EFFECT OF CARBONATE ALKALINITY ON THE FLOCCULATION
BEHAVIOR OF HEMATITE

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BEHAVIOR OF HEMATITE**

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ABSTRACT

EFFECT OF CARBONATE ALKALINITY ON THE FLOCCULATION BEHAVIOR OF HEMATITE

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As high grade iron ore deposits are rapidly depleted, the minerals industry is increasingly obliged to enrich their ores and process lower grade iron ores. Production of large quantities of fine ores as tailings or by-products in mining operations and mineral liberation at fine particle sizes have led to the development of concentration methods employed to fine ores. Selective flocculation is one of the beneficial methods which can be used in recovering of very fine particles

It is obvious that process water chemistry has a significant influence on the flocculation efficiency, and the water chemistry is deeply affected by carbon dioxide dissolution. Carbonate content of natural waters regulated by CO_2, carbonic acid and solid carbonates is known as 'carbonate alkalinity' which may be an important factor in flocculation especially at alkaline pH.

Selective flocculation of iron ores is usually run at around pH 11 where carbonate alkalinity could be rather high. There have been no reports in literature regarding the effect of carbonate alkalinity on the flocculation behavior of iron oxides, mainly hematite. In this study, the flocculation behavior of iron ores with starch under different alkalinities has been investigated. The extent of flocculation has been assessed by settling rate and suspended solid content measurements at different starch doses and pH values. Zeta potential measurements and starch adsorption studies were carried out to explain these effects by carbonate alkalinity.

According to the results, flocculation is enhanced by addition of low amount of carbonate alkalinity, less than 2.4 mEq/L. However, adding the higher amount of alkalinity adversely affected the flocculation of hematite. Similar behavior was also observed during the starch adsorption tests, larger amount of starch was adsorbed by hematite in low alkalinity compared to high alkalinity. Zeta potential measurements indicate that, by increasing the carbonate alkalinity of suspension, zeta potential values of solids will become more negative leading to an increase in the stability of suspension and then adversely affecting flocculation. Therefore, as carbonate alkalinity has a significant effect on the flocculation of hematite, it should be seriously taken into account to optimize the selective flocculation of hematite ores.

Keywords: Carbonate alkalinity, flocculation, hematite, corn starch, zeta potential, starch adsorption.

ÖZ

KARBONAT ALKALİNİTESİNİN HEMATİTİN FLOKÜLASYONUN ÜZERİNDEKİ ETKİLERİ

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Yüksek tenörlü demir cevherleri hızla azaldığından, madencilik sektörü düşük tenörlü demir cevherlerini zenginleştirerek işletmek zorunda kalmıştır. Mineral serbestleşmesinin çok ince boyutta olması veya cevher hazırlama ve zenginleştirmenin atığı veya yan ürününde bulunan fazla miktarlarda ince taneli mineralleri kazanmak için, ince öğütülmüş cevherlere uygulanabilecek zenginleştirme yöntemlerinin geliştirilmesi gerekmektedir. Selektif flokülasyon pülp içindeki çok ince boyuttaki parçacıkların zenginleştirilmesinde kullanılabilecek uygun yöntemlerden biridir.

Proses suyunun kimyası, flokülasyonun etkili bir biçimde uygulanmasında önemli bir rol oynar. Su kimyasının en önemli unsurlarından biri suyun karbonat içeriğidir. Doğal sularda CO_2, karbonik asit ve katı karbonatlar tarafından düzenlenen karbonat içeriği "karbonat alkalinitesi" olarak adlandırılır ve özellikle alkali pH'larda flokülasyon için

önemli bir faktördür.

Demir cevherlerinin flokülasyonu genellikle karbonat alkalinitesinin oldukça yüksek olduğu pH 11'de yapılmaktadır. Literatürde, özellikle hematit gibi demir oksitlerin flokülasyon davranışlarına karbonat alkalinitesinin etkisiyle ilgili bir çalışma bulunmamaktadır. Bu çalışmada, karbonat alkalinitesinin demir cevherlerinin, nişasta ile flokülasyonu üzerindeki etkileri araştırılmıştır. Flokülasyonun etkinliği farklı nişasta miktarları ve pH değerlerinde çökelme hızı ve askıda katı madde miktarı ile belirlenmiştir. Karbonat alkalinitesinin etkilerini açıklamak için zeta potansiyeli ölçümleri ve nişasta adsorpsiyonu çalışmaları yapılmıştır.

Elde edilen sonuçlar, 2.4 mEq/L'den düşük miktarda karbonat alkalinitesinin flokülasyonu olumlu yönde etkilediğini göstermiştir. Ancak, yüksek karbonat alkalinitesinin hematitin flokülasyonunu ters yönde etkilediği anlaşılmıştır. Benzer davranış, nişasta adsorpsiyon deneylerinde görülmüştür; yüksek alkalinitede hematitin daha az nişasta adsorpladığı tespit edilmiştir. Zeta potansiyeli ölçümleri, karbonat alkalinitesinin artması ile hematitin zeta potansiyelinin daha negatif değerlere ulaştığını göstermiştir. Bu durum, hematitin pülp içinde daha güçlü bir biçimde dağıldığını ve flokülasyonun zorlaştığını göstermektedir. Sonuç olarak, karbonat alkalinitesinin hematit flokülasyonunda kayda değer öneme sahip olduğundan hematitin selektif flokülasyonunun optimize edilmesinde dikkate alınması gerekmektedir.

Anahtar Kelimler: Karbonat alkalinitesi, flokülasyon, hematit, mısır nişastası, zeta potansiyeli, nişasta adsorpsiyonu

To My Husband and My Parents

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

Production of fine particles of minerals is almost inevitable in the grinding process for reaching the adequate liberation. Fine particles respond poorly to conventional separation techniques, such as filtration, flotation, and sedimentation. Thus, a large amount of fine minerals are often lost in the process tailings because of lack of effective recovery methods (Wills, 2006). It is without doubt that the treating the fine particles and increasing the size of particles into larger aggregates is an essential process in mineral processing. Coagulation and flocculation are two promising methods for treating fine minerals. The utilization of coagulation or flocculation of fine particles to form large particles is desirable for improving the separation efficiency of some mineral processing methods such as, gravity separation, filtration, and thickening. (Shibataa and Fuerstenau, 2003; Chin et al., 1998;Lu et al., 2005)

Flocculation is affected by several parameters such as the characteristics of solid and flocculants, solution chemistry, temperature, solid-liquid or solid-polymer interaction, environmental factors, mineralogy and particle size, to name a few (Hughes, 1990). Process water chemistry is related by many of these parameters.

One of the important factors that profoundly affects the chemistry of water is existence of carbon dioxide in water. By dissolving the CO_2 in water, a weak acid is formed. This acid and its salts in solution constitute the carbonic system which forms a buffer system that resists pH change. The pH of natural waters on land is partially controlled by this system. Carbonic system of natural waters is composed of: dissolved CO_2, carbonic acid, H_2CO_3, bicarbonate ion, HCO_3^-, and carbonate ion, CO_3^{2-}, (Stumm

and Morgan, 1996).

Alkalinity is the capacity of a natural water to neutralize strong acid and attribute to the species of the carbonic system of water and to species in small quantities like ammonia, borates, silicates, phosphates and organic bases (Snoeyink and Jenkins, 1980).

Flocculation behavior of hematite particles have been widely investigated with several factors such as: pH, particle size and content, flocculant type, agitation type and strength, time of flocculation, dispersant type and concentration and structure of tank. The effect of pH in the flocculation of hematite is an extensively studied phenomenon (Akdemir, 1997; Pascoe and Doherty, 1997; Yin et al., 2011; Shibataa and Fuerstenau, 2003). In the majority of these studies the optimum pH for flocculation of hematite was determined to be between 10-11, where carbonate alkalinity could be rather high. Having Knowledge of the effect of the carbonic system, i.e. alkalinity, on the flocculation of hematite would help remarkably to improve the process efficiency.

The objective of this study was to investigate the flocculation behavior of hematite as a function of carbonate alkalinity. Corn starch as a natural organic flocculant was employed for the formation of flocs of iron-oxide minerals. For this purpose flocculation tests were performed, settling rate and suspended solid content were measured. Zeta potential measurement and starch adsorption tests also were carried out to explain the flocculation mechanism of hematite in the presence of carbonate alkalinity.

CHAPTER 2

LITERATURE REVIEW

2.1 Flocculation

Flocculation is defined as the process of aggregating fine particles by addition of a polymer or a flocculant which is an important stage in mineral extraction processes. Furthermore it is an essential step in effective solid-liquid separation and also important from the economic point of view (Jones et al., 1998). The flocculation phenomenon is aimed at treating fine colloidal particles to create larger units or flocs, which settle rapidly and removed easily by further operational processes such as filtration and thickening (Lu et al., 2005).

Flocculation is a complicated process which includes a number of process or sub processes occurring sequentially or simultaneously, include: (i) mixing of polymers or surfactant and particles and in solution, (ii) adsorption of the polymer or the surfactant molecules on the particle surfaces, (iii) reconformation of adsorbed chains on the surface of partcicle, (iv) formation of flocs due to polymer or surfactant adsorption, (v) floc breakage (Stechemesser and Dobias, 2005; Gregory, 2005)

2.1.2 Stability of colloidal suspension

Stabilisation of a suspension is due to the surface charges carried by colloidal particles. Normally the particles remain dispersed in the stable suspension, whereas the surface property of these particles may be changed by addition of some chemicals. Coagulation and flocculation are the processes of conversion of stable state dispersion

to the unstable state or destabilisation (Hughes, 1990; Gregory, 1993; Akers, 1975).

Van der Waals force which exists in the colloidal particles in suspension is an attractive force between particles. However, the particles are prevented to approach and make agglomerates by the electrostatic repulsion regarding surface charges. Therefore, electrostatic repulsion is the principal mechanism controlling the stability of particles (Montgomery, 1985). Besides electrical repulsion, a suspension may be stable due to the presence of adsorbed water molecules that provide a physical liquid barrier preventing particulates from making collisions and destabilisation. Particles may acquire surface charges due to unequal distribution of constituent ions on the particle surface, preferential adsorption of specific ions, ionisation of surface groups, crystal imperfection, or any combination of these (Tripathy and De, 2006).

2.1.3 Zeta potential and the Electrical double layer

Oppositely charged ions are attracted to the surface of a charged particle in an electrolytic solution and can either be closely associated with the surface or distributed into the solution (Gregory, 1992). Therefore, electrostatic attraction and ionic diffusion produce a diffuse cloud of ions around the particle, which can extend up to 300 nm. This co-existence of original charged surface and the neutralizing excess of counter-ions over co-ions distributed in a diffused manner are known as the electrical double layer (Kruyt, 1952).

Figure 2.1 demonstrates a schematic view of electrical double layer surrounded a colloidal particle in a solution and electrical potentials formed in the electrical double layer. The electrical double layer includes two main layers, an inner layer, called Stern layer, where the ions are strongly bound; and the outer layer, referred to as diffuse layer, where they are less firmly attached. The potential of the Stern layer significantly affects the stability of colloidal suspension. Although it is impossible to directly measure this potential, it can be estimated to the zeta potential, which is the electrical potential between the shear plane and the bulk solution (Shamlou and Titchener-Hooker, 1993).
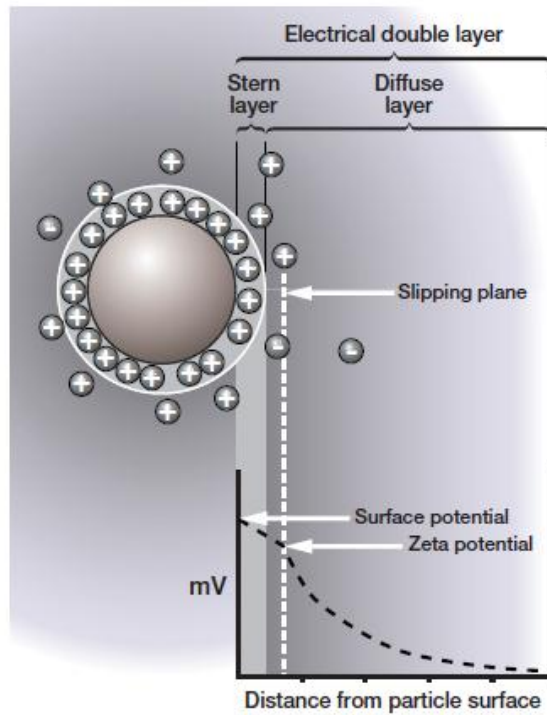
Figure 2.1 Electrical double layer and zeta potential (Malvern, 2009)

Zeta potential is defined as the average potential in the electrical double layer at the zone of shear between a mobile charged particle and the immobile liquid phase in which a particle is suspended. The surface charge and the potential difference of the particles are thought to be an outcome of ionization of surface groups, adsorption of surface active materials, permanent charge associated with crystal structure or combination of these mechanisms (Ward, 2008).

The zeta potential measurement can be applied to estimate and control colloidal suspensions stability. The suspension is more likely to remain stable in higher zeta potential values. In a suspension that particles have a large negative or positive zeta potential, the particles repel each other and there is no tendency to flocculate. However, there is a high flocculation tendency in particles with low zeta potential,

because there is no force to prevent the particles coming together and flocculating. The general dividing line between stable and unstable suspensions is generally taken at either +30mV or -30mV. Thus, stable particles are the particles which the magnitude of their zeta potentials is larger than 30mV (Tripathy and De, 2006; Hunter, 1981; Malvern, 2009).

pH is the most important parameter which affects zeta potential. A zeta potential value without a quoted pH is a virtually meaningless number. The point where the plot passes through zero zeta potential is called the *isoelectric point (iep)* and is very important because it is the point where the colloidal system is least stable. A typical plot of zeta potential versus pH is demonstrated in Figure 2.2 (Malvern, 2009).
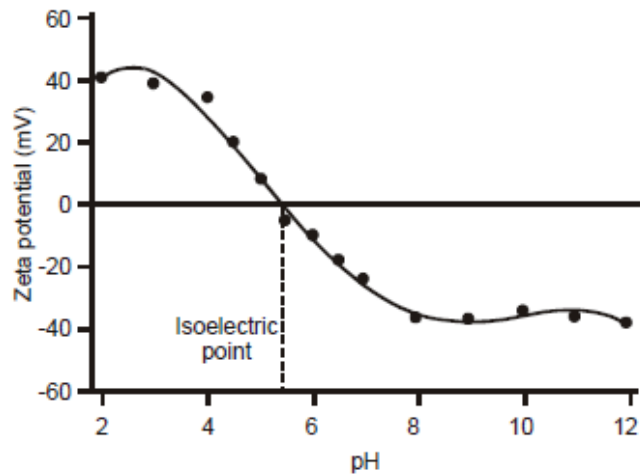
Figure 2.2 A typical zeta potential plot (Malvern, 2009)

Zeta potential is measured using a combination of the measurement techniques: Electrophoresis and Laser Doppler Velocimetry, which is called Laser Doppler Electrophoresis. This method measures how fast a particle moves in a liquid when an electrical field is applied – i.e. its velocity. When the velocity of the particle and the electrical field applied are known, the zeta potential can be determined by using two other known constants of the sample, viscosity and dielectric constant (Malvern, 2009).

2.1.4 Polymer flocculation

Use of polymers as a flocculant has been known for centuries. Synthetic polymers have a wide application as flocculant since they were developed in early 1950's. Also, in the same years, the well-known "bridging action" theory for the flocculation by polymers was developed (Ruehrwein and Ward, 1952). This theory explains that particles are physically held together by the adsorption of long chain polymer molecules on more than one particle (Arol, 1984).

Two essential processes in the flocculation of mineral suspension by means of a polymer are: the adsorption of the polymer and the floc formation.

Adsorption of polymers on minerals is dependent on the polymer properties such as molecular weight and configuration, the number and the nature of functional groups, surface properties of minerals, and the solution properties such as pH, ionic strength, solvent power for the polymer and temperature. Forces responsible for the polymer adsorption arise from the electrostatic bonding, hydrogen bonding, and chemical bonding.

Electrostatic forces play a governing role in the case of polymers with a large number of charged functional groups. Adsorption is always favored when the polymer and mineral are oppositely charged. Similar charges on the mineral and polymer would prevent the adsorption of the polymer due to the electrostatic repulsion. Even when the mineral and the polymer are similarly charged, the adsorption of polymer might still proceed by hydrogen and chemical bonding. The hydrogen bond is relatively weak;

however, the total bonding energy per polymer molecule becomes very large since a great many bonds are formed per polymer molecule. Chemical bonding can be obtained between the functioned groups of the polymer and cations of mineral surface. This type of bonding usually results in rather selective adsorption (Arol, 1984).

In order to flocculate a mineral suspension effectively, the polymer adsorption should be rapid, irreversible and complete. A segment of adsorbed polymers should extend into solution for successful bridging in the formation of large and stable flocs. The effectiveness of floc formation would depend on a number of factors: the amount of the adsorbed polymer on the mineral, the molecular weight and the conformation of the polymer, the pH of the suspension, the presence of dissolved salts, agitation, and the particle size.

The pH and the dissolved salt content of the solution also affect the conformation of polymer molecules, and thus the bridge formation. A cationic polymer will tend to stretch out in acid solution, promoting flocculation, whereas the same polymer will become coiled in basic solution due to the neutralization of the charged functional groups. When a solution contains a high concentration of dissolved salts, the polymer molecules may become highly compressed and even precipitate from the solution (Arol, 1984).

Polymers are usually classified regarding to their action on the particles. If the polymer forms molecular bridges between the particles by adsorbing on several particles simultaneously, it is called *bridging flocculation.* In the case where polymer molecules are branched, or if two or more types of interacting polymer molecules of a linear type are used so that there is a three-dimensional gel-type network enmeshing the particles into a floc, the gel flocculating process is termed *network flocculation.* Under carefully controlled polymer additions as well as hydrodynamic conditions, a compact strong pellet-like floc can be produced, which is called *pelleting flocculation* (Bulatovic, 2007).

2.1.5 Mechanism of flocculation

Polymeric flocculation is a complex physiochemical phenomenon which involves several types of mechanisms. The main mechanisms of polymeric flocculation in the mineral engineering practice were considered to be bridging and patch neutralization mechanisms. Furthermore, an increment in van der Waals attraction or a decline in electrostatic repulsion may lead to some processes like de-stabilization in neutral polymers (Lu et al., 2005). In the following sections bridging and charge-patch neutralization mechanisms will be explained.

2.1.5.1 Bridging

Bridging is associated with high molecular polymers where the tails and loops of the macromolecule can form links between particles. When an optimum dosage of a polymer macromolecule is added to a solution, it can be adsorbed by particles through several segments with the other parts of the molecule extending into the solution (Figure 2.3 a). The bridging mechanism is possible in two ways. The first possible way of bridging can occur between two particles linked by the long chain of one polymer (Figure 2.3 b) or by the association of polymer molecules separately adsorbed on different particle surfaces (Figure 2.3 c).The other situation might happen when there is a high surface coverage of polymer and the degree of association between polymer chains is strong. Therefore the aggregates are formed through these bridging mechanisms (Figure 2.3 d). The polymer uncoiling is influenced by the pH of the solution and the presence of polyvalent ions. On the other hand an increase in the ionic strength could cause the polymer to coil-up and weaken the bridging bonds. In other cases, it is possible that the extended part of the polymer molecule be adsorbed by the same particle on other sites and the polymer molecule might be unable to operate as a bridge (Figure 2.3 e). So the surface may become saturated and as a result no more adsorbable site is available on the surfaces leading the redispersion of the particles in the solution. In other cases, the flocs may be broken up due to agitation and prevent bridging formation. Therefore, the extended parts of the polymer molecules may be adsorbed back on the same particle surface and the particles are dispersed again

(Figure 2.3 f).
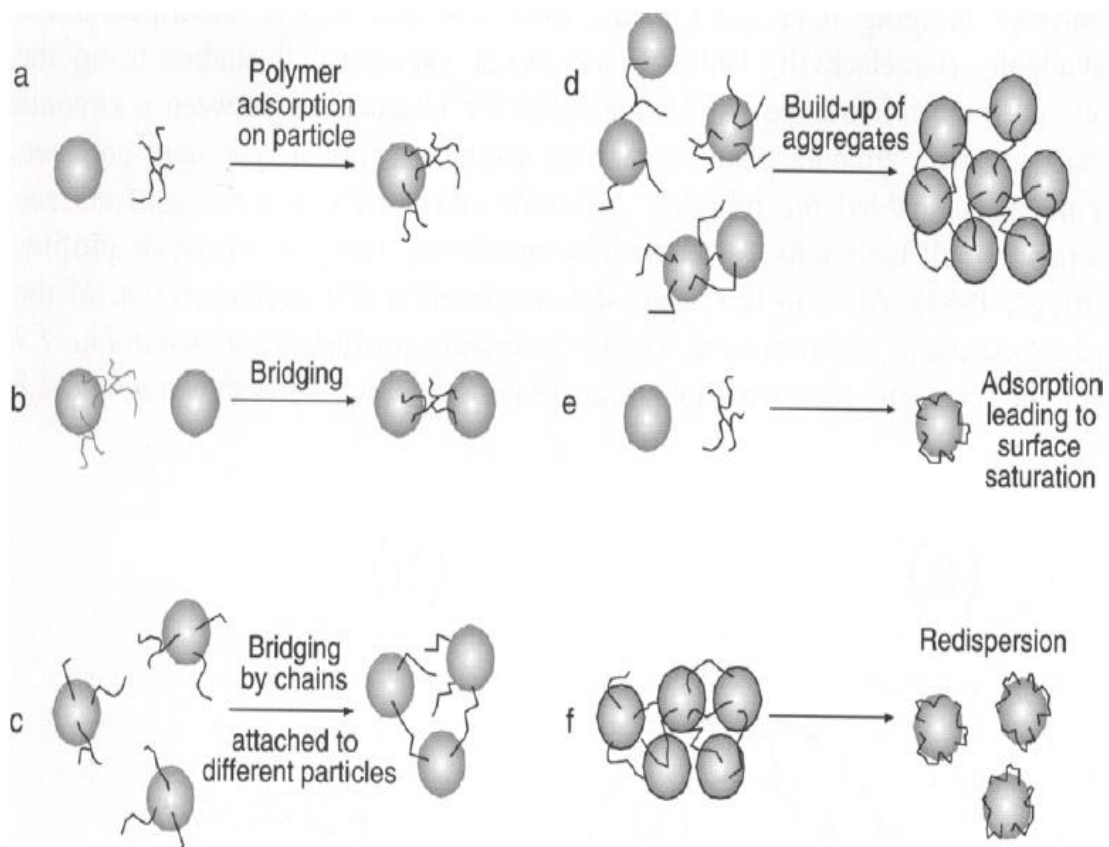
Figure 2.3 Schematic presentation of the influence of polymer on particle adsorption and interactions leading to flocculation or dispersion (Lu et al., 2005)

There are some indispensable conditions for bridging flocculation which are: (1) there should be sufficient uncoated surface on the particle for polymer adsorption. In other words, to reach the effective binding between particles the adsorbed amount should not be too high or too low; otherwise insufficient bridges would be formed between particles. These considerations lead directly to the idea of an optimum dosage of polymer to give the most effective flocculation (Gregory, 2005). (2) Adsorbed polymer on particle surface can extend by chain, loops and tails into solution (Lu et al., 2005)

2.1.5.2 Charge-patch neutralization mechanism

Charge-patch neutralization mechanism was raised by Gregory (1973). According to this mechanism the surface charge of solid material in the pulp is determined and flocculation reagent type is designated. Gregory's theory explains specially that flocculant charge type should be selected as opposite surface charge of the solid material, if the particle is subjected to flocculation has negative surface charge, the flocculant should have positive surface charge for the electrostatic attraction. Moreover, the charged polymer should be much smaller than the surface area of the particle to form patch on the surface. Therefore, this patch system resulted in neutralization of the surface charge of particles and formation of flocs due to collision of particles which is an outcome of charge-patch neutralization mechanism. Figure 2.4 shows the process of charge neutralization and flocculation of particles due to this mechanism (Lu et al., 2005).
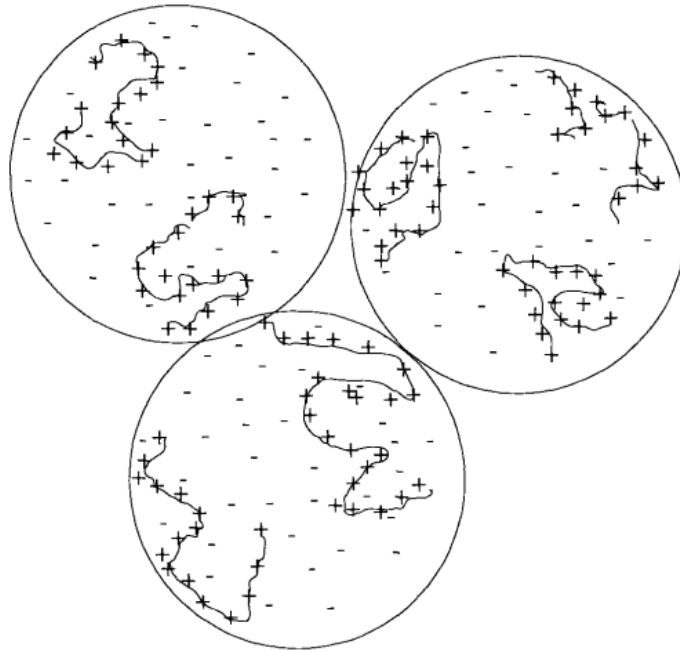
Figure 2.4 Electrostatic patch model of polymer adsorption leading to flocculation (Lu et al., 2005)

2.1.5.3 Flocculation mechanism with different polymers

Flocculation mechanism for various types of polymers in a solution may be different. It might be due to the differences of their molecular constitution or their structure. For example, electrostatic forces can be responsible for the adsorption of anionic corn starch on positively charged surfaces. However, there is evidence of hydrogen bonding and interactions with surface metallic ions, carboxyls in corn starch and phosphate groups in potato starch can chemically react with surface metallic cations.

In the case of anionic polymer flocculants, the polymer molecule chains will be adsorbed by particle surfaces in a developing configuration, due to the structure units

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of the chains electrostatically repelling each. The chain tails which spread into the solution have the greatest probability of connecting to other particles that leads to make a bridge between two particles (Lu et al., 2005).

2.1.6 Flocculating agents

The wide groups of materials used as flocculants are categorized into two groups: inorganic and organic reagents.

2.1.6.1 Inorganic flocculants (coagulants)

In the applications which the source of cationic charge is required inorganic flocculants are utilized. Typical inorganic flocculants are: Calcium salts, typically lime; aluminum salts, such as sulfates or soda alum; and iron salts such as ferrous sulfate and ferric chloride. Inorganic flocculants have some disadvantages such as:

(i) Large amount of inorganic flocculant is required in solid–liquid separation of the dispersion
(ii) Production of large amount of sludge
(iii) Highly sensitive to pH.
(iv) Applicable only to a few disperse systems
(v) Not applicable for coagulating very fine particles

The application of inorganic flocculants is almost limited due to these disadvantages (Sharma et al., 2006; Bulatovic, 2007).

2.1.6.2 Organic flocculants

Organic flocculants can be classified into two main groups: natural and synthetic flocculants. Natural flocculants are derived from natural sources and have the general formula:
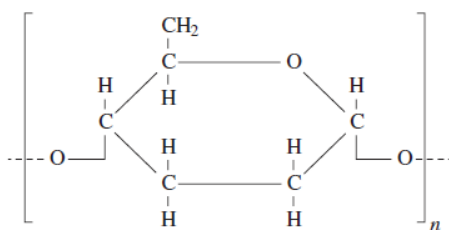
The natural sources of these kinds of flocculants are hydrolyzed starch, guar gums, modified polysaccharides and etc. One of the principal applications of these flocculants is in selective flocculation of iron ores and other oxides. Synthetic flocculants are found in wide variety in comparison with natural flocculants and are generally applied in dewatering processes (Bulatovic, 2007).

There is another classification of flocculants which is according to their physicochemical characteristics (molecular and ionic) as shown in Table 2.1.

Table 2.1 Classification of flocculants according to origin and physicochemical properties (Lu et al., 2005)

Polymer	Non ionic	Ionic character		
		Anionic	Cationic	Amphoteric
Natural	Starch, guar gum, tannin, dextrin	Carboxyl methyl cellulose, sodium humate	Cationized starch, chitosan	Gelatin, protein
Synthetic	Polyacrylamide, polyvinyl alcohol, polyethylene oxide	Highly hydrolysed polyacrylamide, polyacrylate, sodium polystyrene sulfonate	Polyethyleneamine, polyvinylpyridium chloride, aminoethoxylated polyacrylamide	

2.1.6.3 Starch

Starch and its derivatives are widely applied in mineral processing as natural flocculant in flocculation and depressant in froth flotation (Iwasaki et al., 1969; Laskowski et al., 1991; Ravishankar et al., 1995). Starch is a polysaccharide originated from plants as renewable resources. Natural starch consists of two different types of glucose polymers, amylose and amylopectin (Xing et al., 2005). In general, starch contains an abundance of hydroxyl groups, where each anhydroglucose unit contains secondary hydroxyls and a large majority contains primary hydroxyls. These hydroxyls have a potential of reacting with any chemical capable of reacting with alcoholic hydroxyls which includes ions in solution and collectors. Ordinary starch consists of several glucopyranose units formed by D-(1–4) linkages as shown in Figure 2.5 and can have a molecular weight of up to 150,000 (Bulatovic, 2007).
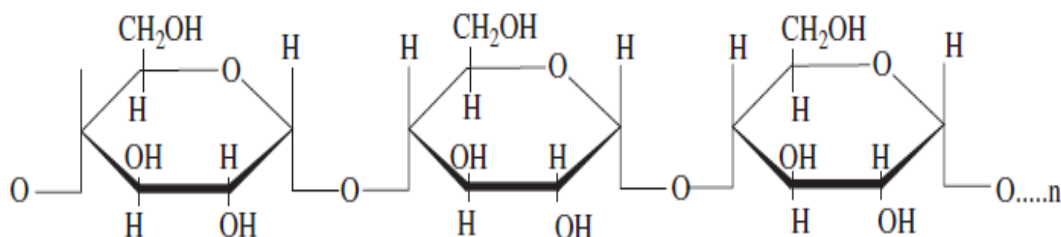
Figure 2.5 General structures of starch (Bulatovic, 2007)

Common corn, potato and tapioca starches show different behaviors in the flocculation which is due to the differences in the amount of straight and branched chain molecules. Also having different molecular weights of the various fractions can be a reason of these differences (Lu et al., 2005).

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Starch is widely used as a flocculant in flocculation and selective flocculation of iron ores. Many researchers have utilized starch as a flocculant in selective flocculation of hematite in the ores containing quartz, silicates, clay minerals, and alumina, etc. Table 2.2 presented the summary of these works. Furthermore, starch is commonly used as a depressant in the froth flotation of hematite, as starch depresses hematite while quartz is floated by means of other collectors (Weissenborn et al., 1994; Liu et al., 2000).

2.1.7 Starch adsorption

Starch adsorbs on iron oxides strongly and irreversibly. Adsorption characteristics vary with the type of starch and preparation method. A number of factors control the effectiveness of starch in the flocculation of iron oxides. Some of these factors are process water chemistry, the amount and the type of dispersants and presence of clayey constituents (Arol and Iwasaki, 2003). It has been reported by many researchers that the adsorption of starch on hematite is a pH dependent factor, where adsorption decreases by an increase in the pH (Bulatovic, 2007).

The adsorption of starch on different types of particles was studied by many researchers and several theories have been suggested to explain the mechanism of adsorption. According to these works it seems to be more than one mechanism involved in the process. The principal mechanisms which are frequently reported in several studies include: hydrogen bonding and hydrophobic interactions (Laskowski et al., 1991; Ravishankar et al. , 1995; Khosla et al., 1984; Weissenborn et al., 1995). However, in some recent works, specific chemical interactions have been proposed as one of the effective mechanisms involved in starch adsorption. For example, electrostatic forces can be responsible for the adsorption of anionic corn starch on the positively charged surfaces. Furthermore, there are reported cases of hydrogen bonding and interactions with surface metallic ions. For instance, carboxyls in corn starch and phosphate groups in potato starch can chemically react with surface metallic cations (Lu et al., 2005).

Table 2.2 Summary of some researches on the application of starch as a flocculant in the selective flocculation of iron ores (Weissenborn et al., 1994)

Authors	Feed minerals and grades	Type of starch	Methods	Grade and recovery of ion or iron-bearing minerals in concentrate
Lien and Morrow (1978)	30% iron as hematite plus a small amount of magnetite, 45% silica	Tapioca	Combination of pulp magnetization, selective flocculation and desliming	65% iron with 75% recovery
Gururaj et al. (1983)	Synthetic mixtures (1:1) of hematite : kaolinite, hematite : illite, hematite : montmorllonite, and a natural iron ore slime consisting of hematite and above clay minerals (~ 45% iron)	Not specified	Single and multiple stage selective flocculation	Best results for hematite : kaolinite mixture 54.6% iron with 78% recovery. Selective dispersion was more effective than selective flocculation
Zuleta et al. (1984)	Iron ore containing 37% iron as hematite and a range of clay minerals and quartz (10%)	Cationic corn	Three stage selective flocculation plus magnetic separation	Selective flocculation only gave a grade of 50% iron with 69% recovery. Adding magnetic separation gave 54% iron with 77% recovery
HanumanthaRao and Narasimhan (1985)	Similar iron ore slimes as for Gururaj et al., 1983. Consisting of 52.5% iron, 7.8% silica and 7.4% alumina	Corn	Two stages selective flocculation followed by floc washing	Variety of results, best was a grade of iron of 65% with 80% recovery
Colombo (1986)	Variety of iron ores containing hematite, geotite quartz, silicates, calcite and apanite. On average containing ~ 35% iron	Pearl	Selective flocculation and froth flotation (pilot plant scale)	On average ~ 62% iron with ~ 70% recovery
Prasip et al. (1993)	Synthetic mixtures (1:1) of hematite : kaolinite and hematite : gibbsite and an iron ore slime containing 46% iron and 11.6% Al_2O_3	Maize	Synthetic mixture – single stage elective flocculation. Slimes – hydrocyclones at 5 μm followed by selective flocculation of - 5 μm fraction and selective dispersion of + 5 μm fraction	Very good selectivity and recovery of hematite from hematite : kaolinite mixture. No selectivity (ie. Bulk flocculation) for hematite : gibbsite mixture. Iron ore slimes – 60% iron, 4.7% Al_2O_3 with 50% recovery of iron.

2.1.8 Factors affecting flocculation performance

Flocculation process are dependent upon both chemical, e.g., flocculant type, pH, ionic strength, dose, etc. and physical factors, e.g., mixing conditions, temperature, etc (Hulston et al., 2004).

2.1.8.1 Polymer molecular weight and charge density

The effect of polymer molecular weight on the flocculation process can be described by bridging and electrostatic patch mechanisms. For the systems in which bridging is the main mechanism of flocculation, by increasing the molecular weight flocculation will be promoted. At higher molecular weight as the polymer gets adsorbed, it can extend further away from the particle surface which causes to reach to equilibrium. This also increases particle radius and collision number and enhance flocculation rate. Although anionic charge on polymer can oppose adsorption onto a negative surface, it helps to improve extension of polymer chain through mutual charge repulsion and increasing its approachability. It has been reported that despite an optimum molecular weight, flocculation efficiency reduces. This is attributed to steric repulsion between polymer molecules. On the other hand, in the systems where the electrostatic patch mechanism is the principle mechanism in rate controlling, the influences of molecular weight are less well defined (Tripathy and De, 2006).

2.1.8.2 Polymer dosage and adding conditions

The flocculation process is widely affected by two parameters of the polymer dosage and the addition technique. It is without doubt that an optimum dosage of polymer is required to reach the most effective flocculation.

It is reported by many researchers that, the settling rate tend to be decreased at high flocculant dosage (Lu et al., 2005). This phenomenon was explained by Healy and La Mer (1964); in high flocculant dosage due to increasing the concentration of the polymer, the number of molecules adsorbed on the surface of the particle does increase as well. However, the surface area that the polymer could attach decreases, which impedes the polymer bridging and floc formation.

The method of addition of polymer to a pulp is as important as the amount of polymer added. For instance, the polymer might be added gradually in several stages rather than added all at once. In multi-stage addition processes, frequently lower polymer amounts are needed which can be defined by more efficient polymer uptake by the particles. Also it has been indicated that the flocs size increase with a faster rate of addition. However, too high rate of addition may cause break up of the flocs and insufficient mixing in the suspension, leading to ineffective flocculation (Lu et al., 2005).

2.1.8.3 pH and ionic strength

pH has a significant role in flocculation process because it can control the charges on the polymer surface and either the particle surface. Ionic strength is also very important, since compression of the double layer leads to a decrease in the inter particle separation. Thus, this would affect flocculation through the charge patch and bridging flocculation mechanisms. The effect of pH is shown in Figure 2.6, where the configuration of adsorbed polymer on clay at different pH values of the suspension is demonstrated (Lu et al., 2005).
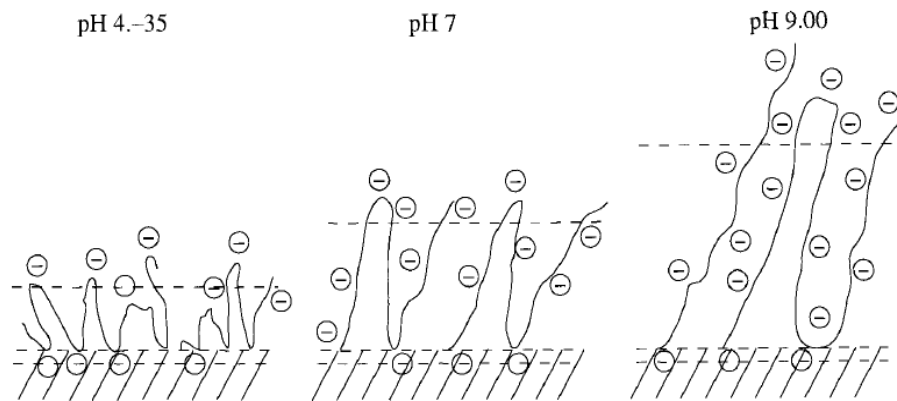
Figure 2.6 Adsorption of anionic polymer on negatively charged clay surface.

Low pH: low surface charge and adsorbed chain extension low. This can cause strong bridging; Medium pH: surface charge increases and polymer begins to extend from surface. Bridging occurs and forming large flocs; High pH: high surface charge and highly extended polymer in solution causing bridging and formation of large and porous loose flocs (Lu et al., 2005).

2.1.8.4 Effect of temperature

It is generally known that temperature increase can improve flocculation process. However, this is not always the case, since a change in temperature will cause different effects in different systems. The flocculant rate of diffusion and the rate of particles collision are expected to increase with an increment in temperature, while the adsorption step, which is exothermic, is negatively affected by high temperature. On the other hand the changing temperature may affect the linear extension of the polymer molecules which depends on the nature of the solvent-solute interactions. Therefore, it is not easy to predict the effect of temperature in a given system (Mathur et al., 2000; Doğu, 2002).

According to a work undertaken by Hulston et al. (2004), increasing the temperature will cause a significant increase in settling rate due to either reducing in solution viscosity or decreasing of the floc size. While an increase in temperature had little effect on the supernatant turbidity of untreated hematite suspensions, it leads to significant reductions in polymer-treated suspensions. It is believed that the decrease in supernatant turbidity is due to reduction in viscosity, causing particles to settle faster.

2.1.9 Applications of flocculation

The flocculation process has a wide range of applications such as mineral and ceramic processing, paper making, treatment of industrial effluents, and municipal sewage sludge purification. Therefore, flocculation has a twofold effect: slowing down the depletion of raw materials and reducing environmental contamination (Stechemesser and Dobias, 2005; Brostow et al., 2007).

2.1.9.1 Application of flocculation in mineral processing

A wide variety of applications are known for (polymeric) flocculation in mineral processing. Almost every mineral processing plant employs polymeric flocculants in order to aid, enhance, expedite or carry out the overall process or certain aspects of it. Therefore, these applications should be explored according to the relevant unit processes. Unit processes such as flocculation/settling, filtration, and centrifugation are required in solid-liquid separation. The aim of separation process may be removal of water from concentrate product, recovery of water process or concentration of the solids, in tailing disposal (Laskowski and Ralston, 1992; Bulatovic, 2007).

Below are some of the important applications of polymer flocculants:

- *Flocculation/settling.* One of the essential applications of polymers is in the clarification of effluents in wastewater treatment or for reusing in mineral processing plants.

- *Filtration.* The polymeric flocculants used in filtration applications have several objectives, including to: (a) reduce size of settling equipment (thickeners), (b) improve

clarity of the thickener effluent and, (c) improve filterability of the filtered material. This application of the flocculants is also designed to obtain slurry that forms a filter cake with an open structure of high permeability with a reduced amount of free fines that tend to block or "blind" the filter medium.

- *Centrifugation*. Polymeric flocculants are also used in de-watering slurry by centrifugation (Bulatovic, 2007).

2.1.10 Flocculation of hematite

2.1.10.1 The mineral hematite

Hematite is widely distributed and is the main iron ore mineral; when pure, it contains the equivalent of 70% metallic iron based on the chemical formula Fe_2O_3. It furnishes the base of the world's most important ores occurring chiefly in sedimentary iron ores and their metamorphosed equivalents. There are several varieties of hematite, the common massive ore is known as *red hematite*. The crystalline material is called *specular* hematite or *specularite*, also referred to as *martite* where replaces magnetite. Hematite is a weak magnetic material (Camp and Francis, 1920; Deer et al., 1962; Petruk, 1930).

A great portion of hematite is extracted in high- grade, 64-68 % iron, with only small amount of impurities such as silica and alumina. However, there are large reserves of low-grade hematite of as low as 20-40 % iron with high silica contents which are not being mined (Aksit, 2004).

2.1.10.2 Flocculation of hematite

As high grade iron ore deposits are rapidly depleted, the minerals industry is increasingly obliged to process lower grade iron ores. Production of large quantities of fine ores as tailings or by-products in mining operations and mineral liberation at fine particle sizes have led to the development of concentration methods employed to fine ores. As treating the fine ores is not possible by ordinary separation methods like gravity separation or flotation, there should be a method applicable to treat minerals in the ultrafine size range. Flocculation is one of the beneficial methods which can be

used in recovering of very fine particles (Arol and Iwasaki, 2003; Addai-Mensah and Ralston, 2004; Pascoe and Doherty, 1997).

During the last two decades, the flocculation behavior of hematite particles have been researched considering wide variety of parameters including pH, particle size and concentration, flocculant type, flocculation time and agitation strength, dispersant type and concentration, etc. For example, in the study which was carried out by Akdemir (1997) the effects of pH, collector concentration and stirring speed on the shear flocculation of fine hematite (38 μm) were determined. In another study the selective flocculation of ultrafine hematite (<10 μm) from quartz with sodium oleate was investigated by Pascoe and Dohertyv (1997). It was reported that pH, oleate concentration, shear rate, and agitation time were the most important factors affecting hematite floc size. Hu et al. (2003) was reported a study on the aggregation and flotation of hematite and wolframite. Flocculation and flotation characteristics of fine hematite with sodium oleate were investigated by Shibata and Fuerstenau (2003). Arol and Iwasaki (2003) investigated the effect of sodium silicate on the flocculation and the selective flocculation of hematite with starch in the presence of calcium. And the effects of sodium oleate concentration, stirring speed and time and pH on the floc size and flotation based on the experiments by Zeta potential measurements and flocculation image analysis were discussed by Wan-zhong et al. (2011). Almost in the all of these studies, the effect of pH in the flocculation of hematite was investigated, whereas there have been no reports on the effect of carbonate alkalinity on the flocculation behavior of iron oxides, mainly hematite, in the literature. Although the study which is done recently by Haselhuhn et al. (2012) is based on the determination of process water chemistry in a selective flocculation–dispersion hematite ore concentrating plant. However, the effect of alkalinity on the flocculation of hematite was not investigated.

1.2 Alkalinity

1.2.1 Carbon dioxide in water

Presence of carbon dioxide in air and its production from microbial decay of organic matter have made it the most important weak acid in water. Furthermore combustion of fossil fuels and volcanic activities are the main source of CO_2 emission in to the atmosphere. Thus, dissolved carbon dioxide exists in all natural waters and waste waters. Rainfall from even an absolutely unpolluted atmosphere is slightly acidic due to the presence of dissolved CO_2 (Manahan, 2011; Stumm and Morgan, 1996).

1.2.2 The carbonate system in aqueous solution

The carbonate weak acid/base system greatly dominates the waters on earth. For example, there are approximately 7×10^{14} moles of living organic carbon in the oceans, but more than 3×10^{18} moles of dissolved carbonate species in the ocean (Brezonik and Arnold, 2011).

The chemical species composing the carbonate system are: gaseous CO_2, $CO_{2(g)}$; aqueous or dissolved CO_2, $CO_{2(aq)}$; carbonic acid, H_2CO_3; bicarbonate, HCO_3^-; carbonate, CO_3^{2-}; and carbonate containing solids. The analytical methods for measuring the neutralization capacity of water to a strong acid or a strong base (alkalinity and acidity, respectively) are based mainly on the specific characteristics of the carbonate system. Carbonate species have a considerable role in water chemistry due to their wide presence and involvement in reactions (Snoeyink and Jenkins, 1980).

1.2.3 The carbonate species equilibria

The various components of the carbonate system are interrelated by the following equilibria. The temperature dependence of the constants is presented in Table 2.3.

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}; \qquad K = K_H = 10^{1.5} \qquad (K_H : \text{Henry's constant}) \qquad (1)$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3; \qquad K_M = 10^{2.8} \qquad (2)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-, \qquad K_1 = 10^{3.5} \qquad\qquad (3)$$

$$H_2CO_3^* \leftrightarrow H^+ + HCO_3^-, \qquad K_{a,1} = 10^{6.3} \qquad\qquad (4)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}, \qquad K_{a,2} = 10^{10.3} \qquad\qquad (5)$$
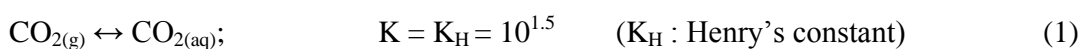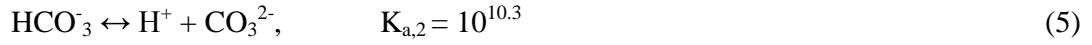
(Snoeyink and Jenkins, 1980)

Since the concentrations of CO_2 (aq) and H_2CO_3 cannot be measured individually via titration, they were combined together as $H_2CO_3^*$:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad\qquad (6)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad\qquad (7)$$

$$[CO_2(aq)] + [H_2CO_3] = [H_2CO_3^*] \qquad\qquad (8)$$

And the total dissolved carbonate is given by (Brezonik and Arnold, 2011):

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \qquad\qquad (9)$$

Table 2.3 Temprature dependance of some important carbonate equilibrium contants (Brezonik and Arnold, 2011)

Reaction	Temperature, °C						
	5	10	15	20	25	40	60
1. $CO_{2(g)} \leftrightarrow CO_{2(aq)}$; pK_H	1.20	1.27	1.34	1.41	1.47	1.64	1.8
2. $H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$; $pK_{a,1}$	6.52	6.46	6.42	6.38	6.35	6.30	6.30
3. $HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$; $pK_{a,2}$	10.56	10.49	10.43	10.38	10.33	10.22	10.14
4. $CaCO_{3(s)} \leftrightarrow Ca^{2+} + CO_3^{2-}$; pK_{so}	8.09	8.15	8.22	8.28	8.34	8.51	8.74
5. $CaCO_{3(s)} + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$; $p(K_{so}/K_{a,2})$	-2.47	-2.34	-2.21	-2.10	-1.99	-1.71	-1.40

Figure 2.7 is a logarithmic equilibrium diagram for a simple aqueous carbonate system.
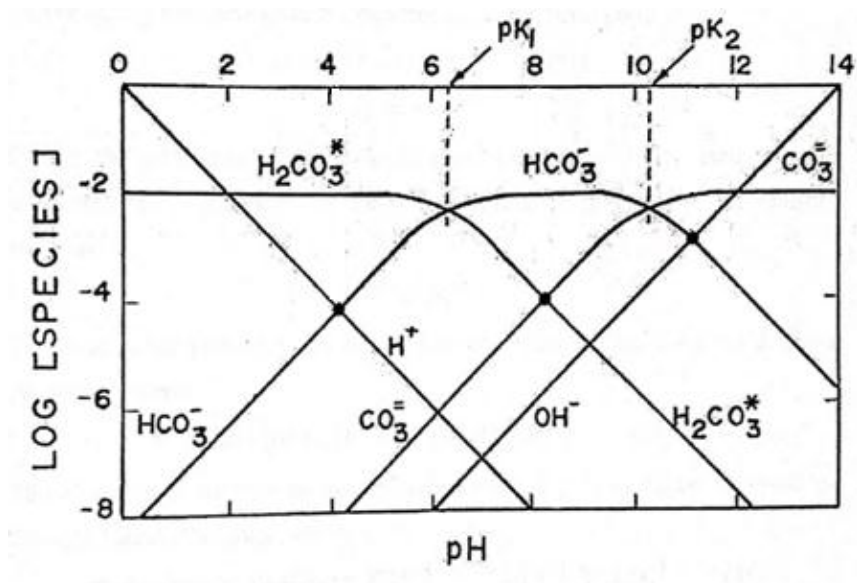
Figure 2.7 Equilibrium diagram for a simple aqueous carbonate system; $C_T = 10^{-2}$ M
(Loewenthal and Marais, 1976)

1.2.4 Determination of the carbonic system species in water

Accurate determination of the relevant properties of water is very important. Without this information no procedures for water treatment or control of water quality can be efficiently applied. Therefore, practical determination of the constitution of water as it is applied to carbonic system is very important. The carbonic species in water is defined by five basic parameters: $H_2CO_3^*$, HCO_3^-, CO_3^{2-}, OH^-, and H^+. To obtain values for the parameters in any particular water, it is necessary to establish five independent relationships linking the basic parameters to solve these equations. To establish the five equations, three are available from the dissociation equation of carbonic species and one is available from the pH measurement. The remaining

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equations are found by establishing some measurable characteristics which are defined in terms of the basic parameters. There are two independent characteristics which can be measured: *total carbonate species*, and *alkalinity* or *acidity* (Loewenthal and Marais, 1976).

1.2.5 Definition of Alkalinity

The acid neutralizing capacity of a water is called the *alkalinity* [alk] (Manahan, 2011; Brezonik et al. 2011; Snoeyink and Jenkins, 1980). Alkalinity is an important factor in treatment of water also in the chemistry and biology of natural waters. Highly alkaline water has a high pH and generally contains elevated levels of dissolved solids.

The basic species which are mostly responsible for alkalinity in water are carbonate ion, bicarbonate ion and hydroxide ion. Other species, which usually exist in small amounts, contributors to alkalinity are ammonia and the conjugate bases of silicic, phosphoric, boric, and organic acids.

At pH values below 7, $[H^+]$ in water detracts significantly from alkalinity, and its concentration must be subtracted in computing the total alkalinity. Therefore, the following equation is the complete equation for alkalinity in a medium where the only contributors to it are HCO_3^- , CO_3^{2-}, and OH^- (Manahan, 2011):

$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{10}$$

As discussed below, this equation is an incomplete definition of the total alkalinity of natural water and is more properly referred to as the *total carbonate alkalinity* (Brezonik et al. 2011).

Actually, three different definitions of alkalinity are in common use in water chemistry:

(1) Analytical definition: Alkalinity is the sum of titratable bases with strong acid to defined endpoint based on the carbonate system. This definition gives rise to the alternative term for alkalinity: *acid neutralizing capacity* or *ANC*.

(2) Chemical definition:

$$ANC = [alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + \sum [B^-] - [H^+], \tag{11}$$

Where B^- represents any other titratable base. In natural waters, these include borate, which is important in sea water, phosphate, silicate, and humic substances.

(3) Geochemical or charge-balance definition:

$$ANC = [alk] = \sum [BC] - \sum [SA], \tag{12}$$

Where BC are base cations (principally Na^+, K^+, Ca^+, Mg^{2+}), and SA are strong acid anions (principally Cl^-, SO_4^{2-}).

Of course, the three definitions define essentially the same property of water, but each emphasizes a different aspect of alkalinity, respectively: (1) the way we measure alkalinity; (2) the chemical species that comprise it; and (3) the fact that alkalinity in natural waters arises from an imbalance between the biogeochemical processes giving rise to strong base cations and strong acid anions (Brezonik et al. 2011).

1.2.6 Determination of alkalinity

The sum of titratable bases to two endpoints defined in reference to the carbonate system: (1) $pH_{HCO_3^-}$, pH= 8.3; where all carbonates have been titrated to bicarbonate and essentially all hydroxide alkalinity, if any was present in the sample, has been converted to water; and (2) pH_{CO_2}, pH= 4.5-5.1; where all bicarbonates has been titrated to $H_2CO_3^*$ (Brezonik et al. 2011).

In determination of alkalinity a known volume of sample is titrated with a standard solution of a strong acid. The quantity of acid required to reach the first endpoint, $pH_{HCO_3^-}$, determines the *carbonate alkalinity* of a sample. This quantity sometimes is called the phenolphthalein alkalinity, in reference to the color indicator commonly used to detect the end point. Then:

$$\text{Carbonate alkalinity} = [CO_3^{2-}] + [OH^-] - [H^+] - [H_2CO_3^*] \tag{13}$$

The total quantity of acid required to reach the second endpoint, pH_{CO_2}, gives the *total alkalinity* of a sample (Equation 10).

And the difference between first and second endpoint gives the *bicarbonate alkalinity* (Brezonik et al., 2011; Loewenthal and Marais, 1976; Snoeyink and Jenkins, 1980).

The titration of water samples containing various forms of alkalinity can be demonstrated as in Figure 2.8.

Apart from the algebraic approach alkalinity or C_T of a process water can also be found by using capacity diagrams. Graphs using variables with conservative properties (like C_T, alkalinity, and acidity) as coordinates can be used to show contours of non conservative variables like pH, $[H_2CO_3^*]$, and $[HCO_3^-]$. Addition or removal of components of the carbonate system on such graphs behaves as vectors and they can be used to facilitate equilibrium calculations. Deffeyes derived several graphs of this type. Here is the most common of his diagrams – a plot of [alk] versus C_T (Figure 2.9). Deffeyes used the relationship between alkalinity, C_T and pH to contrast the diagram relating alkalinity to C_T at a series of constant pH values (Brezonik et al., 2011; Stumm and Morgan, 1996; Snoeyink and Jenkins, 1980).
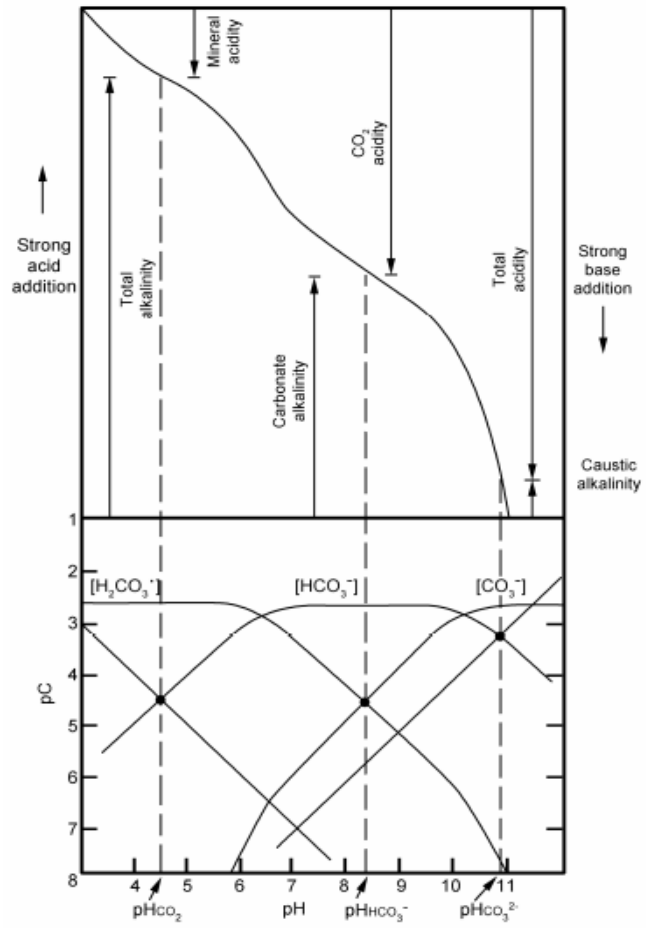
Figure 2.8 Titration curve for the carbonate system at 25˚C (Snoeyink and Jenkins, 1980)

The diagram shown in Figure 2.9 can be used for a wide variety of calculation involving the addition and removal of various species from the carbonate system. If two of three characteristics, pH, C_T, and total alkalinity of a water are given, the third characteristic can be determined using the diagram. It can be seen from the figure that adding strong acid decreases alkalinity without changing C_T. on the other hand the removal of CO_2 can cause a horizontal shift; the addition or removal of bicarbonate and carbonate is represented by movement at angles of $45°$ and $60°$, respectively. Furthermore dilution will cause a $45°$ movement and $[H_2CO_3^*]$ have no effect on the alkalinity.

Normally, dissolution of CO_2 does not change alkalinity however, above pH= 4.5, pH of the solution is lowered upon CO_2 dissolution. In order to keep the pH at a higher value a base has to be added to the solution. As a result in alkaline pH, the alkalinity of water continuously increases in the presence of CO_2 if the pH is to be kept constant (Snoeyink and Jenkins, 1980).
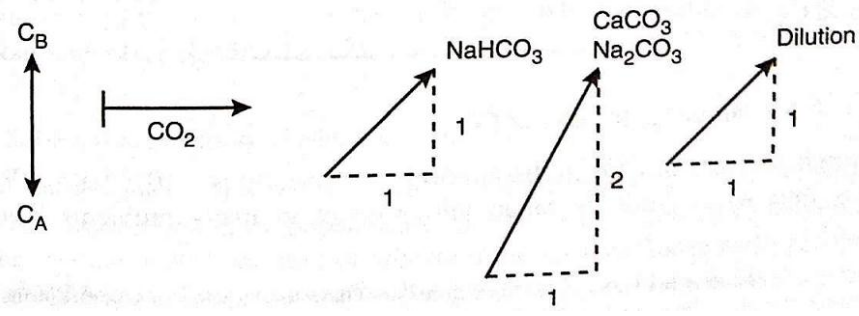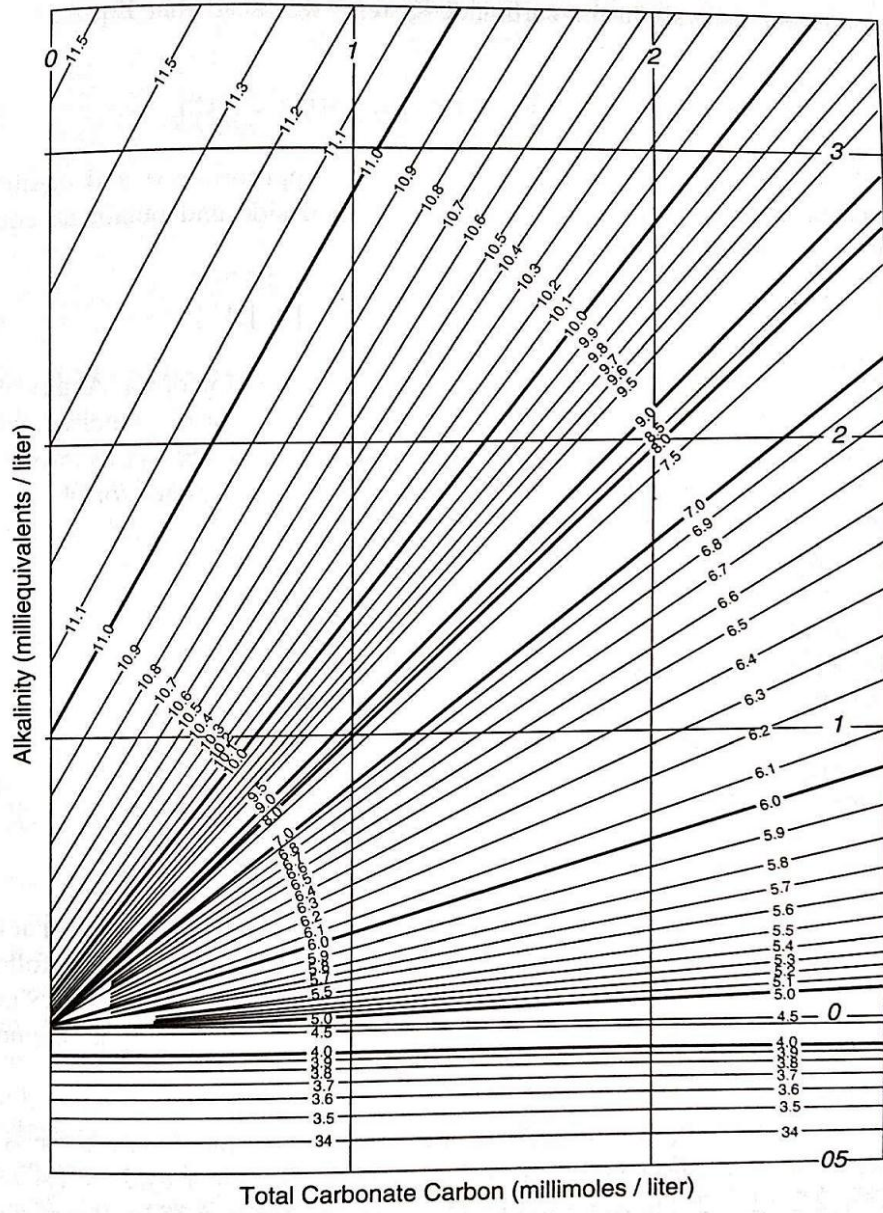
Figure 2.9 Deffeyes diagram (Brezonik et al., 2011)

1.2.7 Alkalinity of various natural waters

Natural water typically has an alkalinity of 1.00×10^{-3} equivalents per liter (Eq/L), meaning that the alkaline solutes in 1 L of water will neutralize 1.00×10^{-3} moles of acid (Manahan, 2011).

Table 2.4 Alkalinity of natural waters (Stumm and Morgan, 1996)

Various waters	C_T (M)*	Alkalinity (Eq liter $^{-1}$)
Sea water	2.3×10^{-3}	$2.3 - 2.6 \times 10^{-3}$
River waters, average	$\sim 10^{-3}$	$\sim 10^{-3}$
River waters, typical range	$10^{-4} - 5 \times 10^{-3}$	$10^{-4} - 5 \times 10^{-3}$
Ground waters, typical range, United states	$5 \times 10^{-4} - 8 \times 10^{-3}$	$10^{-4} - 5 \times 10^{-3}$
Rain water, typical range	$10^{-5} - 5 \times 10^{-5}$	$0 - 4 \times 10^{-5}$

* $C_T = [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

1.2.8 Factors affecting alkalinity and pH in natural waters

Mineral weathering is the primary source of alkalinity in natural waters. Dissolution of carbonate minerals (limestone, dolomite) is important, but so is the incongruent dissolution of silicate minerals (see Table 2.5, reactions 6 and 7). Atmospheric acid deposition of sulfuric and nitric acids can be a significant sink for alkalinity in watersheds with low rates of mineral weathering. Aside from weathering/dissolution reactions and atmospheric inputs, many biochemical processes in water bodies and watersheds also affect pH and alkalinity. Photosynthetic production of organic matter (Table 2.5, reaction 1a) and reverse reaction, respiration,

do not affect alkalinity directly, but they do affect pH by consuming and producing CO_2. If these pH changes cause $CaCO_3$ to precipitate or dissolve, then alkalinity is affected. Plant grow involves more than the production of organic carbon, however; proteins also must be formed, and depending on the inorganic source of nitrogen, this can cause either an increase (NO_3^-) or decrease (NH_4^+) in alkalinity (Brezonik and Arnold, 2011).

Table 2.5 Processes affecting alkalinity and pH in natural waters (Brezonik and Arnold, 2011)

Process		pH/alkalinity change
Photosynthesis and respiration	(1a) $nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2$	Increase in pH No change in alkalinity
	(1b) $106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+$ $\rightarrow \{C_{106}H_{263}O_{110}N_{16}P\} + 138O_2$	Increase
	(1c) $106CO_2 + 16NH_4^+ + HPO_4^{2-} + 108H_2O$ $\rightarrow \{C_{106}H_{263}O_{110}N_{16}P\} + 107O_2 + 14H^+$	Decrease
Nitrification	(2) $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	Decrease
Denitrification	(3) $5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$	Increase
Sulfide and iron sulfide oxidation	(4a) $HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$	Decrease
	(4b) $FeS_2(s) + 3\ 3/4O2 + 3\ 1/2H2O \rightarrow Fe(OH)_3(s) + 4H^+ + 2SO_4^{2-}$	Decrease
Sulfate reduction	(5) $2CH_2O + SO_4^{2-} + H^+ \rightarrow 2CO_2 + HS^- + H_2O$	Increase
$CaCO_3$ dissolution/ precipitation	(6) $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$	Increase
Aluminosilicate mineral weathering	(7) $2NaAlSi_3O_8(s) + 2CO_2 + 11H_2O$ $\rightarrow Al_2Si_2O_5(OH)_4(s) + 2Na^+ + 2HCO_3^- + 4Si(OH)_4$	Increase

Other nitrogen cycle reactions also affect pH and alkalinity. Nitrification (Table 2.5, reaction 2) converts the weak acid NH_4^+ to the strong acid, HNO_3, thus decreasing pH and alkalinity. Denitrification consumes the strong acid, HNO_3, increasing pH and alkalinity. Sulfur cycle redox reactions behave similarly. Sulfide oxidation converts a weak acid, H_2S to a strong acid, H_2SO_4, and sulfate reduction has the opposite effect. Sulfate reduction in lake sediments is an important pH buffering mechanism in some low-alkalinity lakes. Because oxidized forms of elements are stronger acids than reduced forms, we can make the generalization that oxidative biogeochemical processes, such as nitrification, sulfide oxidation, and iron oxidation, consume alkalinity by producing strong acid. Conversely, reductive biogeochemical processes, such as nitrate assimilation, denitrification, and sulfate reduction, produce alkalinity by consuming a strong acid or producing a weak acid from a strong one (Brezonik and Arnold, 2011).

1.2.9 Acid-base systems in natural waters; ranges and controls on pH

The behavior of natural waters in which carbonate species are the main buffering agents, is profoundly affected by some parameters. Below is some important considerations related with natural waters and alkalinity:

- Temperature, pressure, and activity coefficients have no effect on the alkalinity. Whereas pH will be affected with all of these parameters.

- Total alkalinity will be unaffected by addition or removal of CO_2. This statement is valid as long as CO_2 addition or removal does not form or dissolve solid phase $CaCO_3$. If suspended particles of $CaCO_3$ are present in a water sample, CO_2 addition may solubilize them by the reaction $CaCO_{3(s)} + CO_2 + H_2O \rightarrow Ca^{+2} + 2HCO_3^-$, thus increasing alkalinity. Conversely, stripping dissolved CO_2 from water sample may raise its pH enough to precipitate $CaCO_3$, and its precipitation will decrease the alkalinity. Addition or removal of CO_2 may affect the form of alkalinity, however. If a sample has carbonate alkalinity, adding CO_2 decreases this form and increase the bicarbonate: $CO_2 + CO_3^{-2} + H_2O \rightarrow 2HCO_3^-$ (for no net change in total alkalinity) (Brezonik and Arnold, 2011).

-The activities of photosynthetic and respiratory organisms commonly involve the addition or removal of ions such as H_3O^+, NO^{-3} , NH^{+4} , HPO_4^{-2}, etc. Charge conservation requires that the uptake of an ion such as NH^{+4} must be accompanied by the uptake of H^+ or the release of OH^-, either of which will increase the alkalinity. Processes of this kind take place on a large scale in both aquatic and non-aquatic ecosystems. The flow of groundwater and runoff from the land can affect the pH and alkalinity of adjacent bodies of water, especially in areas of intense agricultural activity. (Brezonik and Arnold, 2011; Loewenthal and Marais, 1976; Stumm and Morgan, 1996; Snoeyink and Jenkins, 1980; Butler, 1982; Holland, 1978; Morel and Hering, 1993).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The hematite ore sample of Brazilian origin was first subjected to comminution by jaw and roll crusher to minus 1 millimeter, followed by purification by high intensity magnetic separation. After purification it was ground wet in a ball mill with steel balls for 2 hours to reach 99.9% - 45μm. Then the wet sample was filtered and dried at 105 ˚C and stored in sealed plastic bags.

Commercial corn starch from the local market was employed as a flocculant. Reagent grade Na_2CO_3 and $NaHCO_3$ were used to adjust the carbonate alkalinity. 1 N NaOH and HCl solutions were used to adjust pH. Distilled water was used for all experiments and solutions.

3.1.1 Particle size analysis of the sample

The particle size analysis of sample was carried out by means of Malvern Mastersizer in Central Lab of METU. Figure 3.1 and Table A-1 shows particle size distribution of the sample.
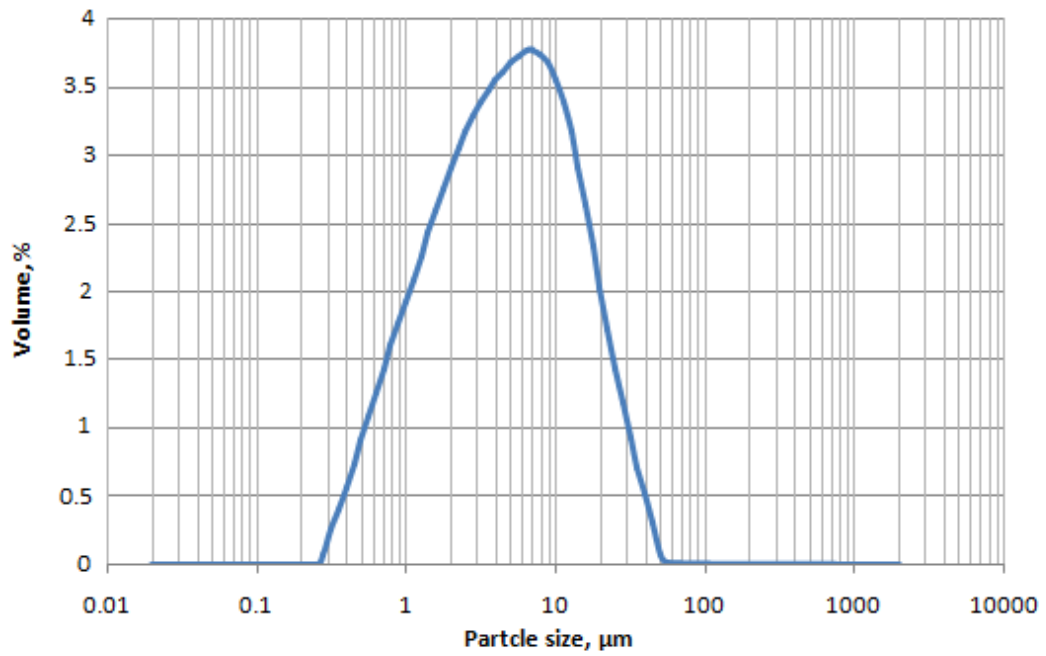
Figure 3.10 Particle size distribution of the hematite sample

3.1.2 Chemical and mineralogical analyses of the sample

The chemical analyses of the sample were carried out by SPECTRO iQ X-Ray Fluorescence Spectrometer. The results are given in Table 3.1 and Table A-2.

Table 3.1 Chemical Analysis of the hematite Sample

Constituent		Weight %
Fe_2O_3	Iron oxide	79.86
SiO_2	Silicon oxide	7.438
Al_2O_3	Aluminum oxide	4.041
MgO	Magnesium oxide	3.564

Mineraloical analyses of sample were carried out by the help of Xray diffraction (XRD) method in Metallurgical and Materials Engineering Department of METU. The results are illustrated in Figure 3.2.

According to the results, hematite is the most common mineral, whereas there are small amounts of gibbsite and cristobalite in the sample.
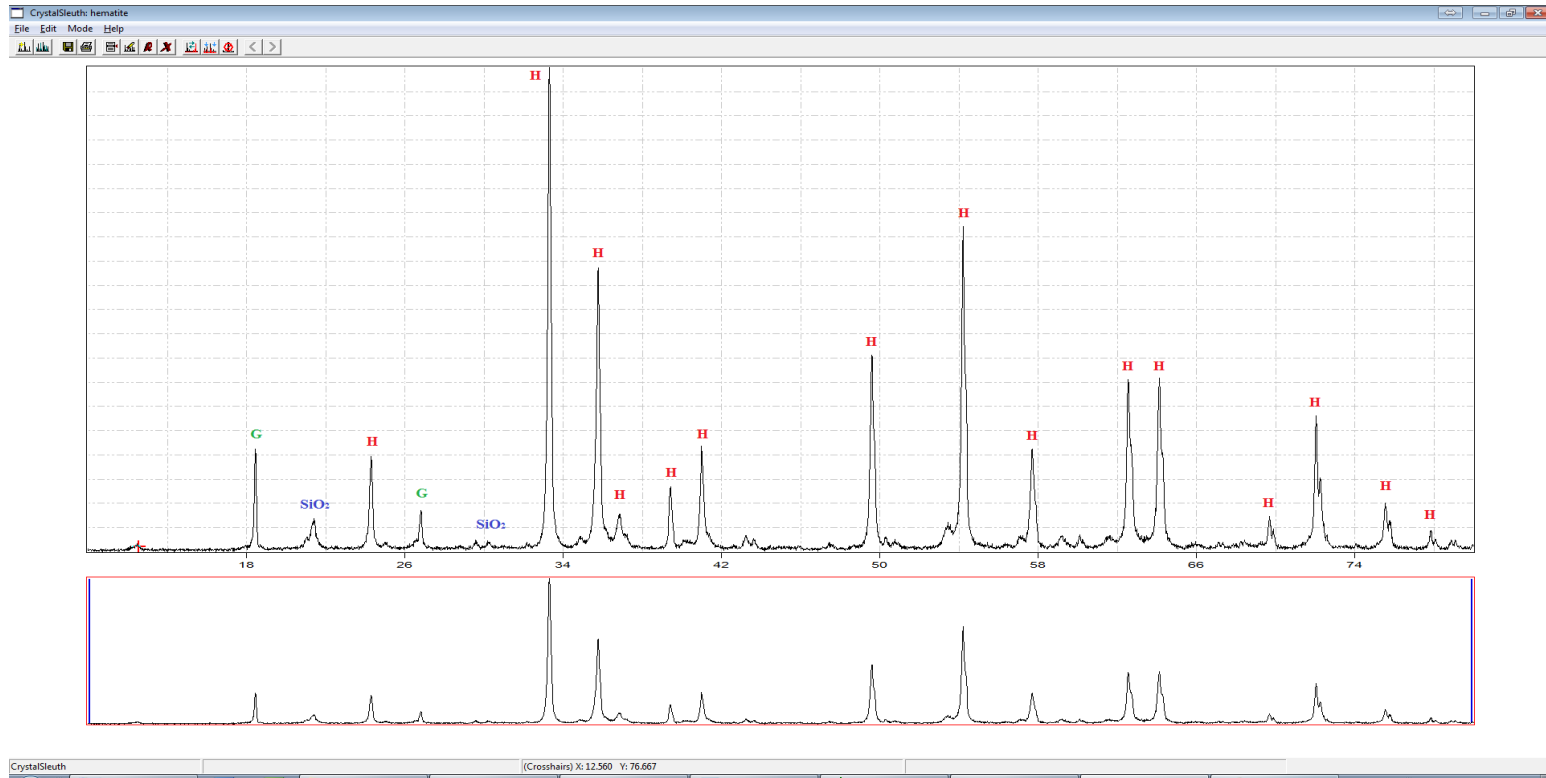
Figure 3.2 Results of XRD analysis of the sample, H: Hematite, G: Gibbsite, SiO_2: Cristobalite

3.2 Methods

3.2.1 Preparation of test waters

Waters with different alkalinities were used in the experiments. Alkalinity of test waters was adjusted by adding a known amount of Na_2CO_3 and $NaHCO_3$. Solutions of different concentration of Na_2CO_3 and $NaHCO_3$ by means of CO_2 free distilled water were prepared. These concentrations were 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} M. Each type of water, with different alkalinity, was prepared in one liter stock solution and kept closed to atmosphere.

3.2.2 Preparation of starch

Starch is not soluble in cold water and must be solubilized in a process known as gelatinization. To reach to this purpose, starch was thermally gelatinized and dispersed. In the cooking process, the starch polymer becomes hydrated and dispersed in the aqueous system.

Starch solutions were prepared daily to minimize the effect of microbial degradation. For preparing starch solution, 0.5 gram of corn starch was placed in 400 mL beaker. Approximately 100 mL distilled water (CO_2 free) was added and the beaker was covered with a watch glass. It was pressure cooked in an autoclave (CETROCLAVE, shown in Figure 3.3) for 30 minutes at 140°C and 30 psi. The cooked and gelatinized starch was cooled for 10 minutes in air followed by 10 minutes in a water bath. It was then homogenized in the blender (Waring Commercial Blender, shown in Figure 3.3) for 30 seconds at high speed and made up to 500 cc in a flask by adding CO_2 free distilled water to obtain 1mg/mL starch concentration.

Figure 3.3 CETROCLAVE used to cook the starch (left) and the blender (right)

3.2.3 Starch analysis

Quantitative starch analysis was carried out by sulfuric acid-phenol method (Dubois et al., 1956). Five different starch solutions with the concentrations of 15, 30, 45, 60, 75 mg/L were prepared. 2 mL of sample solution and 1mL of 5% phenol were pipetted into a 10 mL beaker, followed by rapid and uniform delivery of 5 mL of concentrated (98%) H_2SO_4. The beakers were left to cool for 10 minutes in air and another 10 minutes in cold water. Furthermore, the prepared solutions were analyzed by Schimadzu UV-1610 Spectrophotometer at 490 nm wavelength and the absorbance percent (ABS %) of samples were determined. Then, a graph of ABS% versus starch concentration was plotted (Figure 3.4 and Table B-8). To check the repeatability of experiments, two parallel analyses of every sample were run.
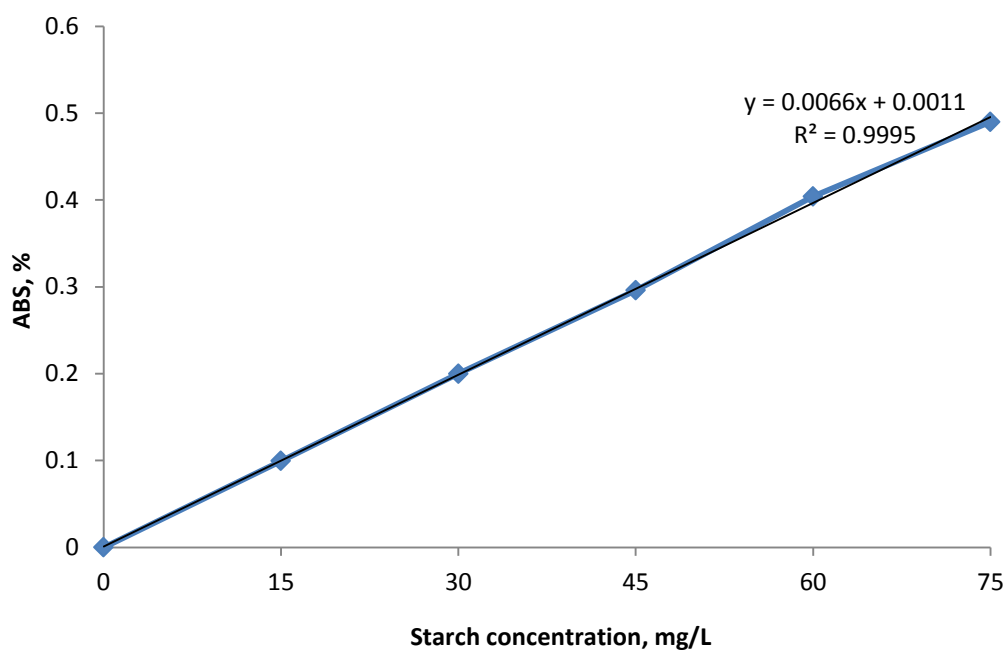
Figure 3.4 Absorbance at 490 nm as a function of starch concentration

3.2.4 Starch adsorption tests

To determine the starch adsorption capacity by hematite particles, 1.25 gram (5%) of hematite sample was put into 50 mL flask and known amount of starch was added. Then, test water which consisted of a predetermined amount of alkalinity was introduced into flask, followed by pH adjustment. After making up the final level of pulp in the flask to 25 mL by means of distilled water, the flask was tumbled at 52 rpm for 30 minutes (Arol, 1984). Finally the suspension was centrifuged at 6000 rpm for 30 minutes and the supernatant was suctioned for starch analysis.

The starch analyses of the samples were carried out as mentioned. However, in this case the concentration of starch is unknown which was simply determined by use of the graph in Figure 3.4. The value that was calculated by this method is the amount of

starch which is not adsorbed by hematite. By subtraction of this amount from the total amount of starch, the desired starch value which is adsorbed by hematite particles will be obtained.

3.2.5 Flocculation tests

The flocculation tests were carried out in 250 mL graduated cylinder. 12.5 grams of hematite sample (5% by weight) were placed in the cylinder and was filled by the test water (with known amount of alkalinity) up to 230 mL mark. pH adjustment was done by 1 N NaOH solution followed by adding the desired quantity of starch in three equal stages. After the last addition of starch; the level of pulp was made up to 250 mL and final pH was adjusted to 11. The cylinder was inverted and shaken five times after each addition of starch and five times more after last addition. Then, the suspension was left to settle down for a predetermined time and the settling time of particles (the mud line) for a known height of the cylinder was measured. The settling rate was calculated by dividing the distance travelled by settling time and expressed as cm/s. Finally, 200 mL of the supernatant was siphoned out by means of a special copper tube with special care of no disturbance would occur in the settled part. The supernatant was placed in an oven to dry the solids at 105-110 ˚C. Dry weight of solids was divided by the supernatant volume to determine the suspended solid content in mg/L.

3.2.6 Zeta potential measurements

The zeta potential of the hematite sample in different pH and different alkalinities were measured with Zetasizer Nano-Z (Figure 3.5). For the measurement, a suspension of 0.5% (w/v) hematite sample in test water (with a given amount of alkalinity) was prepared in a 50 mL beaker. The suspension was mixed continuously for 5 minutes. Prior to the mixing, pH calibration was carried out by solution of 1N NaOH. After mixing, the suspension was left for one minute followed by injection of top surface (supernatant) of the suspension into disposable cuvettes of the instrument (Figure 3.6).
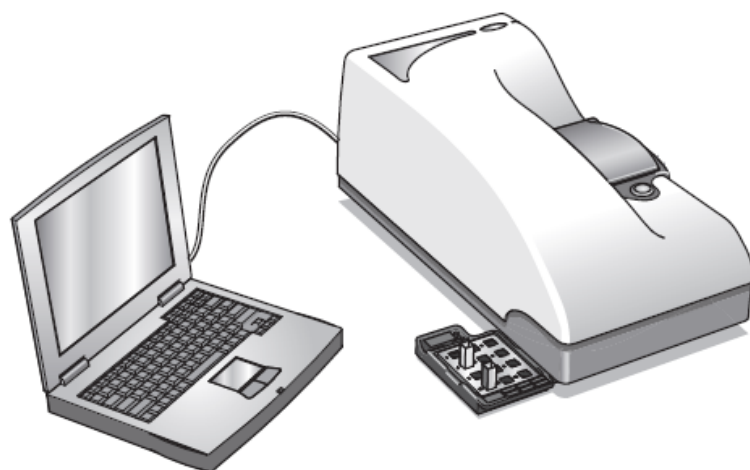
Figure 3.5 Zetasizer Nano-Z (Malvern, 2009)

Then, the disposable cuvettes were placed in Zetasizer and zeta potentials of samples were measured.

Electrode ⊕   ⊖ Electrode

Capillary
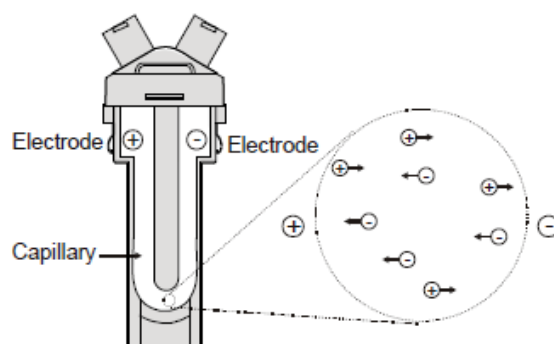
Figure 3.6 Disposable Cuvette of Zetasizer Nano-Z and particle movement according to electrode sign (Malvern, 2009)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Flocculation - dispersion behavior of hematite as a function of pH

In order to determine the effect of pH on the dispersion of hematite in the absence of starch, flocculation tests were carried out at various pH values. The results are shown in Figure 4.1 and Table B-1. As seen in the figure, for 45 seconds settling duration any complete settling of particles was not observed at any pH. However, it seems that in low pH values (around 3) hematite particles have a tendency to coagulation.

Hogg (2000) indicated that the charge in mineral particles dispersed in water typically arises from electrochemical interaction between the solid and surrounding aqueous solution and can usually be controlled through the solution pH. At some pH, the so-called isoelectric point, the particles have no net charge and are unstable with respect to coagulation and flocculation.
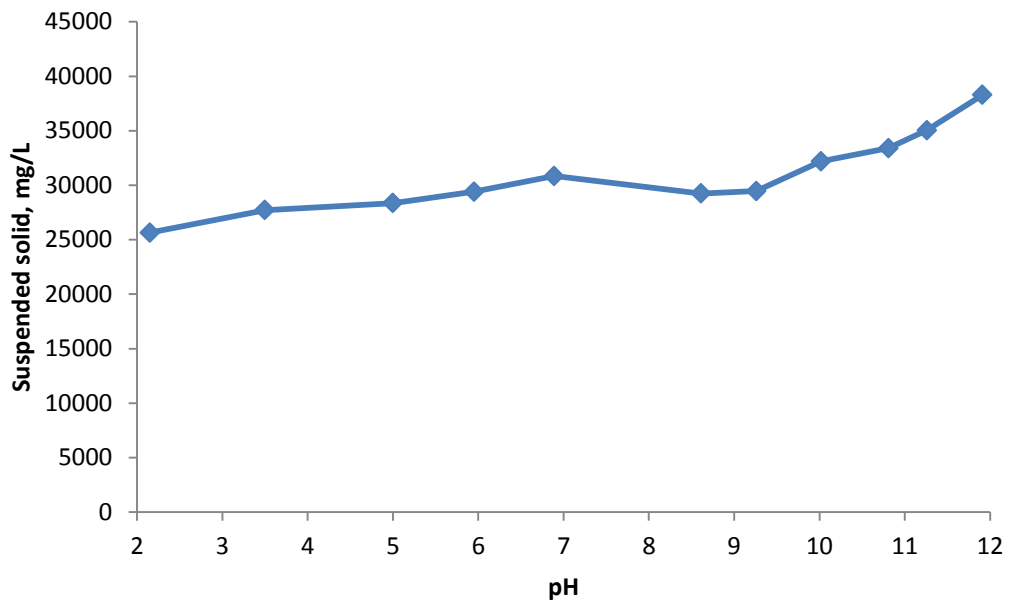
Figure 4.11 Effect of pH on the flocculation - dispersion of hematite, no starch, settling time 45 seconds

Since the selective flocculation and reverse cationic flotation of hematite ore, the most widely used flotation route in the iron ore industry, is generally conducted at pH 10.5-11 (Arol and Iwasaki, 2003; Colombo, 1980; DeVaney, 1985; Haselhuhn et al., 2012; Ma, 2012; Ma, 2011). Thus, all of the following tests were performed at pH 11. This pH was essential especially for selective flocculation because in this pH hematite particles present a net negative surface charge that leads to approximately complete dispersion of the fine silica particles from the hematite surfaces (Haselhuhn et al., 2012).

4.2. Effect of starch concentration on the flocculation of hematite

In order to investigate the effect of different factors on the flocculation of hematite, the first step is to determine the flocculation behavior of hematite particles in the presence of the flocculant and finding the optimum dosage of the flocculant. Therefore, flocculation test of hematite as a function of starch concentration was carried out in the absence of carbonate alkalinity. The pH of pulp was adjusted to 11. The results are illustrated in Figure 4.2 and Table B-2.

According to Figure 4.2 a, the amount of solids that are not flocculated and remained suspended decreases considerably to reach the minimum in the concentration of 15mg/L of corn starch. More increment in starch concentration after the optimum point, 15 mg/L, resulted in increasing in suspended solid content. This behavior is well known as the full coverage of the starch macromolecules on the solid surfaces, which blocks the bridging and prevents the formation of flocs. According to Ma (2011), at low concentration starch destabilizes hematite by bridging flocculation, but it restabilizes hematite at higher concentration as steric forces induced by the polymer molecules start to grow.

The same behavior can be seen in Figure 4.2 b, increasing the settling rate until the concentration of 15 mg/L and then reducing remarkably as a result of increasing the starch concentration.

Since the best results for flocculation parameters, suspended solid amount and settling rate, was observed in 15 mg/L starch. Thus, the optimum addition of starch was determined as 15 mg/L to be used in following flocculation experiments.
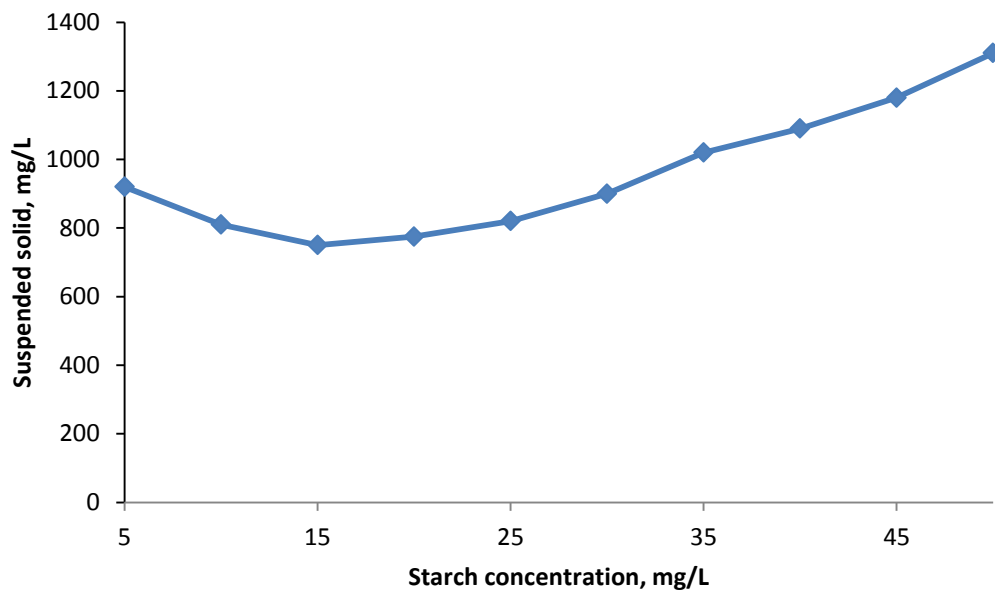
(a)
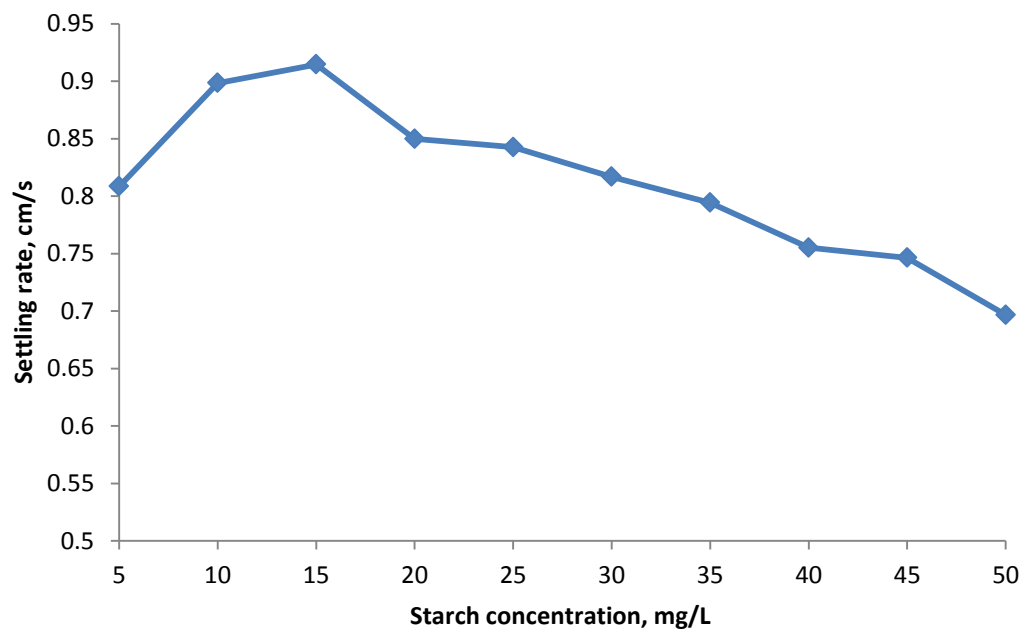
(b)

Figure 4.2 Effect of starch concentration on the flocculation of hematite, pH 11, settling
time 45 seconds

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4.3 Effect of alkalinity on the flocculation of hematite

After determining the optimum conditions for flocculation; i.e., The pH and starch concentration, the effect of carbonate alkalinity on the flocculation of hematite was investigated. Water with different alkalinities were prepeared by adding given amounts of Na_2CO_3 to CO_2 free distilled water and equilibrating the test waters with air at room temperature. All the flocculation experiments were performed with these waters.

4.3.1 The effect of carbonate alkalinity on the dispersion of hematite in the absence of starch

A series of flocculation tests were carried out with waters bearing different alkalinity values in the absence of starch at pH 11. The results were given in Figure 4.3 and Table B-3.
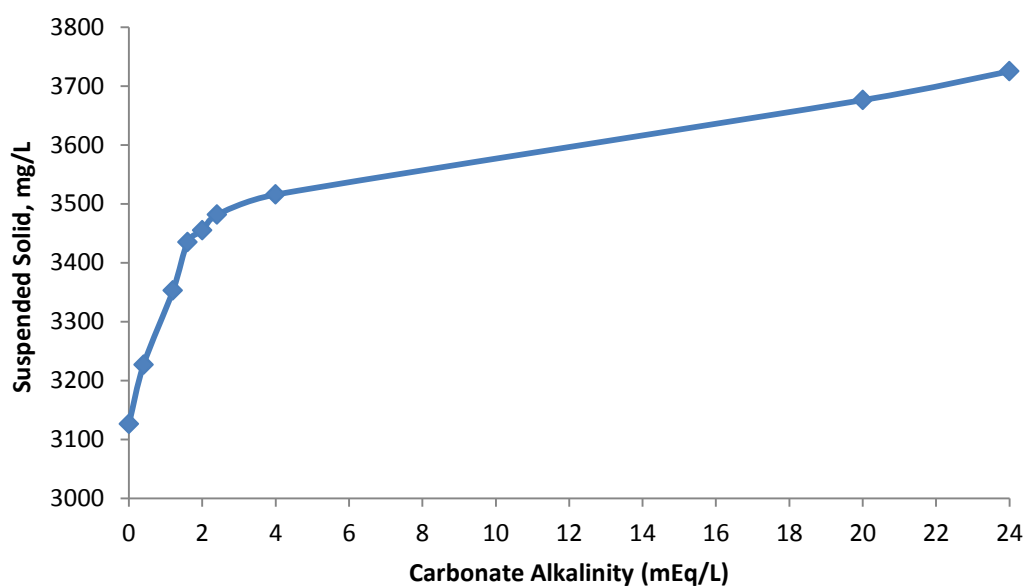
Figure 4.3 Effect of alkalinity on the flocculation of hematite, no starch, pH 11, settling time 45 seconds

As illustrated in the figure, in low alkalinities suspended solid quantity has a sharp increase as a result of rising the alkalinity amount of the pulp. In higher alkalinities suspended solid increase slightly and this trend seems to be continued in higher alkalinities. According to these results carbonate alkalinity leads to increase in the dispersion of hematite particles in the suspension in the absence of starch.

4.3.2 The effect of carbonate alkalinity on the flocculation of hematite in the presence of starch

The flocculation behavior of hematite particles in the presence of 15 mg/L starch as a function of alkalinity was investigated. The purpose of this work is to determine the positive or negative effects of carbonate alkalinity on the flocculation of hematite. The results were given in Figure 4.4 and Table B-4.

It is seen in Figure 4.4 a that suspended solid quantity had a downward trend to reach the minimum in about 1 mEq/L alkalinity. Then, it increased significantly as the suspended solid amount in 24 mEq/L is approximately twice its amount in the flocculation with no alkalinity.

In general, carbonate alkalinity in low quantities has a positive influence on the flocculation of hematite. As in the 1.2 mEq/L alkalinity, the minimum amount of suspended solid was reached. In the alkalinities of 2 mEq/L and 2.4 mEq/L suspended solid quantities were more than 1.2 mEq/L but they are lower than initial value with no alkalinity. Therefore it is clear that by addition of low amounts of alkalinity (lower than 2.4 mEq/L) flocculation behavior of hematite will be improved.

Graph b in Figure 4.4 indicates that, settling rate was significantly affected by the carbonate alkalinity. By adding a small amount of alkalinity to the test water a steep increase was observed in the settling rate. Following this sharp rise the settling rate was almost leveled out in higher alkalinities. It seems that, the seetling rate was more effected by presence of the carbonate alkalinity and the quantity of carbonate alkalinity had not considerable effect on the settling rate at higher carbonate alkalinity.
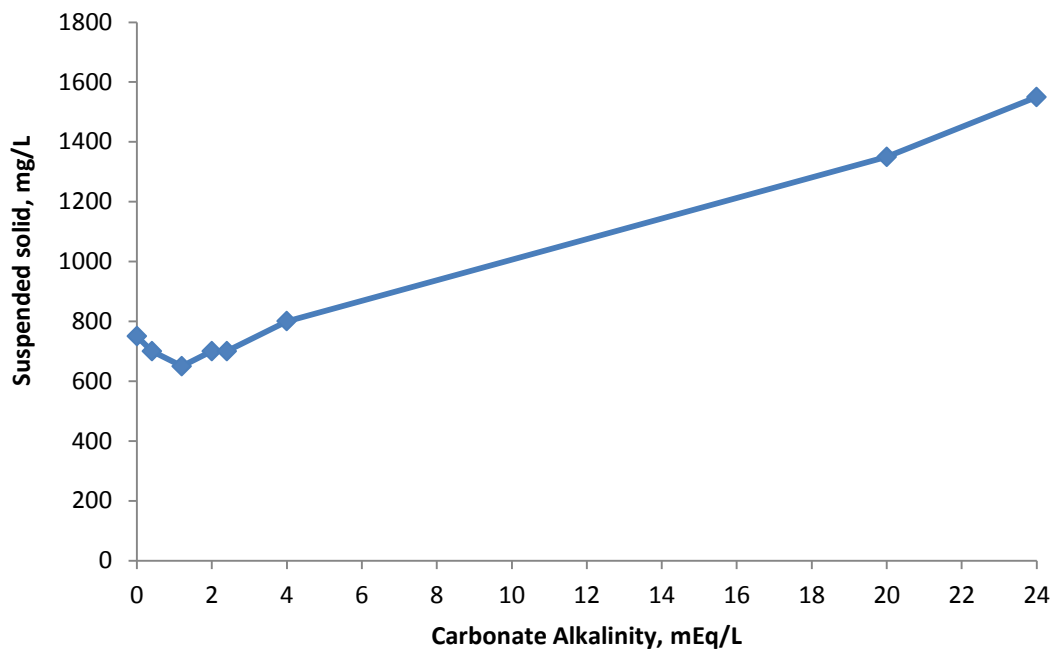
(a)
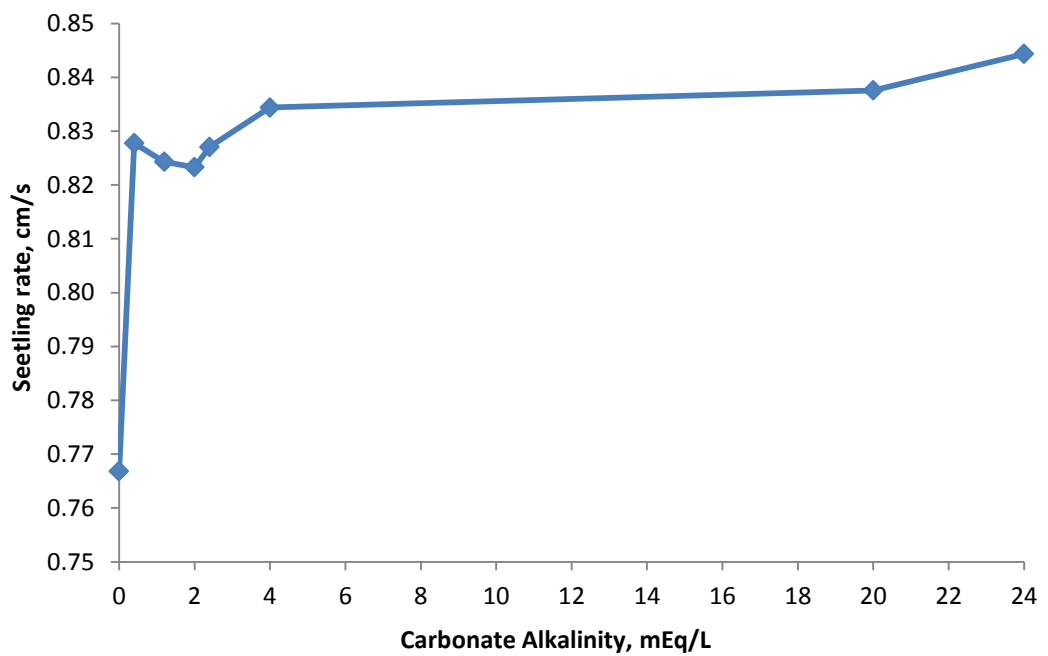
(b)

Figure 4.4 Effect of alkalinity on the flocculation of hematite, starch = 15 mg/L, pH 11, settling time 45 seconds

4.3.3 The effect of carbonate alkalinity on the flocculation of hematite in different starch concentration

To realize flocculation behavior of hematite as a function of carbonate alkalinity in different starch concentration series of flocculation tests were conducted. As it is illustrated in Figure 4.5 and Table B-5, flocculation experiments were performed in three different starch concentrations and five different alkalinity levels.
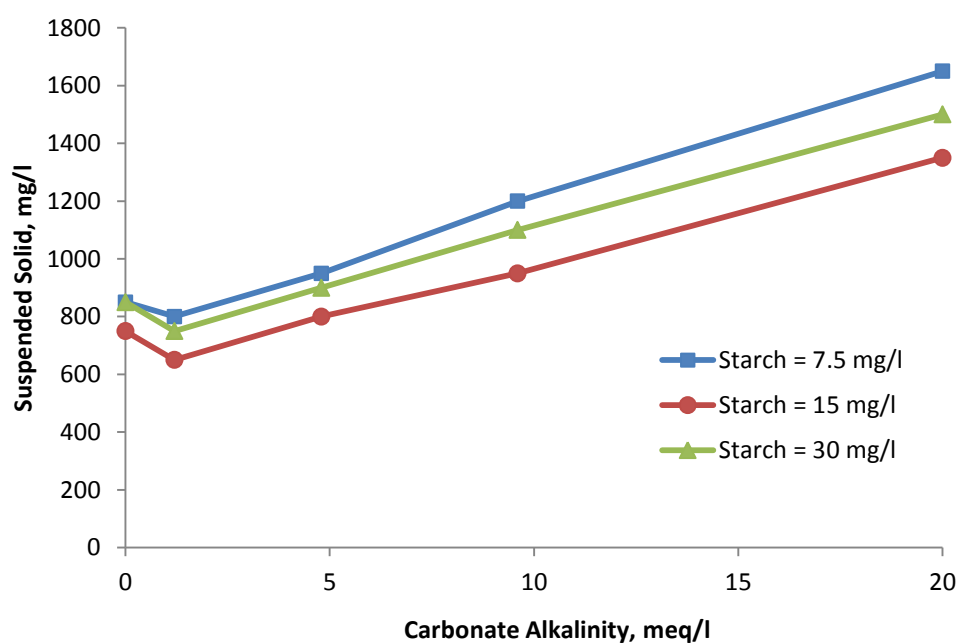
Figure 4.5 Effect of alkalinity on the flocculation of hematite in different alkalinities and different starch concentrations, pH 11, settling time 45 seconds

According to the results it was found out that, carbonate alkalinity in general adversely affects the flocculation of hematite with any starch concentration. However,

existance of carbonate alkalinity in low quantities has possitive effect on the flocculation of hematite. Furthermore, the results confirm the selection of optimum value of 15 mg/L for starch concentration.

4.4 Zeta Potential measurements

Zeta potential of hematite as a function of pH and alkalinity was measured to investigate the effect of carbonate alkalinity on the electrical potential between the charged particle and the bulk solution.

4.4.1 Effect of pH on the zeta potential of hematite particles

The most important factor that affects zeta potential is pH. The zeta potential of hematite sample at different pH values as given in Figure 4.6 and Table B-6.
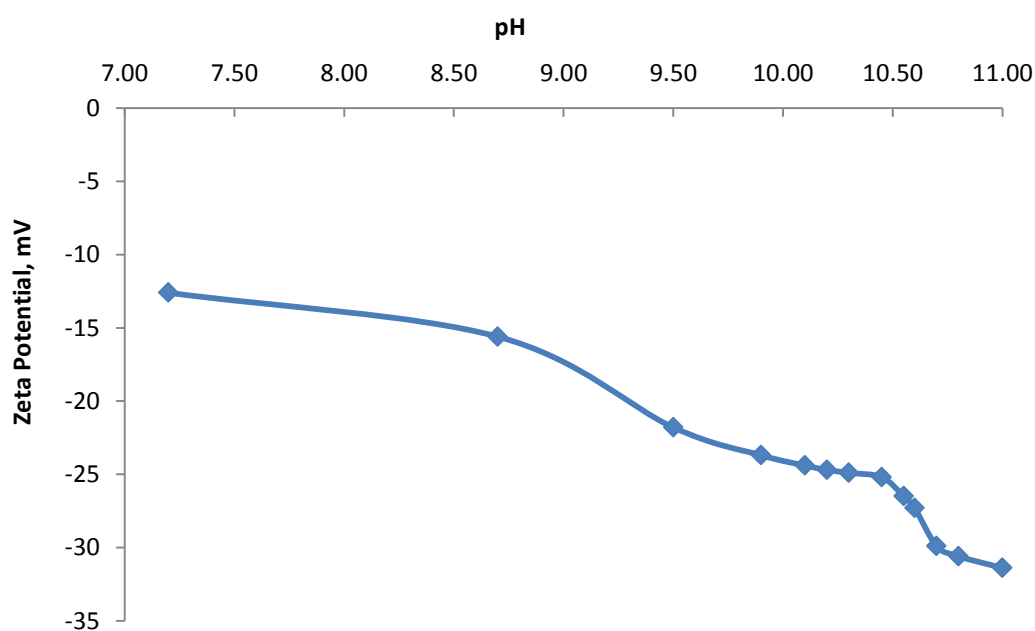
Figure 4.6 Zeta potential of hematite as a function of pH, no alkalinity

The figure indicates a downward trend for zeta potential which is as a result of increasing the pH of suspension. According to the figure hematite particles in the distilled water (pH 7.2) have a zeta potential of -12.6 mV; by increasing the pH of suspension, particles tend to acquire more negative charge, then zeta potential will be more negative to reach the minimum of -31.4 mV at pH 11. It seems that, this trend will continue in higher pH values.

4.4.2 Effect of alkalinity on the zeta potential of hematite particles

A series of zeta potential measurements at pH 11 in different carbonate alkalinity was carried out. The results are given in Figure 4.7 and Table B-7.
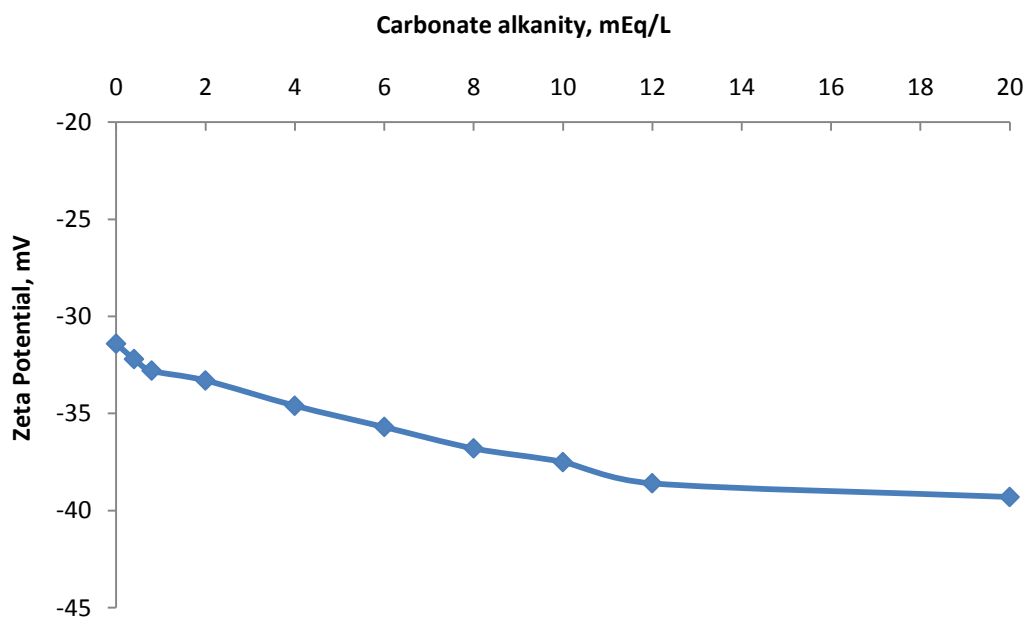
Figure 4.7 Zeta potential of hematite as a function of alkalinity, pH 11

As illustrated in the figure, there is a noticeable decline in zeta potential as a result of increase in carbonate alkalinity until 12 mEq/L carbonate alkalinity then it seems to level out. This decrease could be due to a shell made up of hematite/carbonate complexes formed around the hematite particles (Carlson and Kawatra, 2011).

As flocculation tendency of particles decreases by increasing of the magnitude of zeta potential, these outcomes confirm the negative influence of carbonate alkalinity on the flocculation of hematite.

4.5 Starch adsorption tests

Flocculation behavior of hematite with starch in the presence of carbonate alkalinity suggests that the carbonate alkalinity influences adsorption of starch by hematite. To elucidate this point, starch adsorption by hematite was determined in constant amount of starch and various concentration of starch as a function of carbonate alkalinity.

4.5.1 Effect of carbonate alkalinity on the starch adsorption in a constant amount of starch

Starch adsorption capacity of hematite as a function of carbonate alkalinity was investigated. The tests were performed in 15 mg/L starch concentration at pH 11. The results are presented in Figure 4.8 and Table B-9.
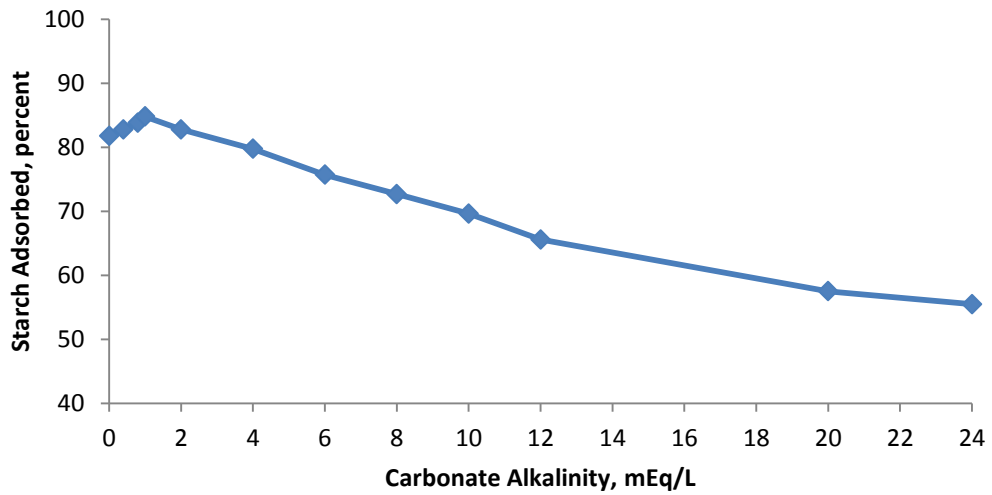
Figure 4.8 Effect of carbonate alkalinity on the starch adsorption, starch = 15 mg/L, pH 11

It was found out that the amount of starch which was adsorbed by hematite increased slightly in the response of carbonate alkalinity addition to reach the maximum in 1mEq/L carbonate alkalinity. But by addition of more alkalinity to the suspension, starch adsorption percent reduced remarkably from 84% to 55%. This reduction affected the flocculation performance of hematite.

The adverse influence of carbonate alkalinity on the starch adsorption could be due to the modification of surface of hematite particles or it could be related to the structural change of starch because of alkalinity. This needs to be studied in more details to exactly explain the mechanisms involved in the process.

In the comparison of Figure 4.4 a with Figure 4.8, the main reason of improving the flocculation performance in the low carbonate alkalinity values is supposed to be the rise in starch adsorption by hematite particles. Therefore, it is clear that the considerable decline in starch adsorption in higher carbonate alkalinities is responsible for decreasing the flocculation performance and increasing the suspended solid quantity.

4.5.2 Effect of carbonate alkalinity on the starch adsorption at different starch concentrations.

To investigate the influence of carbonate alkalinity on the flocculation of hematite with different starch concentrations, a series of experiments were performed. The tests were carried out at the same conditions as in Figure 4.5. The results are given in Figure 4.9 and Table 4-10.

Figure 4.9 gives new information about the influence of carbonate alkalinity on the starch adsorption. According to the experiments, starch adsorption is reduced with the increasing alkalinity (except for low alkalinities).

It is interesting to see that larger percentages of starch were adsorbed from the suspension with higher starch concentrations at higher carbonate alkalinity. This point needs to be further studied to understand the underlying mechanism.

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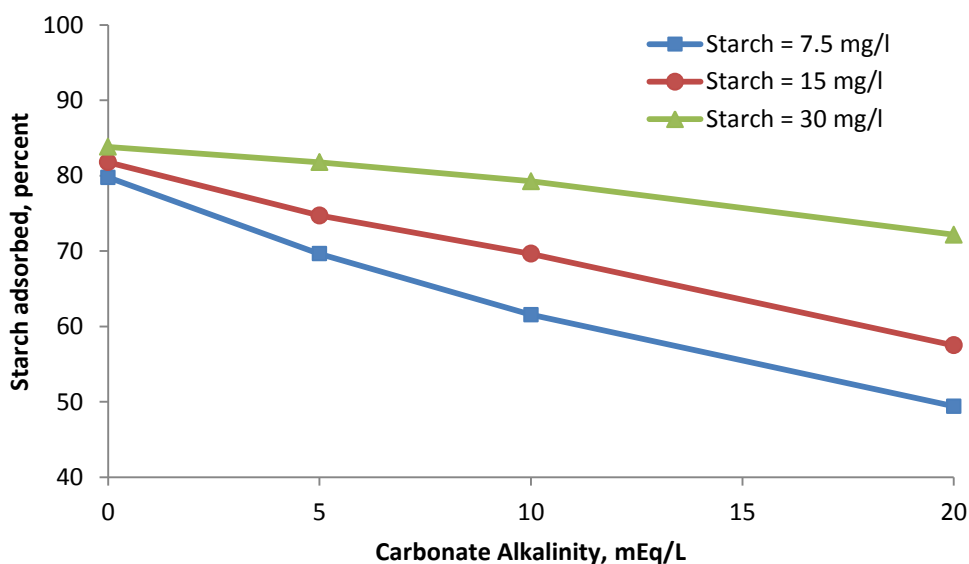
Figure 4.9 Effect of carbonate alkalinity on the starch adsorption at different starch concentrations, pH 11

CHAPTER 5

CONCLUSIONS

Based on the results obtained in this study, the following outcomes can be derived:

- In the absence of starch, hematite suspension was found to be stable (dispersed) in almost all pH values. However, in low pH values (around 3) hematite particles have a tendency to coagulation.

- Flocculation experiments with various starch concentrations indicated that the best starch concentration for the flocculation of hematite at pH 11 was 15 mg/L (300 g/ton of hematite)

- Carbonate alkalinity in low quantities (less than 2.4 mEq/L) has a positive influence on the flocculation of hematite, however in the high concentrations flocculation of hematite was adversely affected by carbonate alkalinity.

- Carbonate alkalinity demonstrates opposite effect on the zeta potential of hematite. The magnitude of zeta potential of hematite increases as a result of carbonate alkalinity increase at pH 11. High zeta potential means the suspension is more stable and the probability of flocculation in low.

- According to starch adsorption tests in 15 mg/L starch, the principle reason of improving the flocculation performance in the low alkalinity values is

supposed to be the increase in starch adsorption and the reduction in starch adsorption in higher carbonate alkalinities is responsible for the lower flocculation performance.

- The negative influence of alkalinity on the starch adsorption was more considerable in low starch concentrations while alkalinity slightly affected the starch adsorption at higher concentrations of starch.

To sum up, carbonate alkalinity has a considerable effect on the flocculation of hematite. This effect can be observed in both zeta potential measurements and starch adsorption test. Therefore, carbonate alkalinity should be taken into account in the flocculation/selective flocculation processes for a successful operation.

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APPENDIX A

DETAILED PARTICLE SIZE AND CHEMICAL ANALYSIS

Table A-1 Particle size analysis of hematite sample

Size (μm)	Volume undersize, %	Size (μm)	Volume undersize, %
0.020	0.00	3.991	47.03
0.283	0.06	5.024	54.34
0.317	0.32	5.637	58.07
0.356	0.72	6.325	61.84
0.399	1.28	7.096	65.62
0.448	2.01	7.962	69.37
0.502	2.92	8.934	73.05
0.564	4.01	10.024	76.61
0.632	5.27	11.247	80.00
0.710	6.71	12.691	83.18
0.796	8.32	14.159	86.10
0.893	10.09	15.887	88.74
1.002	12.02	17.825	91.08
1.125	14.11	20.000	93.11
1.262	16.37	22.440	94.84
1.416	18.80	25.179	96.28
1.589	21.39	28.251	97.46
1.783	24.15	31.698	98.39
2.000	27.06	35.566	99.10
2.244	30.12	39.905	99.62
2.518	33.30	44.774	99.92
2.825	36.60	50.238	99.99
3.170	39.99	56.365	100.00

Table A-2 Detailed chemical analysis of hematite sample (Method: XRF)

Symbol	Element	Weight %
Fe_2O_3	Iron oxide	79.860
SiO_2	Silicon oxide	7.438
Al_2O_3	Aluminum oxide	4.041
MgO	Magnesium oxide	3.564
CaO	Calcium oxide	0.628
Cr_2O_3	Chromium oxide	0.442
SO3	Sulfur trioxide	0.328
Ta_2O_5	Tantalum oxide	0.293
MnO	Manganese oxide	0.224
NiO	Nickel oxide	0.149
P_2O_5	Phosphorus oxide	0.117
Na_2O	Sodium oxide	<0.11

APPENDIX B

LIST OF EXPERIMENTAL RESULTS

Table B-1 Flocculation-dispersion behavior of hematite as a function of pH in the absence of starch, settling time 45 seconds

pH	Suspended solid (g)	Suspended solid (mg/L)
2.15	5.13	25650
3.5	5.544	27720
5	5.673	28365
5.95	5.882	29410
6.89	6.17	30850
8.61	5.85	29250
9.26	5.892	29460
10.02	6.44	32200
10.81	6.68	33400
11.26	7.01	35050
11.91	7.657	38285

Table B-2 Effect of starch concentration on the flocculation of hematite, no carbonate
alkalinity, pH 11, settling time 45 seconds

Starch Concentration		Settling Time (s)	Settling Rate (cm/s)	Suspended Solid (mg/L)
(mg/L)	(g/ton)			
5	100	24.49	0.808	920
10	200	22.04	0.898	810
15	300	21.65	0.915	750
20	400	23.3	0.850	775
25	500	23.5	0.843	820
30	600	24.24	0.817	900
35	700	24.93	0.794	1020
40	800	26.22	0.755	1090
45	900	26.53	0.746	1180
50	1000	28.42	0.697	1310

Table B-3 Effect of carbonate alkalinity on the dispersion of hematite in the absence of
starch, pH 11, settling time 45 seconds

Carbonate Alkanity (mEq/L)	Suspened Solid (mg/L)
0	3125.85
0.4	3226.71
1.2	3352.62
1.6	3434.82
2	3454.70
2.4	3481.28
4	3515.61
20	3676.04
24	3724.94

Table B-4 Effect of carbonate alkalinity on the flocculation of hematite, starch = 15 mg/L, pH 11, settling time 45 seconds

Carbonate Alkanity (mEq/L)	Settling Time (s)	Settling rate (cm/s)	Suspended Solid (mg/L)
0	25.82	0.77	750
0.4	23.92	0.83	700
1.2	24.02	0.82	650
2	24.05	0.82	700
2.4	23.94	0.83	700
4	23.73	0.83	800
20	23.64	0.84	1350
24	23.45	0.84	1550

Table B-5 Effect of carbonate alkalinity on the flocculation of hematite in different starch concentration, pH 11, settling time 45 seconds

Carbonate Alkanity (mEq/L)	Suspended solid (mg/L)		
	Starch = 7.5 (mg/L)	Starch = 15 (mg/L)	Starch = 30 (mg/L)
0	850	750	850
1.2	800	650	750
4.8	950	800	900
9.6	1200	950	1100
20	1650	1350	1500

Table B-6 Effect of pH on the zeta potential of hematite particles, no alkalinity

pH	Zeta Potential (mV)
7.20	-12.6
8.70	-15.6
9.50	-21.8
9.90	-23.7
10.10	-24.4
10.20	-24.7
10.30	-24.9
10.45	-25.2
10.55	-26.5
10.60	-27.3
10.70	-29.9
10.8	-30.6
11	-31.4

Table B-7 Effect of alkalinity on the zeta potential of hematite particles, pH 11

Carbonate Alkanity (mEq/L)	Carbonate Alkanity (mg/L as $CaCO_3$)	Zeta Potential (mV)
0	0	-31.4
0.4	20	-32.2
0.8	40	-32.8
2	100	-33.3
4	200	-34.6
6	300	-35.7
8	400	-36.8
10	500	-37.5
12	600	-38.6
20	1000	-39.3

Table B-8 Starch analysis results

Starch concentration (mg/L)	ABS %
0	0
15	0.0995
30	0.2000
45	0.2960
60	0.4040
75	0.4900

Table B-9 Effect of carbonate alkalinity on the starch adsorption in a constant amount of starch, starch = 15mg/L, pH 11

Carbonate Alkanity (mEq/L)	ABS%	Starch Concentration in the Process Water (mg/L)	Starch Adsorbed percent
0	0.019	2.732	81.79
0.4	0.018	2.580	82.80
0.8	0.017	2.428	83.81
1	0.016	2.277	84.82
2	0.018	2.580	82.80
4	0.021	3.035	79.76
6	0.025	3.642	75.72
8	0.028	4.098	72.68
10	0.031	4.553	69.65
12	0.035	5.160	65.60
20	0.043	6.374	57.50
24	0.045	6.678	55.48

Table B-6 Effect of carbonate alkalinity on the starch adsorption in the different amount of
starch, pH 11

Carbonate alkanity (mEq/L)	ABS %			Starch Concentration (mg/L)			Starch Adsorbed Percent		
	Starch = 7.5 mg/L	Starch = 15 mg/L	Starch = 30 mg/L	Starch = 7.5 mg/L	Starch = 15 mg/L	Starch = 30 mg/L	Starch = 7.5 mg/L	Starch = 15 mg/L	Starch = 30 mg/L
0	0.011	0.019	0.033	1.518	2.732	4.857	79.76	81.79	83.81
5	0.016	0.026	0.037	2.277	3.794	5.464	69.65	74.71	81.79
10	0.020	0.031	0.042	2.884	4.553	6.222	61.55	69.65	79.26
20	0.026	0.043	0.056	3.794	6.374	8.347	49.41	57.50	72.18