered, dried, and taken to iron analysis to determine the iron grade and recovery using UV-VIS spectrometry at 510 nm. This procedure consisted of digestion of solids in

hydrochloric acid (HCl), dilution in distilled water, and addition of a neutral pH buffer, hydroxylamine hydrochloride reductant, and 1, 10-Phenanthroline indicator solutions. All Fe^{+3} ions are reduced to Fe^{+2} ions which turn orange when they react with the indicator. Following Beer-Lambert's law, the absorbance of the solution is proportional to the concentration of iron in solution.

The grade and recovery targets for the desliming process were communicated to us by the plant engineers during sample collection. These targets are 40-45% iron grade and 70-80% iron recovery. The best results obtained in the lab yielded a grade of $40.2 \pm 0.5\%$ and a recovery of $76.2 \pm 4.0\%$ by adding 3 lb/ton of the Cyquest 3223 antiprecipitant - anionic polyacrylamide dispersant and 0.0625 lb/ton of the corn starch flocculant solution.

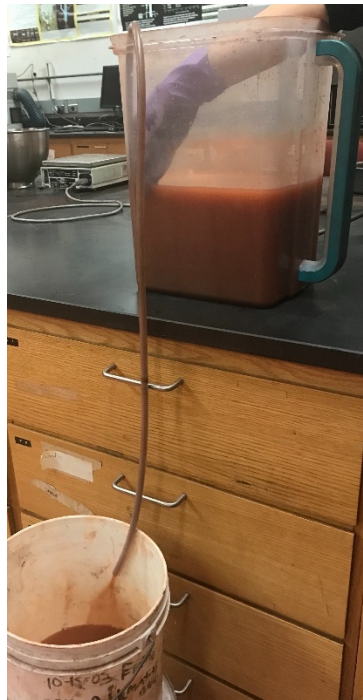


Figure 3.3: Desliming set up in the MTU laboratory. Tailings were siphoned out onto the white bucket and the concentrate was flocculated to the bottom of the deslime cell.

Reverse cationic flotation of hematite:

Flotation tests at MTU are performed using a 2-L Denver flotation cell shown in Figure 3.4. The feed for this process is the concentrate from the desliming stage. Once the slurry coming from desliming is added, more feed water is added (15% solids). The reagents added in this stage are sodium hydroxide (NaOH) for pH control (10.5), causticized corn starch (3% solution) as a depressant, and primary ether amine 30% neutralized with acetic acid (1% solution) as a collector/frother.

The grade and recovery targets for a single-stage flotation process (not including scavenging stages) were also given to us by the plant engineers during sample collection.

These targets are 63-64% iron grade and 60% iron recovery. The best results obtained in the lab yielded a grade of $63.4 \pm 1.8\%$ and a recovery of $56.7 \pm 2.8\%$ by adding 1.5 lb/ton of the corn starch depressant solution and 1.5 lb/ton of the primary ether amine collector/frother.



Figure 3.4: Flotation set up in the MTU laboratory. Tailings were recovered in the froth product and the concentrate was recovered at the bottom of the flotation cell.

A brief summary of plant targets, MTU laboratory results, and important findings such as grinding time and optimum reagent dosage are shown in the table below (Table 3.2). Note that the grinding time and the optimum reagent dosages determined were kept constant for the rest of the experiments described in Section 3.3.

Table 3.2: Summary of results for the initial task of recreating grinding, desliming and flotation in the MTU laboratory

	Plant Targets	Michigan Tech Lab Results	Method / Findings
Grinding Process Initial size: 0.8 mm	25 μm at 80% passing	25.57 \pm 0.3 μm at 80% passing	Achieved by grinding for 50 minutes in the rod mill.
Desliming Process	Grade: 40-45% Recovery: 70-80%	Grade: 40.2 \pm 0.5% Recovery: 76.2 \pm 4.0%	Optimum dosages: 3 lb/ton Dispersant (anionic polyacrylamide) 0.0625 lb/ton Flocculant (corn starch)
Single Stage – Flotation Process	Grade: 63-64% Recovery: 60%	Grade: 63.4 \pm 1.8% Recovery: 56.7 \pm 2.8%	Optimum dosages: 1.5 lb/ton Depressant (corn starch) 1.5 lb/ton Collector (Ether Monoamine)

3.3 Experimental Methods

Flotation / Entrainment Analysis:

Exactly as described in the previous section, the samples were ground and the slimes (ultrafine silica less than 25 μm) were removed during the selective flocculation and dispersion process using feed water with calcium and magnesium concentrations of 7.5 ppm and 1.5 ppm respectively. Past this point, the flotation procedure was adjusted. One of the main changes to the flotation procedure was the water used. Instead of using the feed water used during grinding and desliming, a specific concentration of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) or magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were mixed with deionized water to prepare water solutions of 0, 45, 60, 100, and 200 ppm of calcium and at 0, 7, 15, and 30 ppm of magnesium.

For the flotation / entrainment tests, the 15% solids slurry composed of the concentrate from desliming and flotation water at specific concentrations of calcium or magnesium (depending on experimental desing) was adjusted to a pH of 10.5 with sodium hydroxide (NaOH) and conditioned for 3 minutes with 1.5 lb/ton of etheramine 30% neutralized. Then, the solution was conditioned for 1 more minute with 1.5 lb/ton of starch depressant. Once all the reagents were added, the air was turned on and the froth product was collected during 165 seconds swapping collection pans at intervals of 15, 30, 60, 120, and 165 seconds. After flotation, all tailings and concentrate products were weighed for water recovery analysis, filtered, and dried. The dried weight of each product was recorded and all samples were analyzed for iron content by UV-VIS spectroscopy at 510

nm following the same procedure described in Section 3.1.2. Each test was repeated 3 times for reproducibility.

Zeta Potential Analysis:

The samples of freshly ground, filtered and dried ore were split into representative samples of approximately 1 gram. Each sample was hydrated with deionized water, adjusted to a pH of 10.5 with sodium hydroxide (NaOH), and sealed for 24 hours. Once hydrated, a 1-gram sample was placed in a 250 ml plastic beaker and 200 ml of deionized water adjusted to pH 10.5 was added. The particles were kept suspended in solution by a magnetic stirrer at 600 RPM. Only plastic instruments were used to prevent surface adsorption to laboratory equipment as described by Haselhuhn (2012b).

A 1000 ppm solution of calcium and 1000 ppm solution of magnesium were prepared using calcium chloride dihydrate ($\text{CaCl}_2 \cdot \text{H}_2\text{O}$) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) respectively. Also, a 0.15% corn starch solution was prepared in a hot plate at 240°C for 30 minutes and treated with 0.5 ml of a 10% NaOH solution.

Zeta potential tests were performed at 25, 50, 100, and 200 ppm of calcium and magnesium both with and without starch. Depending on the calcium and magnesium concentrations desired a micropipette was used to add the predetermined dosage of calcium or magnesium chloride solution. For the test with starch, 1.5 lb/ton of cooked starch was then added and conditioned. The zeta potential was measured using a Zetasizer Nano ZS (Malvern) unit at the MTU lab. For reproducibility, each measurement was repeated 3 times.

Settling Tests:

Settling analysis helps indicate the dispersive stability of a slurry. Particles that are flocculated will settle much faster than particles that are highly dispersed. The method used monitors the total suspended solids (silica and hematite) concentration in solution over time using a Hach DR5000™ UV/VIS spectroscopy at 810 nm properly calibrated (Hach, 2010; Haselhuhn, 2013; Krawczyk and Gonglewski, 1959). The total suspended solids concentration will decrease as the solids settle.

The slurry preparation was exactly the same as for the zeta potential tests described above. Tests were performed at 25, 50, 100, and 200 ppm of calcium and magnesium at a pH of 10.5 and 1.5 lb/ton of corn starch. Once prepared, the mixed slurry was carefully placed in a 10 mm light path cuvette design for the UV/VIS. The settling rate plots were determined by measuring the total suspended solids (silica and hematite) concentration in solution every 10 seconds for a total of 5 minutes with the UV/VIS measurement at 810 nm. For accuracy, each measurement was repeated 3 times. The absorbance at 810 nm was calibrated by measuring the total suspended solids gravimetrically and using various concentrations of the iron ore samples in deionized water at 10.5 pH.

3.4 Results and Discussion

Flotation / Entrainment Analysis:

The main function of starch in flotation is to depress the hematite to inhibit collector adsorption and to flocculate the hematite so it settles faster. If magnesium is affecting starch adsorption, it means that the mechanisms of hematite recovery in the froth could be altered. Analyzing entrainment plots at different concentrations of calcium and magnesium in flotation can lead us to the different repercussions of high calcium and magnesium concentrations in the reverse cationic flotation of iron ore.

The entrainment analysis method selected for this investigation is known as the simple correlation method (Lynch et al., 1981). It consists of plotting the cumulative water recovery percent in the froth against the cumulative iron recovery percent in the froth. A straight line in the plot indicates that the hematite is being recovered in the froth by entrainment. Any deviation from linearity indicates that some of the hematite particles are being recovered by true flotation.

As observed in Figure 3.5, as the concentration of calcium increases, the level of entrainment decreases, represented as a decrease in the slope. This means that calcium is not only activating the starch adsorption, but it is promoting the flotation performance by improving the depression of hematite. In Figure 3.6, it also clear that the level of entrainment is decreasing as the magnesium concentrations increase. When the hematite depression is improved, it enhances collector selectivity and efficiency as the collector will adsorb less to the hematite and more to the silica which is the main purpose of the reverse cationic flotation of iron ore. Additionally, as the settling rate of hematite increases there are less hematite particles located at the pulp/froth interface and hence, less hematite particles will be recovered by entrainment.

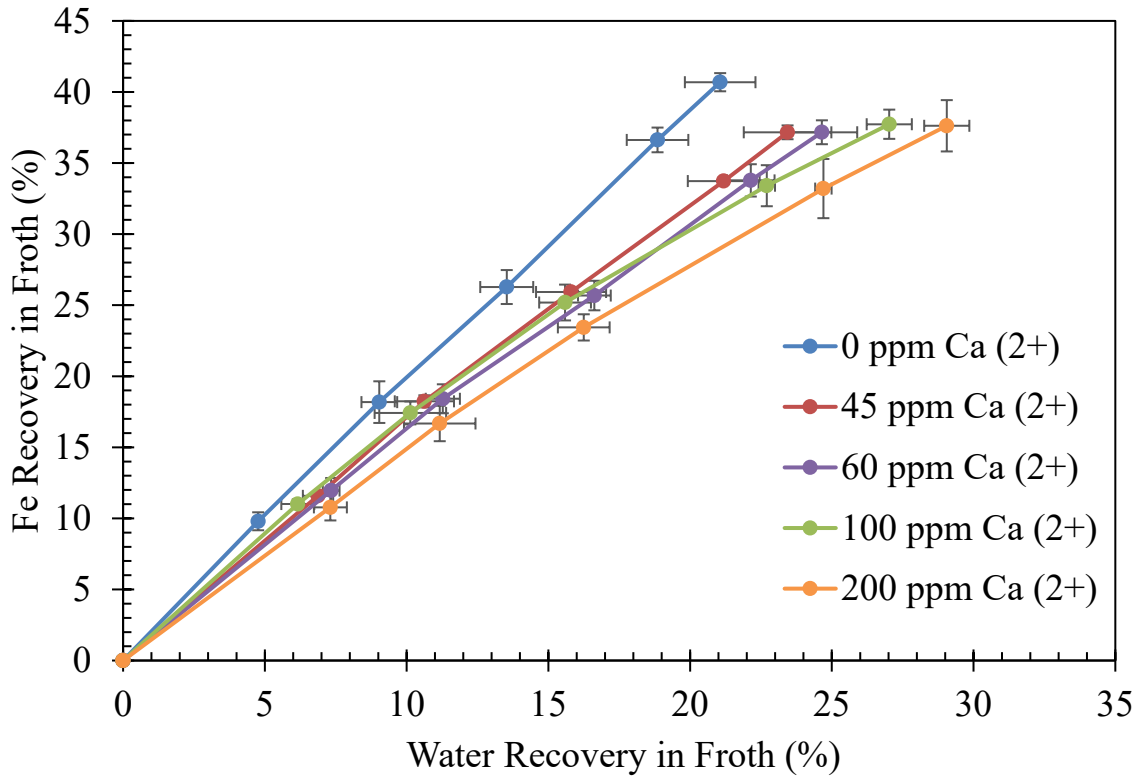


Figure 3.5: Entrainment tests for hematite ore at various concentrations of calcium. Error bars are standard deviation over 3 replicates.

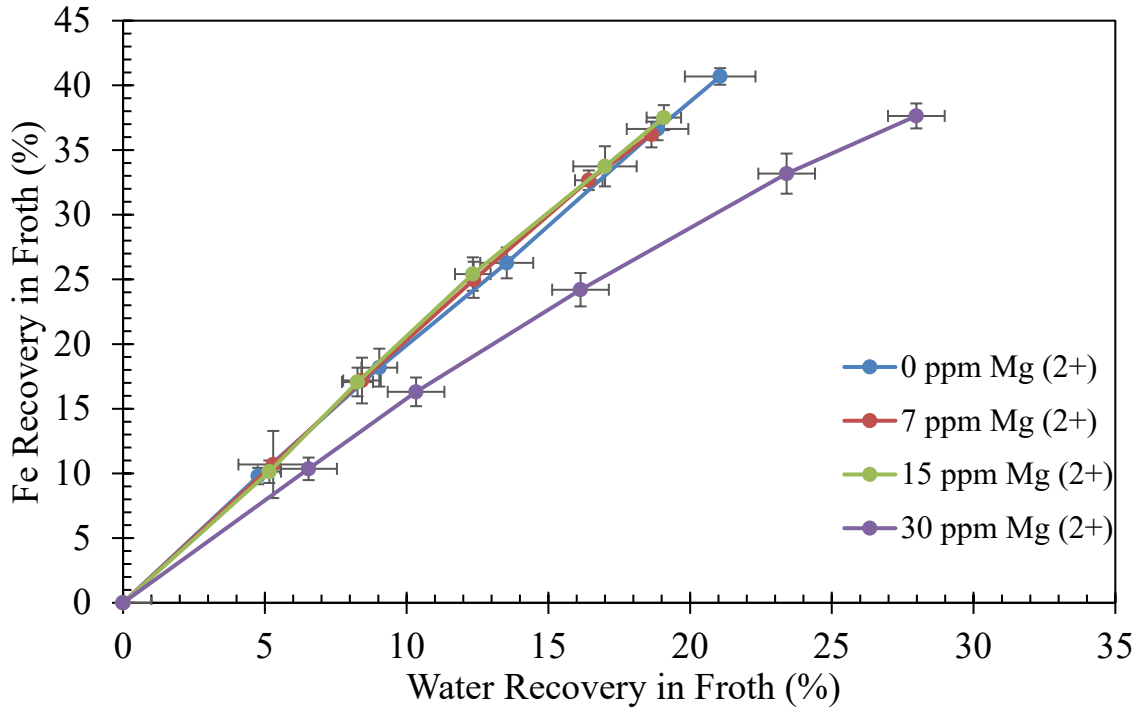


Figure 3.6: Entrainment tests for hematite ore at various concentrations of magnesium. Error bars are standard deviation over 3 replicates.

Better hematite depression means higher iron recovery in the final product, however, to analyze the true flotation performance it is important to consider both the grade and recovery simultaneously. As it is well known a high recovery could mean a low grade and vice versa. Thus, the best flotation performance is found at a balance between grade and recovery. In a grade/recovery curve, points that are higher and towards the right have a better performance than points that are lower and towards the left (Kawatra, 2009). As observed in Figure 3.7, the best performance achieved in this experiment was at 45 ppm Ca which had a grade of 58.9 +/- 0.3% Fe and an iron recovery of 63.7 +/- 0.5%.

The grade/recovery curve in Figure 3.8 shows that initially magnesium is promoting flotation, however after a very small increase in concentration it starts hurting the process. The best performance achieved in this experiment was at 7 ppm Mg which had a grade of 58.0 +/- 1% Fe and an iron recovery of 63.8 +/- 1%. These results prove how much stronger the interactions and repercussions of magnesium can be in flotation compared to calcium due to atomic size differences. Note that in both instances increasing past the optimal dosage decreases both recovery and grade. This is due to the calcium and magnesium decreasing the difference between hematite and silica.

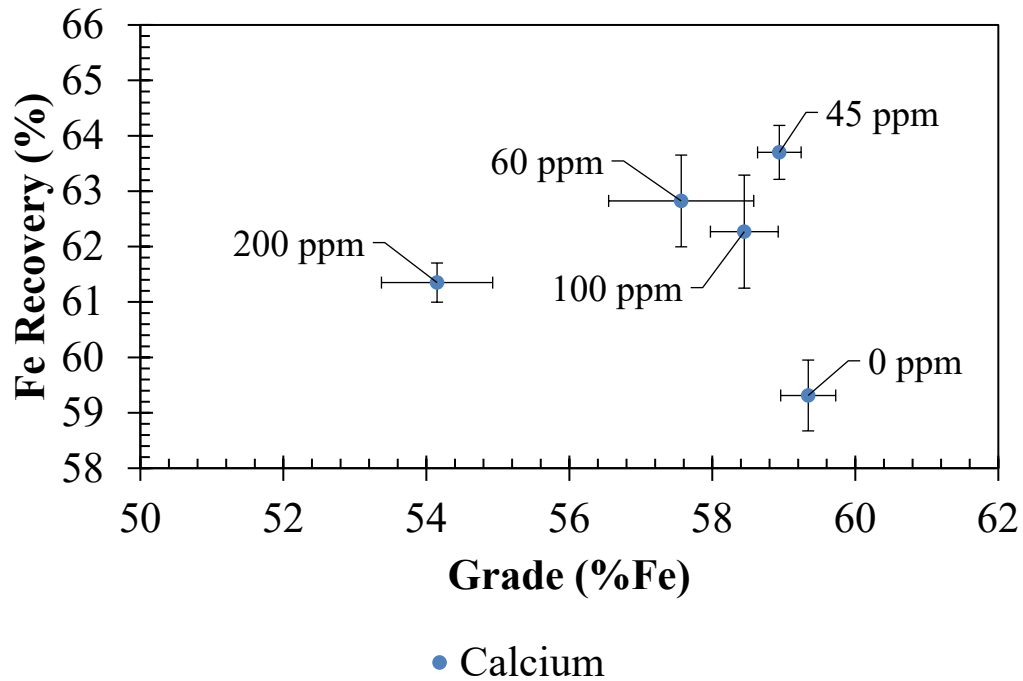


Figure 3.7: Grade/Recovery curve at various concentrations of calcium. Error bars are standard deviation over 3 replicates.

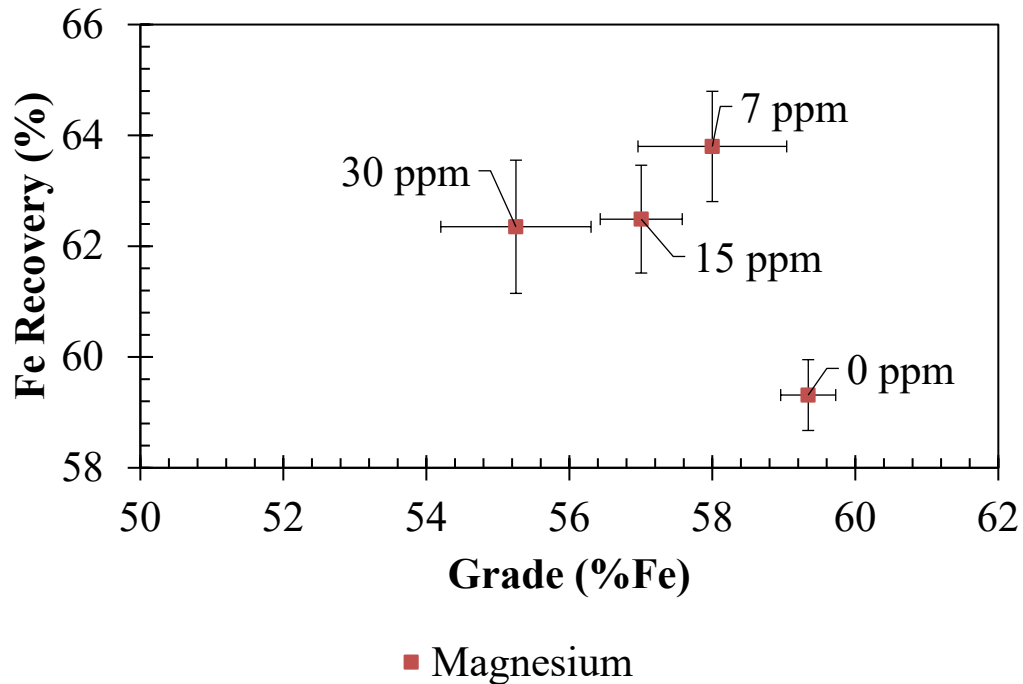


Figure 3.8: Grade/Recovery curve at various concentrations of magnesium. Error bars are standard deviation over 3 replicates.

Zeta Potential Analysis:

Zeta potential tests were performed to determine if calcium and magnesium interact with starch during flotation. In Figure 3.9, it is clear that without starch, magnesium has a stronger impact than calcium in the zeta potential of the hematite ore. Both calcium and magnesium ions have a positive charge, which means that at a pH of 10.5 they can adsorb to the negative surface of the hematite and eventually change the sign of the zeta potential. Within the range of concentrations studied during these tests only magnesium caused a charge reversal from negative to positive around 90 ppm, whereas calcium did not cause a charge reversal at the concentrations analyzed. Figure 3.10 shows the same tests in the presence of starch. In this case magnesium did not cause a charge reversal on the surface of the hematite. By comparing Figure 3.9 and 3.10 it is clear that the starch is limiting the effect of magnesium on the hematite surface. The most probable mechanism is that the starch is capturing the magnesium.

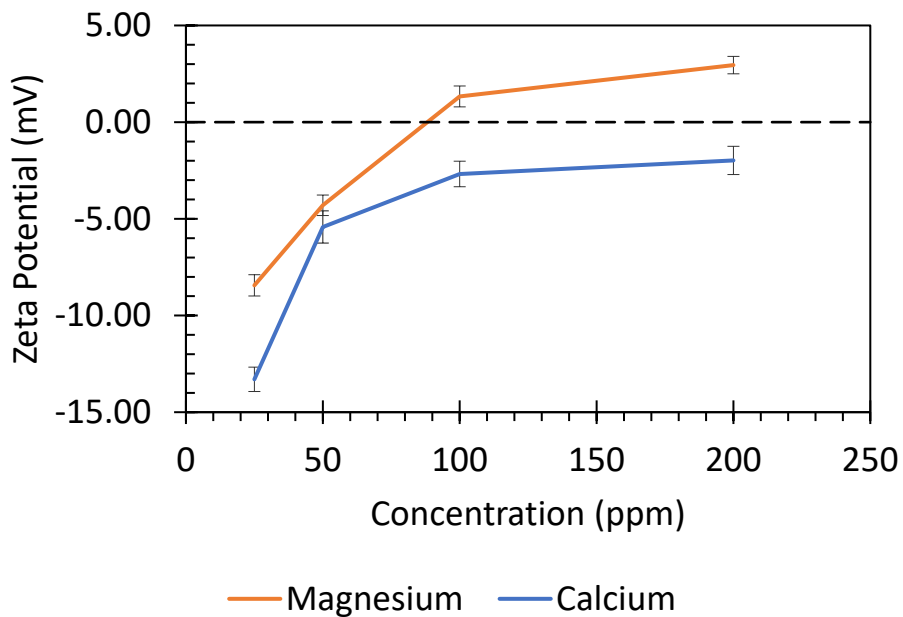


Figure 3.9: Zeta potential of hematite ore conditioned with various concentrations of magnesium or calcium at a pH of 10.5 (no starch added). Error bars are standard deviation over 3 replicates.

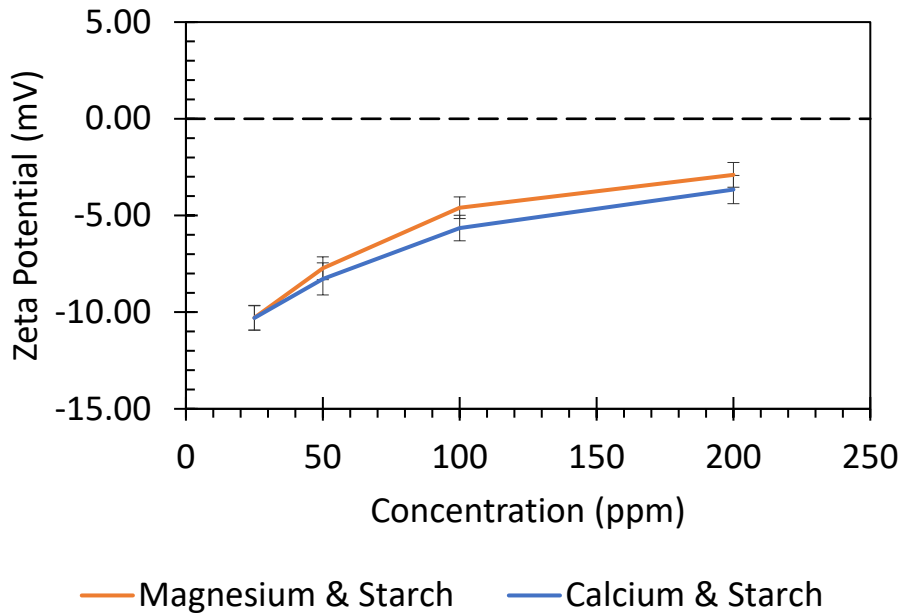


Figure 3.10: Zeta potential of hematite ore conditioned with various concentrations of magnesium or calcium, and 1.5 lb/ton of starch at a pH of 10.5. Error bars are standard deviation over 3 replicates.

Settling Tests:

Settling tests were performed to determine if calcium and magnesium affect the starch adsorption differently. As shown in Figure 3.11, the settling rate of solids (silica and hematite) does not vary significantly between 0 ppm calcium, 50 ppm calcium, and only starch when considering the error bars. Without starch, an increase in the calcium concentration seems to slightly improve the settling rate. This could be due to the addition of positively charged calcium ions to the negatively charged hydroxyl groups of hematite, causing flocculation of particles that were once suspended. The addition of sodium hydroxide (NaOH) increases the negativity of the mineral particles so the forces of repulsion acting between them prevent natural flocculation and settling (Green & Colombo, 1984). If the charge becomes less negative then the electrostatic repulsion is reduced, decreasing dispersion and provoking flocculation.

In Figure 3.12, the settling rate of solids (silica and hematite) does not vary significantly between 0 ppm magnesium, 50 ppm magnesium, and only starch when considering the error bars. But contrary to calcium, an increase in the magnesium concentration seems to slightly reduce flocculation without the presence of starch, which means that magnesium is slightly dispersing the ore. This behavior could be explained by the changes in zeta potential as the magnesium concentration increases. Since magnesium is a specifically adsorbed ion, it is expected to continue adsorbing to the hematite even if the surface has started to carry a positive charge. Hence, at some point, magnesium should begin to lead towards the dispersion of hematite (Claremboux, 2020).

In the presence of starch and 50 ppm of either calcium or magnesium, these ions activate the starch and increase flocculation of particles (either silica or hematite) as observed in Figure 3.11 and 3.12. Modified corn starch is slightly negative due to the presence of the carboxylate group (Green and Colombo, 1984). Thus, starch will adsorb (perhaps non-selectively) to the positively charge surface sites created by divalent ions. It is important to mention that due to site spacing and the surface degree of hydration, starch is more selective towards hematite surfaces than silica (Peçanha et al. 2019), but too high concentrations of calcium and magnesium may affect the selectivity (Haselhuhn and Kawatra, 2015).

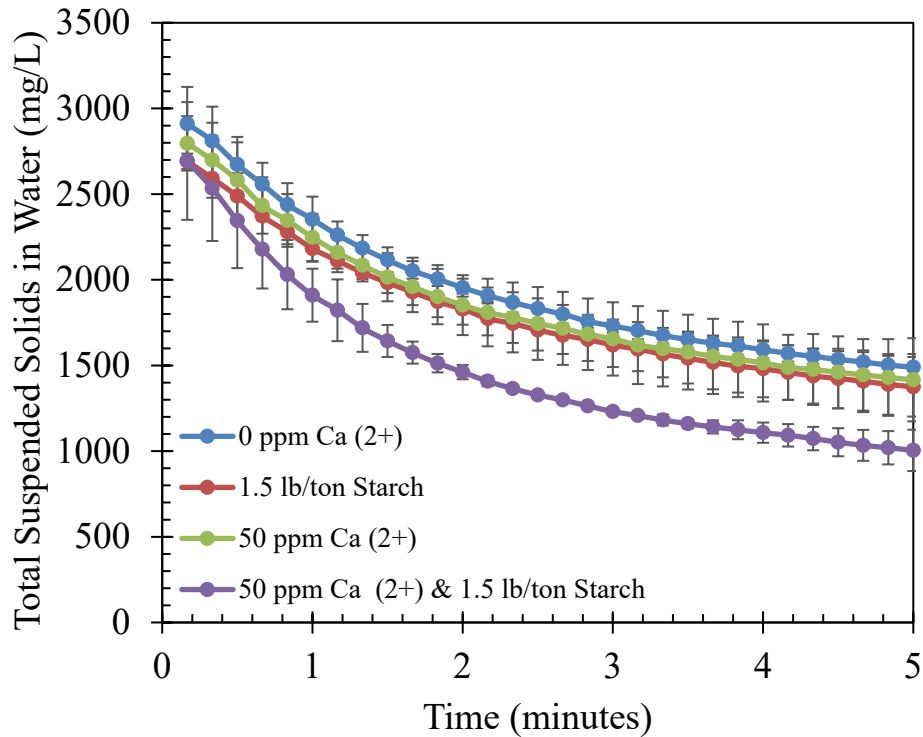


Figure 3.11: Settling tests for a fully hydrated iron ore at 10.5 pH with 0 ppm calcium, 50 ppm calcium, only 1.5 lb/ton of starch, and both calcium and starch combined. Calcium activates the starch for adsorption and increases flocculation of particles. Error bars are standard deviation over 3 replicates.

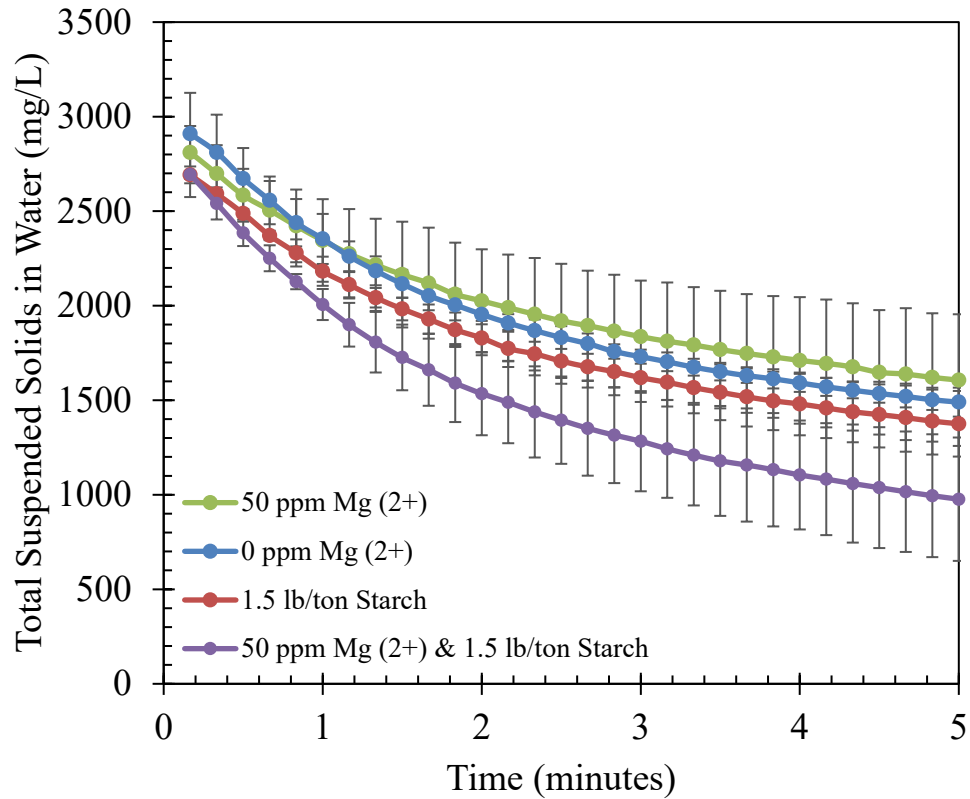


Figure 3.12: Settling tests for a fully hydrated iron ore at 10.5 pH with 0 ppm magnesium, 50 ppm magnesium, only 1.5 lb/ton of starch, and both magnesium and starch combined. Magnesium activates the starch for adsorption and increases flocculation of particles. Error bars are standard deviation over 3 replicates.

In Figure 3.13, the settling rate of solids is not significantly affected by an increase in the calcium concentration at a constant dosage of starch. The settling rate slightly increased as the calcium concentration went from 25 to 200 ppm. This can be attributed to the starch flocculating the ore even further as the calcium ions reduce repulsion or activate more sites for starch adsorption (either hematite or silica sites). On the contrary, an increase in the magnesium concentration at constant starch dosages cause the settling rate of solids to decrease (Figure 3.14), which tells us that magnesium is affecting the adsorption of starch to the ore. As the magnesium concentration continues increasing the settling rate decreases. This is likely due to the magnesium decreasing the amount of starch available by collecting it and causing it to precipitate as it was discussed in the zeta potential tests. Another possible mechanism is that the high concentrations of magnesium result in a positive charge being expressed on all of the available surfaces, resulting in dispersion.

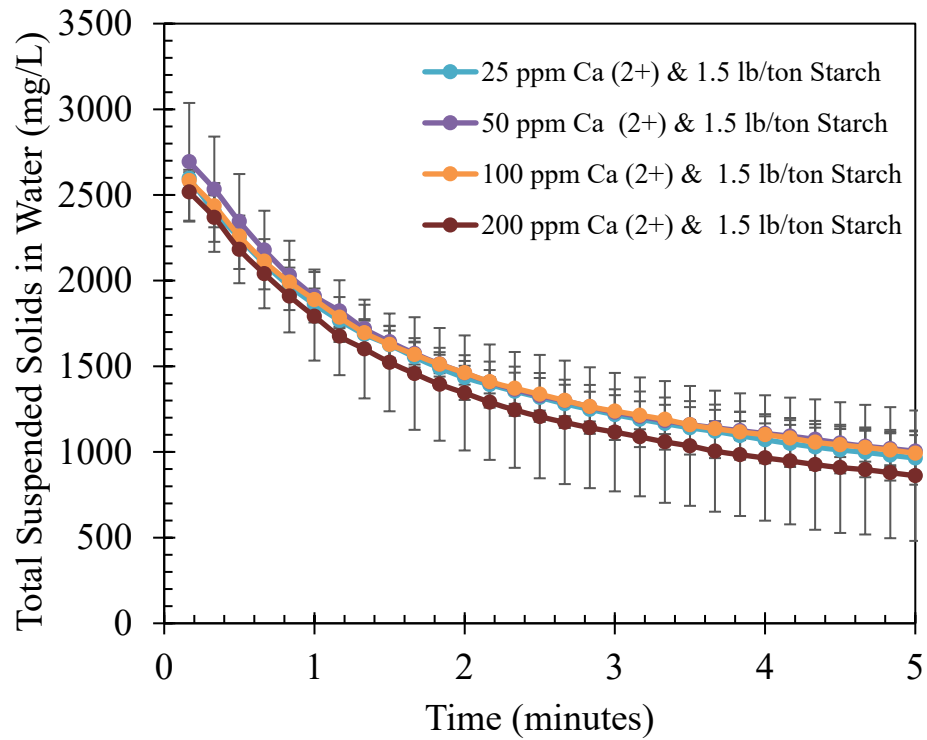


Figure 3.13: Settling tests for a fully hydrated iron ore at 10.5 pH conditioned with 1.5 lb/ton of starch and various concentrations of Calcium. An increase in calcium will not change the settling rate of solids significantly. Error bars are standard deviation over 3 replicates.

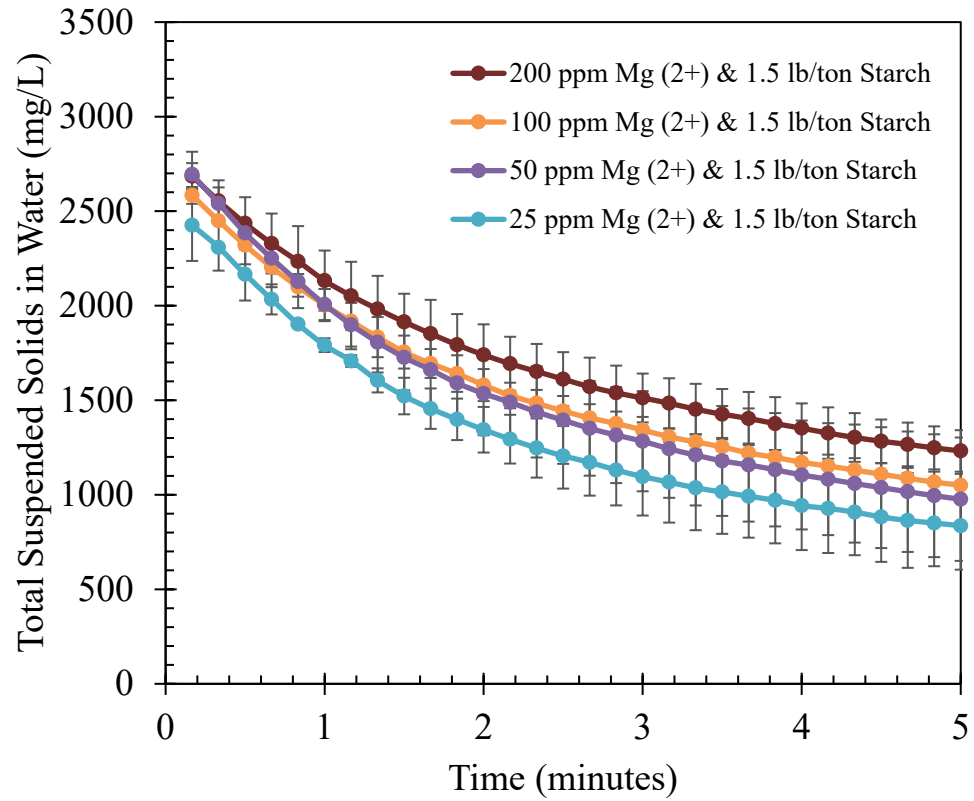


Figure 3.14: Settling tests for a fully hydrated iron ore at 10.5 pH conditioned with 1.5 lb/ton of starch and various concentrations of Magnesium. As magnesium increases, it affects the adsorption of starch to the ore. Error bars are standard deviation over 3 replicates.

4 Conclusions

Specifically adsorbed ions, such as calcium and magnesium in iron ore flotation, are ions that can chemically bind with the mineral surfaces and alter the surface properties. Calcium and magnesium are unavoidable in process water and as their concentrations increase due to water recirculation and reagent additions they are becoming detrimental to the flotation process. Calcium has always been the main focus in research yet magnesium has been found to be more detrimental in flotation due to its smaller atomic size and greater surface charge density.

Starch adsorption in iron ore flotation is key for the effective depression of hematite. It has been determined by flotation, zeta potential, and settling tests, that increasing calcium concentrations promote starch adsorption and reduce entrainment of hematite. As positively charged calcium ions adsorb onto the hematite, they attract the slightly negative starch and promote hematite depression. The effect of magnesium appears to be mechanically very similar to calcium, but with much higher kinetic rates resulting in much lower selectivity. Calcium appears to preferentially promote the adsorption of starch to hematite. The addition of magnesium appears to promote the interaction of starch with everything in solution: hematite, silica, and even starch's interactions with itself resulting in lower selectivity. This should be further tested by evaluating the interaction of magnesium with silica.

Magnesium and calcium must be individually controlled in flotation. Current industry practice focuses heavily on calcium only. For this flotation setup the best performance achieved was at 45 ppm Calcium and 7 ppm Magnesium. Increasing past the optimal dosage decreases both recovery and grade as calcium and magnesium decrease the difference between hematite and silica.

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