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RECOVERY OF PHOSPHATE MINERALS FROM PLANT TAILINGS USING DIRECT FROTH FLOTATION PROCESS

by

ASHRAF ALSAFASFEH

A Thesis

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Approved by
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Dr. Zeshan Hyder

ABSTRACT

The wastes produced from phosphate industry presents many challenges due to the economic and environmental impacts of their disposal. In the meantime, scarcity of high-grade phosphate ores persuades researchers to find novel methods of upgrading these wastes (secondary sources) and recycling them in the production plant circuit. The goal of this study is to investigate the potential to upgrade the phosphorus content in the tailing produced from a phosphorous production plant using direct froth flotation process. Characterization studies such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and mineral liberation analysis (MLA) were first conducted to identify the mineralogical and morphological characteristics as well as grain liberation and locking for a better understanding of the behavior of the flotation feed. It is important to mention that this research primarily discusses the role of reagents rather than other operational parameters. For this purpose, bench scale flotation tests were carried out using a Denver flotation cell in the presence of different reagents. These reagents include sodium silicate which is a commercially-used gangue dispersant and in-house synthesized novel gangue depressant, Hy-PAM. Moreover, several influencing parameters such as solid contents of the flotation pulp, pulp pH and pulp residence time were investigated to optimize the flotation outcomes in terms of the recovery and the grade of the concentrate products. Studies using a dual dispersant/depressant system, at a specific mass ratio, were also conducted to figure out if the synergy could improve the overall flotation performance. Results indicated that the phosphorus content in the plant tailings can be upgraded by> 3% at > 70% recovery.

ACKNOWLEDGMENTS

I would like to express my greatest acknowledgment to my advisor Dr. Lana Alagha for her precious advice, motivation, and continual support throughout this study. She made my dream come true by giving me the opportunity to study in the United States. This thesis was impossible to be completed without her academic guidance, fairness, and responsiveness. Her modest and prudent spirit always influences me and reminds me to work harder.

I would like to extend my deep gratitude to the thesis committee members, Dr. Michael Moats, Associate Professor of Material Science and Engineering and Dr. Zeshan Hyder, Assistant Professor of Mining Engineering for accepting to be members in my Master's thesis committee. My appreciation is also expressed to all the staff members in the departments of Mining and Nuclear Engineering and Material Science and Engineering for their help. My appreciation is also extended to the graduate students in Dr. Alagha's research group; Mr. Mostafa Khodakarami, Mr. Muhammaed Badar Hayyat, and Mr. Ontlamenste Kenneth Molatlhegi for their support and useful discussions.

Finally, I would like to dedicate this thesis to my dearest family. The constant support and encouragement from my father and mother were always the greatest motivation for me to accomplish all. I want to thank my wife, Ala Alzidaneen, for her love and constant support, for all the late nights and early mornings, and for keeping me sane over the past few months. Most of that work occurred on weekends, nights, while on vacation, and other times that were inconvenient to my family. Thank you for being my wife. I owe you everything.

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1. INTRODUCTION

1.1. BACKGROUND

Phosphate is one of the most common minerals which is essential to human, animal and plant life. Phosphate is naturally present in all important daily requirements such as food, water, and even human bodies. In human body, phosphorus is present in genes, teeth, and bones. Phosphate rock is an important mineral commodity used in the production of phosphoric acid which is used to make phosphate salts for fertilizers (Jasinski, 2009).

Phosphate rock resources are generally classified into two major types based on origin and deposition (Jasinski, 2013).

- Sedimentary phosphate deposits: These are considered as higher grade deposits and account for approximately 80% of phosphate-containing rocks in the world.
- Igneous phosphate deposits: This type is usually a lower grade deposit in comparison to sedimentary.

More than 90% of the phosphate rock reserves in the world are in Morocco, China, Jordan, and the United States. China became the world's leading producer of phosphate in 2015, producing far more than any other country at 100 Million tons annually. China's phosphate production remains the same since 2014. Aside from Morocco and the Western Sahara, China holds the second-largest phosphate reserves in the world, with approximately 3.7 billion tons of phosphate (INN, 2016). U.S. phosphate output showed a slight increase from 25.3 million tons in 2014 to 27.6 million tons in 2015. Florida and North Carolina account for roughly 80 percent of phosphate rock production in the US (Cisse and Mrabet, 2004).

The phosphate ore bodies are usually found associated with other minerals (gangue minerals) such as siliceous ores, calcareous ores, and clayey ores. These minerals are usually removed during the enrichment processes of phosphate ores (Adbel-Zaher, 2008; Lehr and McClellan, 1973).

There are several approaches to enrich or beneficiate phosphate-bearing oresthat have been adopted by different companies depending on the type of the ore and the associated gangue minerals they are working with. These techniques include size reduction and screening, electrostatic separation, and froth flotation. Froth flotation is often used as a highly selective technique to separate the gangue from the phosphate minerals. Almost 60% of the phosphate production in the world comes from flotation (Sis and Chander, 2003; Hanna, 1964). The most common flotation technique used is the anionic-cationic flotation, especially when processing silicate-rich phosphate ores (Sis and Chander, 2003; Adbel-Zaher, 2008).

Tailings and wastewaters produced in phosphate industry are the main secondary sources of phosphorus, as shown in Figure 1.1, a picture of phosphate mine tailings produced in Florida. Also, it is found in municipal wastewaters in low-range concentrations (Bashan, 2004; Sorensen et al. 2015). The low-grade sources could be enriched to meet the requirements for manufacturing of phosphorus and its derivative products. Several separations and beneficiation techniques such as heavy media, calcinations, leaching, and flotation have been used for enrichment and recovery of phosphorus (Abouzeid, 2008; Issahary and Pelly, 1985; Sadeddin and Abu-Eishad, 1990; and Singh et al, 1992). Thermal processes such as calcination are mostly used for enrichment of phosphate rocks through decomposition and evaporation of impurities present in the rock. Enhancing phosphorus grade requires higher temperature (above 1000 ^{0}C) which will produce more calcined phosphate which is not suitable for manufacturing superphosphates due to slow reaction of highly calcined phosphates with acid (Freeman et al, 2014). Acidic dissolution is also used to decompose phosphate containing sources. Nitric acid and sulfuric acid are two main acids used in leaching of phosphates (Sultonov et al, 2014). One disadvantage of the acidic leaching is the formation of large amount of acidic wastes. Precipitation is also used for separation of phosphorus from wastewaters and effluents produced by phosphate industry (Seckler et al, 1996, Onstott et al, 1973).

Figure 1.1. A picture of phosphate mine tailings produced in Florida (nytimes, 2007).

In order to be more environmentally sustainable and reduce the production of wastes, extensive characterization of wastes is very important to figure out the appropriate processing method. Lower phosphorus grade and higher contents of gangue minerals such as silicates, carbonates, and clays present more technical challenges and higher processing cost.

1.2. OBJECTIVES

This work aims to investigate the potential to upgrade the phosphorus content in the tailings that are produced from a phosphorus production plant by froth flotation process. The work mostly discusses the role of reagents rather than operational parameters. The specific objectives of the current work were:

1- To investigate the effect of solids content of the flotation pulp, on the recovery of phosphate minerals and the grade of the concentrate products.

2- To investigate the effect of the pulp pH and the type of pH modifier on the overall flotation performance.

3- To compare the effect of different flotation reagent, mainly dispersants, and depressants on the flotation recovery and the grade of the concentrate products.

4- To investigate the potential to use organic-inorganic hybrid polyacrylamide polymers as quartz and slime depressants in phosphate flotation.

5- To study the effect of residence time on the flotation outcomes in both of recovery of phosphate minerals and phosphorous grade content in a concentration tank for the purpose of finding the most cost effective approach to enrich phosphate tailings.

It is anticipated that this study would contribute to the existing efforts to develop robust technologies to re-process mine wastes and other wastes produced from metal production plants. The froth flotation approach proposed in this study seems to offer a significant potential for metal enrichment in the case of phosphate mine tailings processing.

2. LITERATURE REVIEW

2.1. BENEFICIATION OF PHOSPHATE ORE

There are two major types of phosphate deposits (Gharabaghi et al. 2010): 1) sedimentary phosphate deposits and 2) igneous phosphate deposits (Zapata and Roy 2004). About 80 % of phosphate mined in the world is found in sedimentary rock. While 15-20 % comes from igneous deposits. Figure 2.1 shows the different global locations of major phosphate deposits.

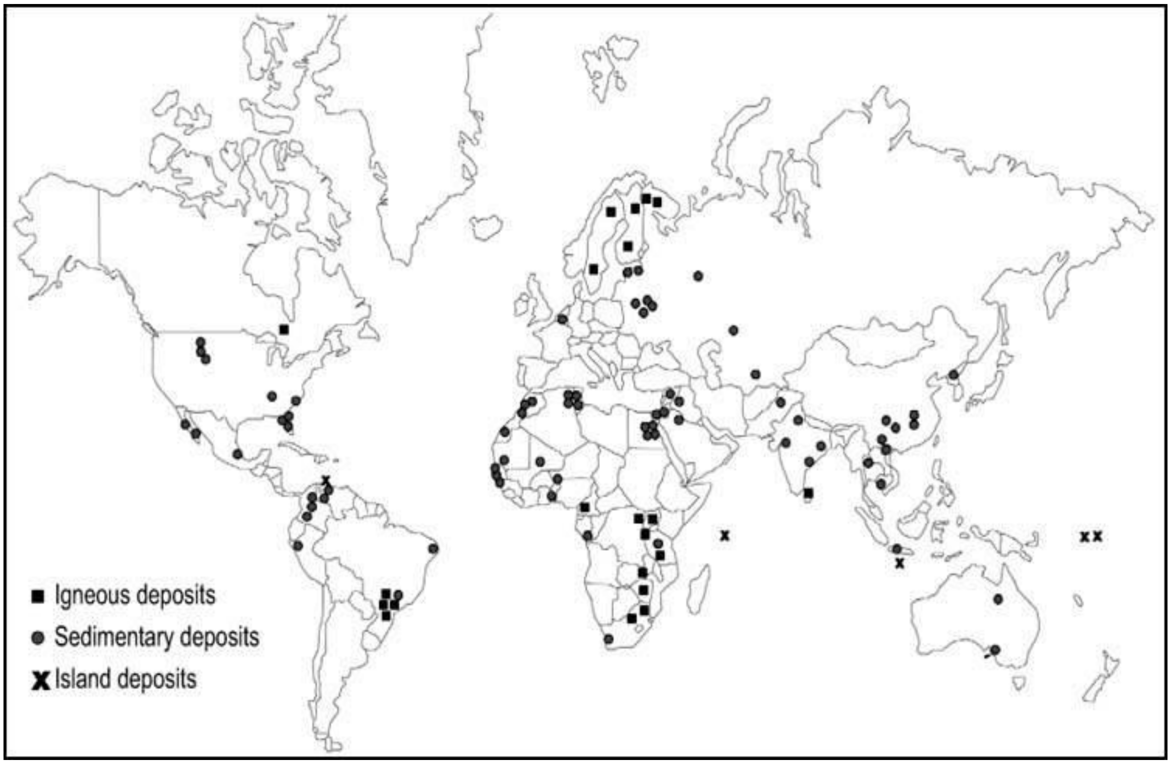


Figure 2.1. Global locations of the phosphate deposits (Emich, 1984).

In general, the largest sedimentary phosphate deposits are located in China, the Middle East, and the United States. However, the largest igneous phosphate deposits are located primarily in Brazil, Canada, and Russia (Zhang, 2013; Cisse and Mrabet, 2004).

Phosphates are inorganic salts of phosphoric acid. Figure 2.2 shows the chemical formula of phosphates. Phosphate ores are classified into three groups that depend on their phosphorus pentoxide (P_2O_5) content (Anonymous et al, 1979; Sengul et al, 2006; Zhang, 2013):

1- Low grade ores that contain approximately 12 to 16% of P_2O_5;

2- Intermediate grade ores with total P_2O_5 grade about 17–25% and;

3- High grade ores that contain up to 35% of P_2O_5.

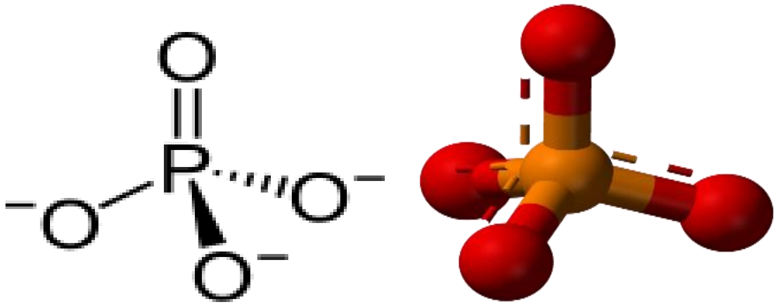


Figure2.2. Chemical formula of phosphates ($PO4^{-3}$).

There are different groups of phosphate-bearing minerals such as apatite, francolite, collophane, and dahllite (Straaten, 2002; Abu-Eishah et al., 1991). Apatite is the major group of minerals and it is mostly found in igneous and metamorphic environments.

Depending on the ionic substitution in the Apatite crystal lattice, Apatite mineral group is subdivided into Flourapatite, Chrloroaptite and Hydroxyapatite (McClellan, 1980).

Phosphate minerals are usually found in association with other minerals. These minerals are known as gangue minerals (Kawatra and Carlson, 2013; Snow, 1979.). And they usually have no economic value. The most common gangue minerals found in phosphate-bearing ores are clay minerals, such as montmorillonite, palygorskite, and kaolinite; quartz; dolomite; and calcite. Dolomite content is very critical and it is always desirable to minimize it because of its low solubility that may cause blinding or blogging of filters (Zhang, 2013). As reported by many phosphate-producing companies, the Dolomite content should be less than 1.0% (McClellan, 1980; El-Shall et al, 2003).

Mineral, chemical and elemental characterizations of phosphates are of crucial importance in order to figure out the appropriate beneficiation approach (Zhang, 2013 and Abouzeid, 2008). There are several analytical techniques that are currently used for mineral characterization in general. Among these techniques are: optical microscopy, cathode luminescence (CL) microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), inductively coupled plasma optical emission spectrometry (ICP-OES) and mineral liberation analysis (MLA).

In the current study, tailing samples and flotation products will be characterized using XRD, SEM, and MLA. XRD is a fundamental spectroscopic technique that has been used widely to reveal both qualitative and quantitative information about the mineral matter. Scanning electron microscopy (SEM) (Evans et al, 1992) images can give detailed information about the topography of mineral surfaces. Moreover, the new microanalysis techniques such as EDS or WDS offer a big advantage for SEM since it can give information about the chemical composition and elemental distribution of the sample (Abouzeid, 2008). Figure 2.3 shows an SEM-EDS micrograph of a phosphate mineral sample and its elemental composition. MLA is a scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectrometers and computer software that automates microscope operation and data acquisition. MLA gives valuable information about mineral associations within the sample, elemental distributions (assay); grain size distribution, degree of liberation and grain locking which is critical to optimize consequent separation processes.

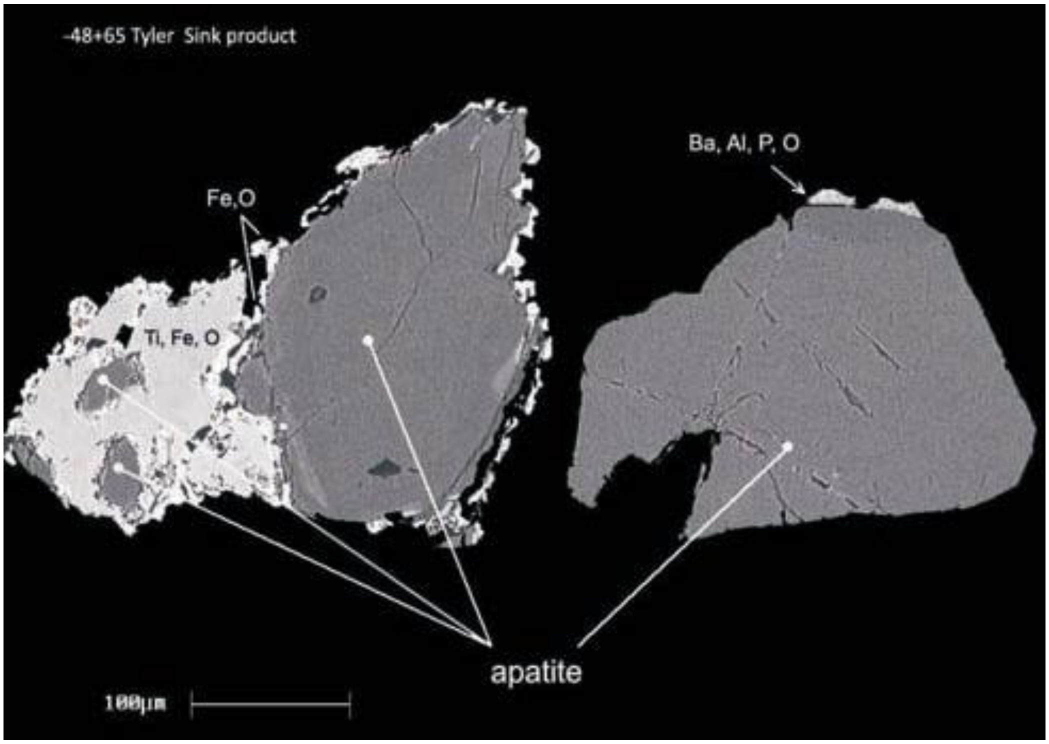


Figure 2.3. A sample SEM micrograph of phosphate minerals (Zhang, 2010).

As mentioned earlier, phosphate minerals are found associated with other minerals in the ore body. These minerals are called gangue minerals. To upgrades the phosphate minerals, several beneficiation techniques can be applied depending on the mineral and elemental composition of the ore body. Size reduction and screening, electrostatic separation, magnetic separation, chemical dissolution of carbonates, and froth flotation are commonly used in phosphate ore beneficiation (Abouzeid, 2008). However, most of these techniques did not give the required upgrading efficiency due to the similarity of the physico-chemical characteristics of the constituent minerals. Therefore, froth flotation process is the most selective technique that can achieve the best separation efficiency compared to other physical separation methods (Abouzeid, 2009).

2.2. FROTH FLOTATION FUNDAMENTALS

The froth flotation of mineral ores is one of the most selective methods for minerals separation. Froth flotation utilizes the differences in wettabilities of minerals in a three-phase system that consists of solids, gas, and water. In this process, hydrophobic particles attach to air bubbles to form a froth which is basically solid-air aggregates that also contain entrapped water. Hydrophilic minerals tend to stay in the pulp as waste products or flotation tailings (Snow, 1979 and Wang and Scanlon, 1983). Figure 2.4 represents the concept of the ore flotation process.

There are three closely correlating components in any flotation system (Sis and Chander, 2003): chemical, mechanical, and operational. The chemical component includes the selection of appropriate flotation reagents such as collectors, frothers, depressants, and activators as well as the adjustment of the pH of the flotation pulp. The mechanical component includes cell design, agitation speed (mixing), air flow rate, cell bank configuration, and cell bank control. Finally, the operational part which includes feed flow rate, particle size distribution of the feed, pulp density, and temperature (Klimpel, 1995).

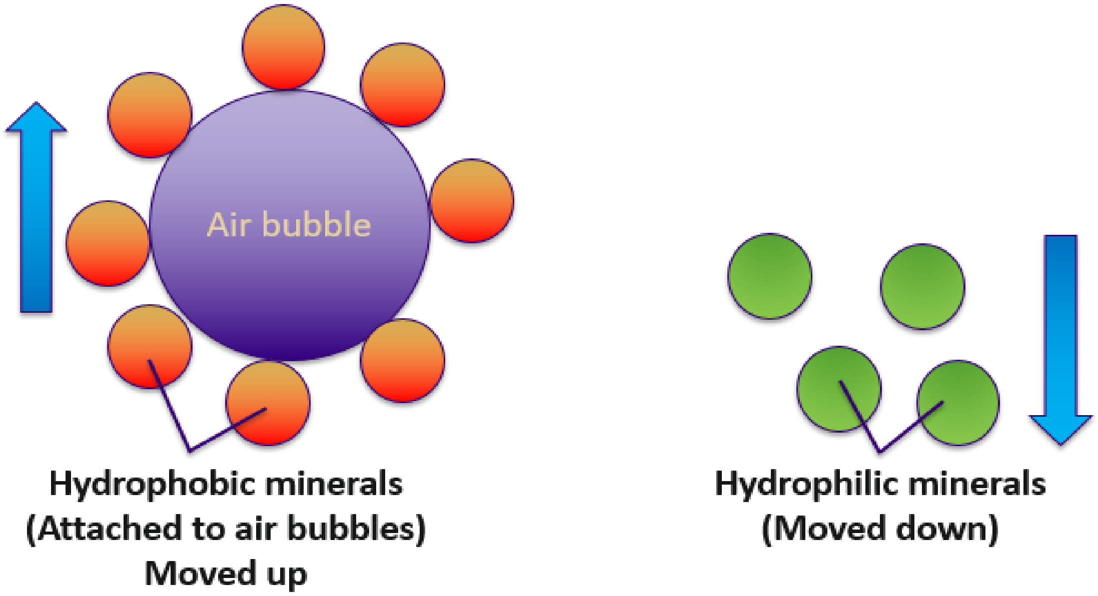


Figure 2.4. Illustration of the froth flotation process.

Mechanical flotation cells are usually implemented in industrial scale flotation operations due to their relatively high recovery rates. In mechanical flotation cells, the slurry is mixed and conditioned with chemical reagents by using an impeller before air is introduced to the pulp through an air inlet. In the pulp zone, the mineral-bubble aggregates move up to surface as a froth and then collect in the concentrate zone. Hydrophilic gangue particles move down in the tailing zone (Bakker et al, 2010). Figure 2.5 shows a general schematics of a mechanical flotation cell.

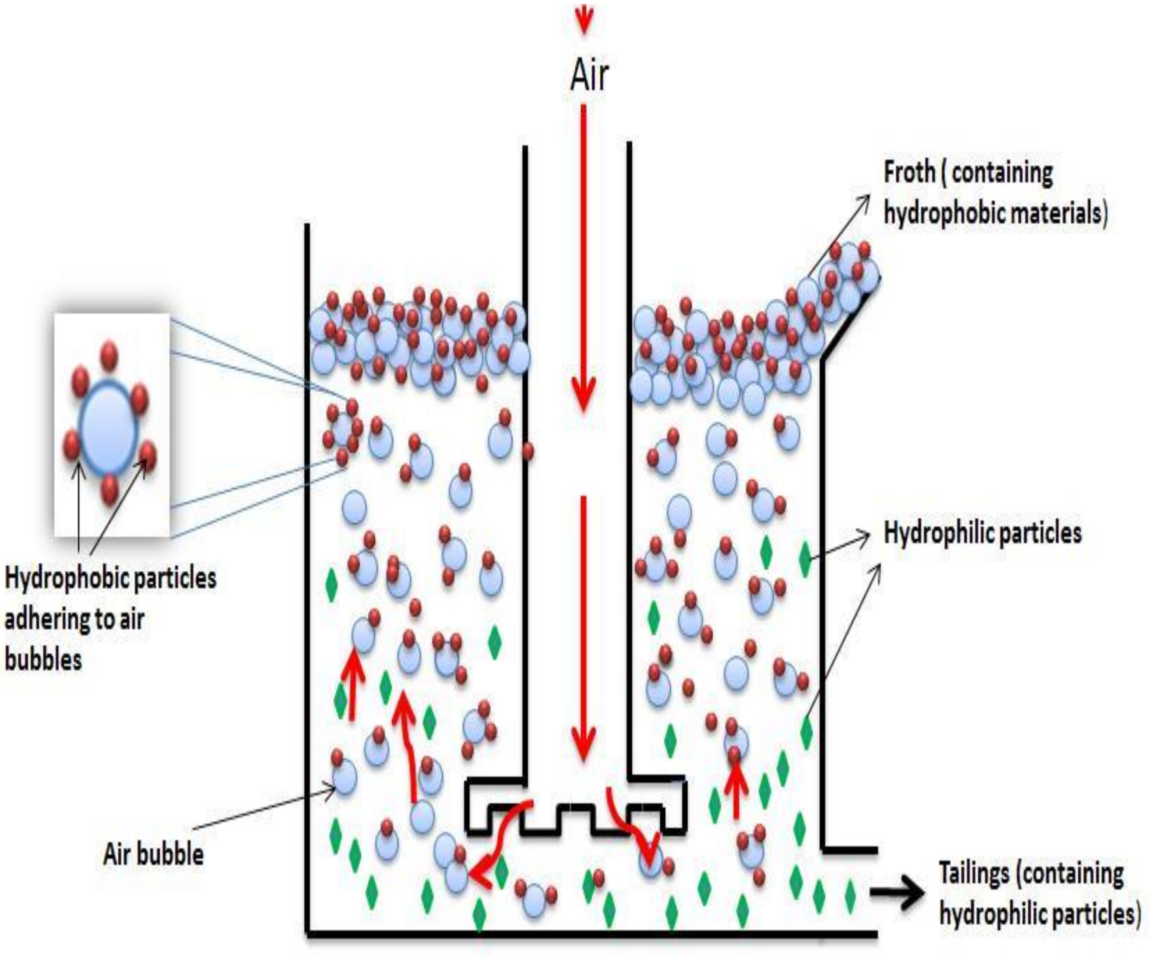


Figure 2.5. General schematics of mechanical flotation cells (Molatlhegi and Alagha, 2016).

2.3. PHOSPHATE FLOTATION TECHNOLOGY

Flotation of phosphate ores is a technically challenging process because of the variations in composition of phosphate-bearing minerals and because of the similar physicochemical properties of phosphate minerals and their associated gangue minerals (Houot, 1982). Therefore, to obtain a desirable enrichment ratio, fundamental understanding and interpretation of the different sub-processes involved in this process is a key factor. Many efforts have been devoted to deal with the difficulties present in this process in order to develop robust processes to improve the phosphate recovery and enrichment efficiency (Al-Thyabat et al, 2011; Yehia et al, 1990; and Efrosyni, 2006). Currently, there are two major processes have been adopted by the phosphate industry to enrich phosphate minerals through froth flotation: direct flotation process and reverse flotation process.

2.3.1. Direct Flotation.

In the direct froth flotation process, the value mineral is rendered hydrophobic, is floated and collected in the froth layer while the gangue minerals are depressed or remain dispersed in the pulp. The direct flotation process is preferred for phosphate enrichment because of its relatively higher separation efficiency (Zhang, 2013).

Direct flotation is generally used to process phosphate ores that are rich in silica and dolomite minerals. This technique was successfully applied to float feeds containing 15–18% P_2O_5, 4–6% MgO, and 20-25% SiO_2. The grade of P_2O_5 increased up to ~ 30-34% in concentrate products at > 80% recovery while the MgO content was reduced to < 2 % (Wang 2005).

Direct flotation process of phosphates has been used by Florida’s phosphate mines for a long time. In general, fatty acids and sodium silicates are used as collectors and dispersants, respectively. Figure 2.6 shows the flow diagram of the flotation plant at the IMC Four Corners mine in Florida. Initially, phosphates are floated with fine silicates at pH 9-9.5 (Kawatra, 2014). In order to upgrade the phosphate concentrate to a salable product, initial concentrates are further cleaned in the second stage of the flotation process where fine silica is floated by reverse flotation using amine-based collectors at pH ranges from 6.5 -8.

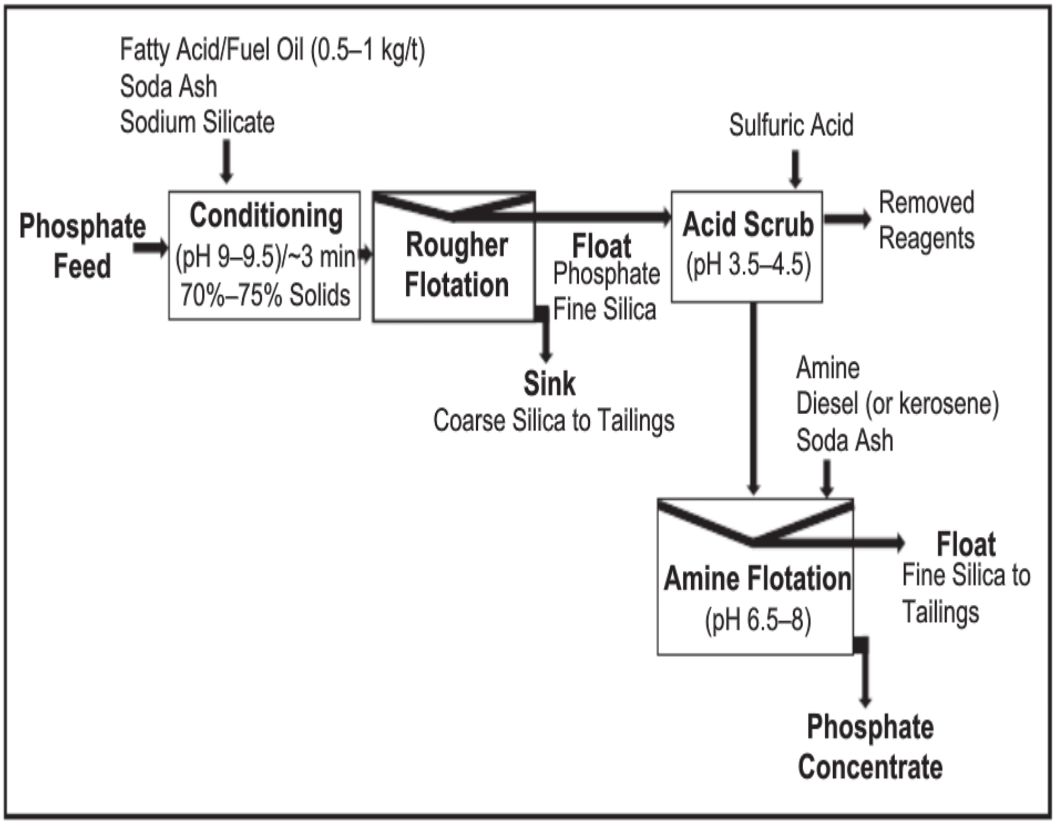


Figure 2.6. Simplified process flow diagram of direct flotation process at IMC Four Corners Mine-Florida (Kawatra, 2014).

2.3.2. Reverse Flotation. In reverse flotation process, the value mineral is depressed using specially designed chemical depressants while the gangue minerals are floated. Therefore, in the reverse flotation of phosphates, the phosphate minerals remain in the pulp and are collected as tailings. Reverse flotation of phosphates is mostly used in processing carbonate-rich ores (Zhang, 2013).

Reverse flotation can be applied for phosphate ores that have high carbonate and low silica content. The grade of P_2O_5 in the tailing products depends on silicate content in the feed. When silicate content is lower in the feed, the P_2O_5 grade is higher in the tailings, and vice versa. The recovery of P_2O_5 is usually more than 80% (Wang 2005).

Figure 2.7 shows the flow diagram of reverse flotation process of phosphate in Florida phosphate mines (Kawatra, 2014). Amines and their derivatives are usually used as collectors to float the fine silica at neutral pH followed by dewatering and conditioning the phosphate tailings with fatty acid/fuel oil collectors at pH 9. After conditioning, the phosphate minerals are floated from coarse silica.

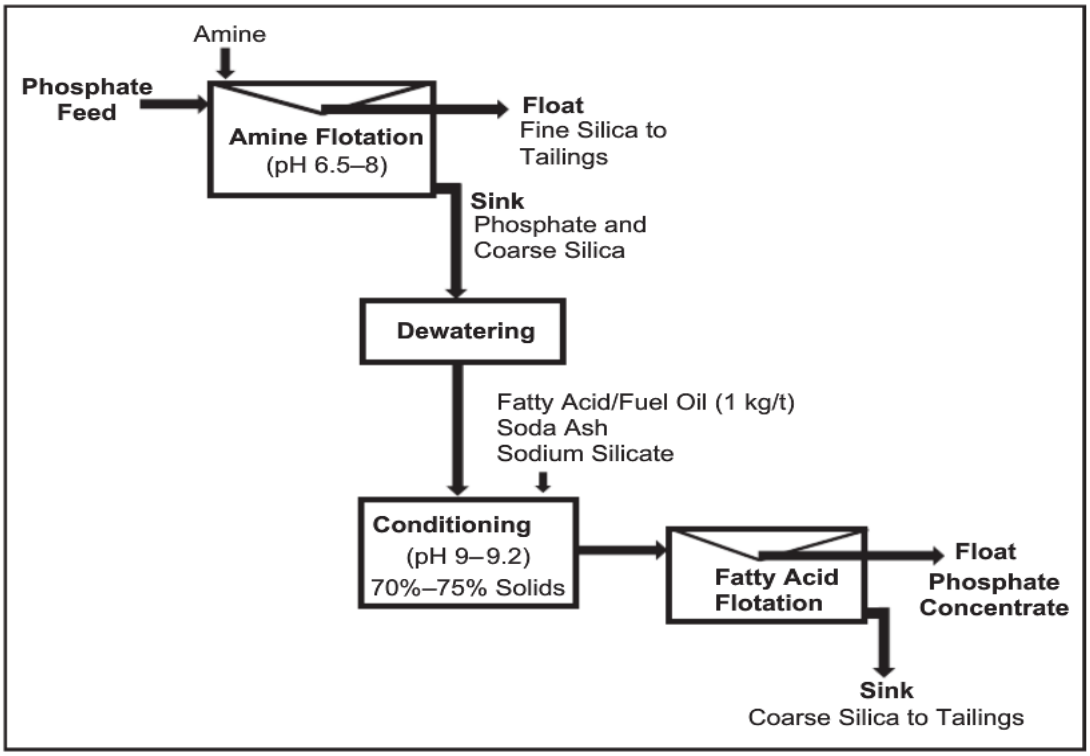


Figure 2.7. Simplified process flow diagram of reverse flotation process at IMC Four Corners mine-Florida (Kawatra, 2014).

2.4. REAGENTS USED IN THE FLOTATION OF PHOSPHATE MINERALS

Aside from all the factors that affect the flotation performance, the reagents used in the flotation process play a major role in controlling the physical and chemical interactions in the flotation pulp. Reagents can alter the surface properties of different minerals at the three interfaces: solid/liquid, solid-air, and liquid/air. Various types of collectors, depressants, dispersants, frothers, etc. have been tested to address the challenges that are present and to solve the problems encountered during phosphate flotation operations (Sis and Chander, 2003).

2.4.1. Collectors. "Fatty Acids" are often used as collectors in the direct flotation process of phosphates. Fatty acids are carboxylic acids with long aliphatic chains that have even number of carbon atoms such as oleic acid, linoleic acid, and capric acid (Huang, 2014). Usually, fatty acids collectors are used for phosphate minerals that contain almost 20-25% of silicates in the feed because they possess negatively charged carboxylate groups (at basic pH) that can repel the silicate minerals. In this case, fatty acids would selectively adsorb on phosphate particles rather than silicate particles (Zhang, 2002). Anionic collectors are generally used in direct flotation process. On the other hand, cationic and amphoteric collectors, such as amines, are used in the reverse flotation process to float silicates and calcite minerals. Aminopripionic acid is used to float carbonates. Table 2.1 shows the different types of collectors used in phosphate flotation operations.

2.4.2. Depressants. Depressants are most often used to depress either the gangue minerals in direct flotation process or the phosphate minerals in the reverse flotation (Pearse, 2005). The selection of depressants depends on the collector that is used as well as the type of flotation process being implemented (Sis and Chander, 2003). Table 2.2 shows some examples of different depressants used in phosphate flotation.

Table 2.1. Collectors used in phosphate ores flotation. (Sis and Chander, 2003).

Floated mineral	Ionic property	Collector
Phosphate minerals	Anionic	Oleic acid
		Fatty acids
		Disodium dodecyl phosphate
	Cationic	Armac T amine
		Tallow amine acetate
Carbonates	Anionic	Fatty acids
		Sulfonated fatty acids
	Amphoteric	Aminopripionic acid
		Carboxyethyl imidazoline
Silica	Cationic	Amines

Table 2.2. Depressants used in phosphate ores flotation. (Sis and Chander, 2003).

Depressed mineral	Depressant
Phosphate minerals	Aluminum sulfate and sodium
	Sodium carbonate
	Phosphoric acid
	Starch
Carbonates	Sodium silicate
	Hydrofluoric acid
	Polysaccharides

Table 2.2. Depressants used in phosphate ores flotation. (Sis and Chander, 2003) “cont.”.

Silica	Sodium silicate

2.4.3. Frothers. Frothers are heteropolar surface-active compounds made up of a polar group and a non-polar hydrocarbon tail and are capable of adsorbing at air-water interface (Molatlhegi and Alagha, 2016). Frothers are generally used to disperse air into fine bubbles and to increase the froth stability. The quality of the froth can be effected by the type and the concentration of the frother used. Frothers that are commonly used in phosphate flotation include methyl isobutyl carbinol (MIBC), pine oil, and polyglycol types.

2.4.4. Dispersants. Dispersing are surface charge modifiers. The function of the dispersant in any direct froth flotation process is to disperse the unwanted minerals, increase their hydrophilicity and depress their flotation. In the phosphate flotation process, the sodium silicate (Na_2SiO_3) is commonly used to disperse the silicate minerals.

2.4.5. Recent Research Work on Flotation Reagents. Several studies have been conducted to investigate the mechanism of reagent adsorption on mineral surfaces. Various techniques have been employed such as zeta potential, contact angle measurements, quartz crystal microbalance with dissipation, etc. These techniques can provide both qualitative and quantitative information about the change of the surface properties of mineral particles as a result of changing the pulp pH, reagent type, reagent dosage, etc.

Hernainz, et al. (2004) studied the direct flotation of phosphate ores with oleic acid as a collector using Denver D-12 with 1.25 L flotation cell. Results indicated that when the pulp pH was increased to 11 and the particle size of the feed was under 200/230 mesh, phosphate minerals were able to float from carbonate minerals at a shorter residence time.

Qi, et al. (1992) reported that using sodium oleate as a collector enhanced apatite flotation from iron oxides in the presence of sodium silicate as an iron depressant. Qi, et al. (1992) used a pH range from 7.5 to 11 and ore particle size of less than 100 microns. Results indicated that the P_2O_5 content of the ore was enriched to 38.6% at 81% recovery. The recovery of Fe_2O_3 in the concentrate products was approximately 2.7% as reported in the study.

Qinbo et al. (2015) studied the synergistic effect of using mixed collectors on the direct flotation of phosphate ores. Qinbo el al (2015) used three different collectors: oleic acid (HOl), linoleic acid (LA) and linolenic acid (LNA) at pH 9.5. Results indicated that the P_2O_5 recovery increased to 88.44% at a specific mass ratio of the mixed collectors: 54 wt. % HOl, 36 wt. % LA and 10 wt. % LNA. Furthermore, the researchers studied the effect of pH on the mixed collector adsorption on apatite. The reasonable pH for the mixed collector regime used was determined to be ~ 9.5 confirmed by both contact angle measurements and results obtained from flotation experiments.

2.4.6. Applications of Hybrid Polymers in Mineral Processing. Polymers have received considerable attention due to their tunability and the opportunity that they provide to enhance the flotation performance at a lower cost (Chen et al, 2003; Huang, 2014; Liu et al, 2000).

Polyacrylamide-based polymers are widely used in ore flotation processes as multifunctional reagents. Depending on the integrated functional groups, polyacrylamides and their derivatives are being used as collectors, depressants, activators or modifiers. Hybrid polyacrylamide polymer (Hy-PAM) was successfully applied in fine coal flotation to enhance the combustible recovery and reduce the ash contents of coal concentrates

(Molatlhegi and Alagha, 2016). Hy-PAM is an organic-inorganic hybrid polymer which consists of polyacrylamide organic chains grafted on nano-size Al(OH)3 inorganic particles (Figure 2.8).

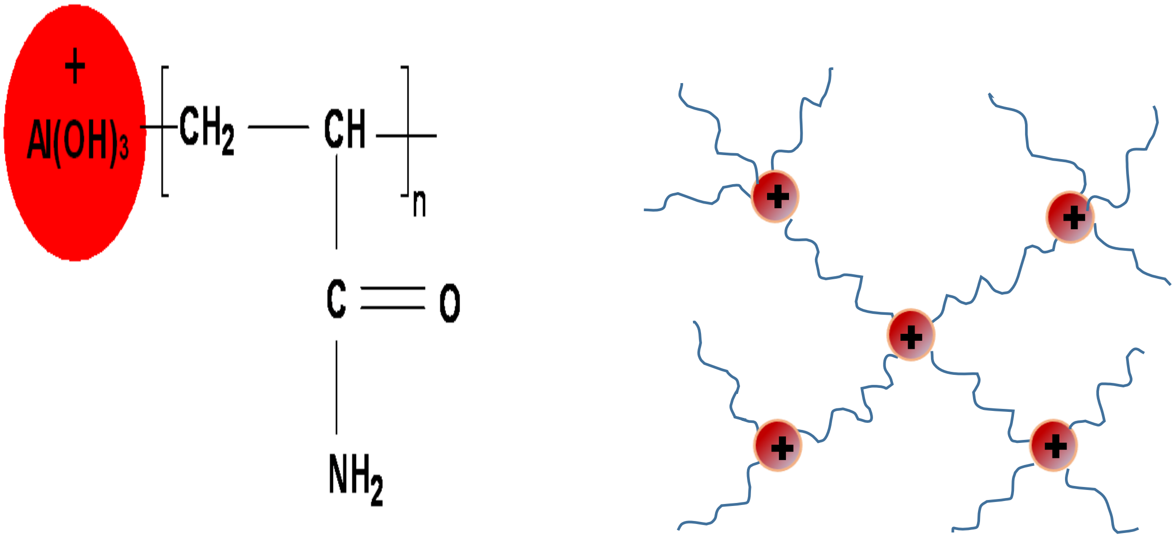


Figure 2.8. Structure of hybrid polyacrylamide polymer (Hy-PAM) used in this study (Molatlhegi and Alagha, 2016).

Hy-PAM was anticipated to adsorb on the surface of slime-forming minerals in coal and depress their flotation and mechanical entrainment to the froth layer (Molatlhegi and Alagha, 2016). Alagha et al., 2012, reported the capability of Hy-PAM polymers to adsorb on the surface of ultrafine silica particles, flocculate them and enhanced their sedimentation in solid-liquid separation processes.

The success of Hy-PAM in the previously mentioned research work along with its unique structural characteristics have brought the motivation to use this polymer in this study as a quartz depressant in the flotation of phosphate-bearing tailing samples.

3. MATERIALS AND METHODS

3.1. MATERIALS

3.1.1. Mineral Samples and Flotation Reagents. Representative tailings samples were provided from a phosphate production plant located in North America. All chemicals used in the flotation experiments were purchased from Fisher Scientific Company, USA. This Includes: sodium oleate which was used as a collector, methyl isobutyl carbinol (MIBC) which was used as a frother, sodium silicate which was used as a dispersant, and sodium carbonate (Na_2CO_3) which was used to adjust the pH of the flotation pulp. In addition, pure apatite and quartz used in the zeta potential experiments were purchased from Ward's Science Company, USA.

3.1.2. Polymer Preparation and Characterization. The hybrid polyacrylamide Hy-PAM was synthesized in-house according to a procedure described elsewhere (Molatlhegi and Alagha, 2016). Hy-PAM was synthesized by the polymerization of acrylamide monomers in an $Al(OH)_3$ colloidal suspension using $(NH_4)_2S_2O_8NaHSO_3$ as a redox initiator. The aluminum content by weight in Hy-PAM polymer was measured using the PerkinElmer inductively coupled plasma system 2000 DV instrument equipped with optical emission spectrophotometer and WinLab32 for ICP version software for measurement of aluminum metal at a wavelength of 396.153nm.

The RF power used was 1500 watts, plasma flow was 15L/min, auxiliary flow was kept at 0.2L/min, and nebulizer flow was kept at 0.8L/min. Pump rate was kept at 2 ml/min. The calibration curve plotted using 7 different concentrations of solutions diluted in 1% HNO_3 (0 mg/L, 0.1 mg/L, 0.5 mg/L, 1 mg/L, 5 mg/L, 10 mg/L, and 25 mg/L) made by using high purity standards purchased from Fisher-Scientific. The correlation coefficient was 0.9999. Sample measurements were repeated 3 times. The sample contains 0.14 wt. % aluminum.

The molecular weight of Hy-PAM was determined by static light scattering (SLS) using Zetasizer Nano (Malvern Instruments Ltd., USA). Polymer stock solution of 10, 15 and 20 ppm were prepared and then filtrated by a Millex-AA Filter Unit with a pore size of 20 microns before the SLS measurements. Before measurements were conducted, calibration was made by using pure (>99.5%) toluene. SLS measures the intensities of the scattered light of the polymer sample and automatically calculates the molecular weight.

The molecular weight of Hy-PAM was determined to be approximately 6 million Dalton. The polymeric structural transitions (compositions and functional groups) of Hy-PAM was further confirmed by FTIR analysis. FTIR spectra showed a primary amine group $-NH_2$ (N-H stretch) peak observed at ~ 3495 cm^{-1}. Methylene ($-CH_2$) group was observed at 2925-2850 cm^{-1}.

The spectrum also exhibited primary amides $–CONH_2$ (NH_2 deformation and C=O stretch) at about 1650 cm^{-1}. C–N stretching appeared at about 1550 cm^{-1}. The $Al\ (OH)_3$ absorbance peaks were observed at wavenumbers of 460 cm^{-1}, 750-800 cm^{-1} assigned to $Al\text{-}O_6$ and -OH, respectively. Freshly prepared 5000 mg/L (ppm) stock solutions of Hy-PAM polymers in deionized water were used in all the flotation experiments.

3.2. METHODOLOGY

3.2.1. Sieves Analysis. Screens of 5, 10, 35, 60, 120, 230, 325, and 400 US mesh were used for sieving. Sieves were selected to furnish information required by specification. The sieves are usually nested in order of decreasing size from the top to the bottom and the sample is placed on the top sieve. Sieves are shaken in a mechanical shaker for the time determined by ASTM C136-14 protocols to provide complete separation for the sieve shaker being used.

3.2.2. X-Ray Diffraction (XRD). X-ray powder diffraction (XRD) was conducted on the flotation feed and products to investigate the crystallinity minerals associated with the samples. The intensities of the XRD pattern of an individual mineral are known to be proportional to the concentrations of the different minerals present. Therefore, by measuring the intensities of patterns, information about the relative amounts of each mineral phase can be obtained. The XRD spectra were obtained by scanning in the 2θ range of 5–90°. A Phillips XRD apparatus with Cu-Kα radiation was used to obtain the X-ray diffraction patterns.

3.2.3. Scanning Electron Microscope (SEM). Scanning electron micrographs were obtained using a SEM instrument combined with energy dispersive X-ray spectroscopy (EDS). Qualitative and semi-quantitative chemical analysis in the EDS mode were performed to support the SEM characterization. All samples were prepared to appropriate size to fit the specimen chamber. Samples were coated with a 2-3 nm gold layer and mounted rigidly on specimen stub. The SEM equipment used in this study is shown in (Figure 3.1).

3.2.4. Mineral Liberation Analysis (MLA). MLA data was obtained using the XBSE method where the acquired backscattered electron (BSE) image is used to differentiate the mineral phases based on the gray level as the gray level intensity varies, dependent on the phase composition. The acquired X-ray spectrum obtained from each phase was compared to the X-ray mineral database to qualitatively determine mineral phases and the surface area data for each mineral was used for quantitative determination of the minerals identified. MLA results were provided by the Center for Advanced Mineral & Metallurgical Processing (CAMP) in Montana Tech of the University of Montana, USA.

Figure 3.1. Picture of scanning electron microscope used in this study (Hitachi S4700) at Missouri S&T, Rolla, MO.

3.2.5. Zeta Potential Measurements. Zeta potential measurement is a critical step to figure out the appropriate reagents that can give the best selectivity. The aim of any direct froth flotation process is that the mineral of interest should selectively attach to air bubbles while leaving the gangue minerals in the pulp. Measuring the surface charge of different minerals in the flotation pulp at varies pH is used to determines the optimum pH range for a specific mineral/reagent system. For that reason, isoelectric graphs of pure apatite and quartz were obtained at a pH range of 2-12. Zeta potential measurements were performed on pure mineral samples (apatite and quartz) before and after mixing with different flotation reagents (collector, dispersant, and depressant). The measured zeta values revealed important fundamental information about the interactions of both apatite and quartz with sodium oleate, sodium silicate and Hy-PAM that were used as a collector, a dispersant, and a depressant, respectively. Zeta potential measurements were performed using a Zetasizer Nano ZS instrument (Malvern Instruments, Inc., Westborough, MA, USA) (Figure 3.2).

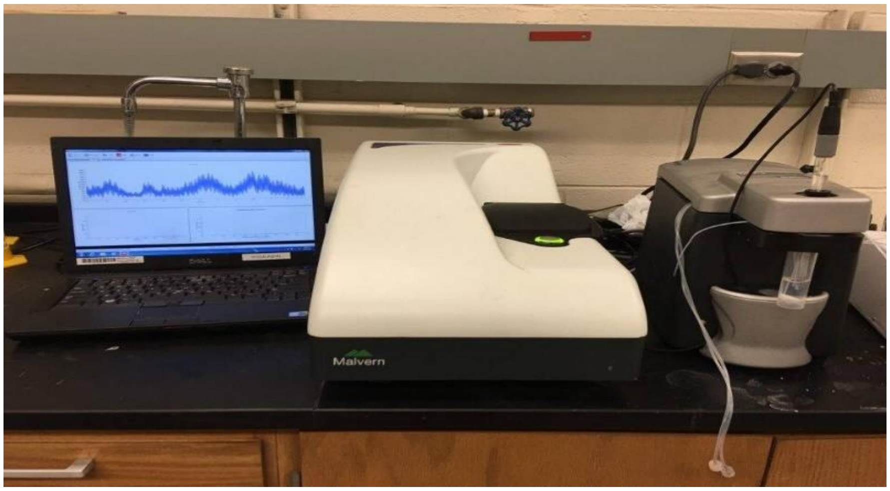


Figure 3.2. Picture of Zetasizer Nano ZS Malvern used for zeta potential measurements.

All measurements were obtained at room temperature. Samples were prepared at 0.1 wt. % of mineral in a 0.1M KCl background solution. The prepared mineral suspension was agitated using an IKA RW20 mechanical stirrer for 45 min at a constant agitation rate of 250 rpm. The suspensions were allowed to settle for overnight. The supernatant liquid was considered for all the zeta potential measurements. In all experiments, the solution pH was adjusted using either 1M HCl or 1M NaOH as needed. Figure 3.3 shows the general protocol used in sample preparation for zeta potential measurements.

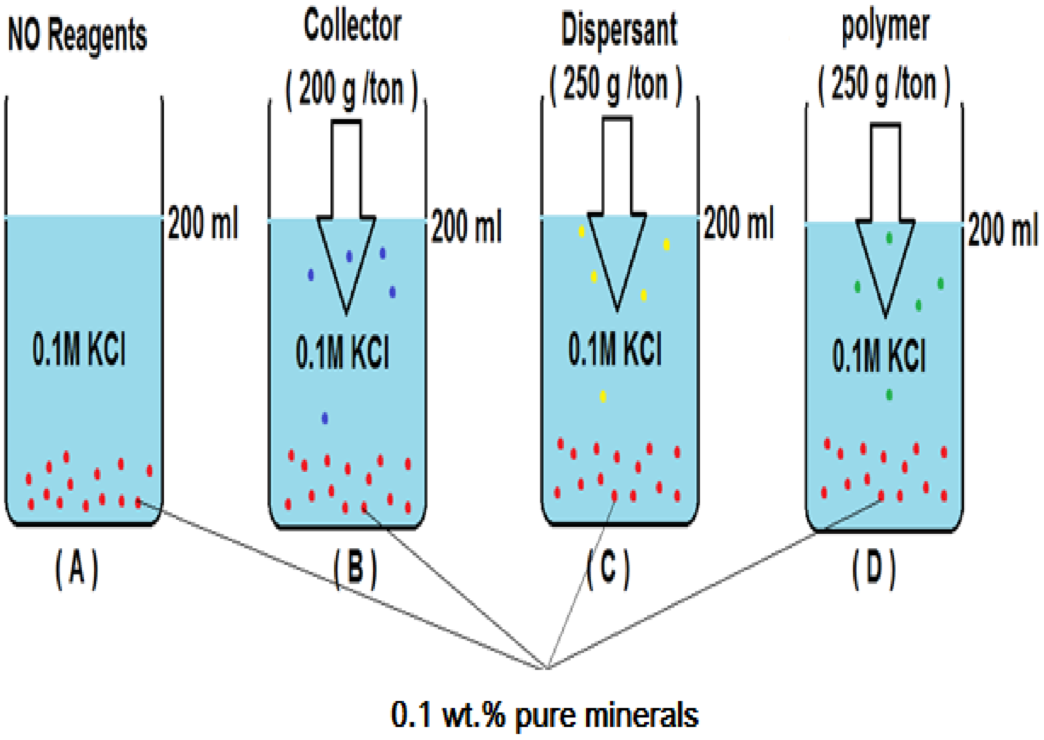


Figure 3.3. Schematics of the general protocol used in sample preparation for zeta potential measurements.

3.3. FLOTATION EXPERIMENTS

As mentioned earlier, this research work investigated the effect of different reagents on the flotation outcome of phosphate plant tailings. The different reagents used in the flotation experiments are presented in (Table 3.1). Batch flotation tests were conducted under various experimental conditions as presented in (Table 3.2).

Table 3.1. The reagents were used in the flotation experiments.

Reagent type	**Reagent name**	**Concentration of stock solutions (mg/L)**
Collector	Sodium Oleate	$10*10^4$
Dispersant	Sodium Silicate	$40*10^4$
Depressant	Al(OH)3-PAM (Hy-PAM)	$5*10^3$

The different experimental conditions studied include: 1) addition of a dispersant at a fixed dosage, 2) changing the solid contents of the pulp in the presence of dispersant, 3) changing the pulp pH in the presence of dispersant, 4) changing the dosage of Hy-PAM depressant, 5) changing the froth collection time and 6) dual addition of Hy-PAM/dispersant system. Flotation outcome was evaluated in terms of the recovery and the grade of the concentrate products obtained. The grade of the concentrate products was presented in terms of elemental phosphorus content (% P). All calculations were made based on XRD analysis.

Table 3.2. Different conditions tested in the flotation of phosphate tailings.

Experiment	Collector (g/ton)	Dispersant (g/ton)	Frother (g/ton)	Polymer (g/ton)	Time of floatation	%solid	pH modifier
Baseline (Frother and collector only)	200	0	63.5	0	10 min	60%	Na_2CO_3
					6 min		
Effect of pH with dispersant	200	250	63.5	0	10 min	60%	NaOH
							Neutral pH ~ (6.87)
Effect of solid contents with dispersant	200	250	63.5	0	10 min	40%	Na_2CO_3
						20%	
Effect of residence time with dispersant	200	250	63.5	0	10 min	60%	Na_2CO_3
					6 min		
Effect of polymer dosage	200	0	63.5	150	10 min	60%	Na_2CO_3
				200			
				250			
				300			
Effect of residence time with polymer	200	0	63.5	250	10 min	60%	Na_2CO_3
					6 min		
Effect of dual use of polymer/ dispersant system at a specific ratio.	200	250	63.5	250	10 min	60%	Na_2CO_3

3.3.1. Preparation of the Flotation Feed. Tailing samples were mixed using a mechanical agitator for 24 hours to ensure sample homogeneity. Representative samples were then collected, dried and sieved according to ASTM C136-14 protocol. In general, the optimum feed size in direct flotation of phosphate minerals reported in literature is between 45 to 125 micrometers. Thus, the flotation feed size used throughout this study was the – 125 + 45 size fraction obtained from sieving.

3.3.2. Experiments. Flotation tests were conducted using a Denver D-12 flotation machine (Figure 3.4) equipped with a 1-liter tank and a 3.88-inch diameter impeller.

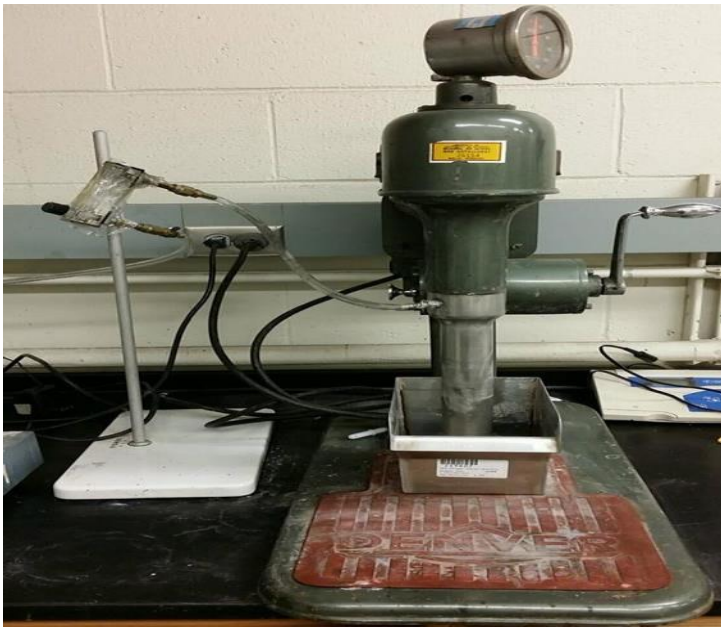


Figure 3.4. Picture of the Denver cell used in the bench-scale flotation experiments.

The slurry was conditioned at 60 wt. % solid in tap water unless otherwise stated. Either Na_2CO_3 or NaOH was used to adjust the pH to ~9. The rotor speed of the flotation machine was set at 1,200 RPM in all flotation experiments. The pulp was conditioned for

5 min prior to any reagent addition. Collector (i.e., Sodium Oleate) was added at a predetermined dosage as shown in (Table 3.2), and the suspension was conditioned for an additional 3 min. The dispersant (sodium silicate), Hy-PAM or the mixed reagents (Hy-PAM/$NaSiO_4$) were added after the slurry was conditioned with the collector and the pulp was agitated for another 3 min. The frothing agent (MIBC) was added thereafter. The pulp was further conditioned for 2 min before the air was introduced. The froth products were collected at different time intervals as shown in (Table 3.2). The concentrate fractions were dried in the oven for overnight at 80°C. After drying, the phosphate minerals contents of the concentrates were determined using XRD analysis. A flow chart of the procedure used in flotation experiments is shown in Figure (3.5).

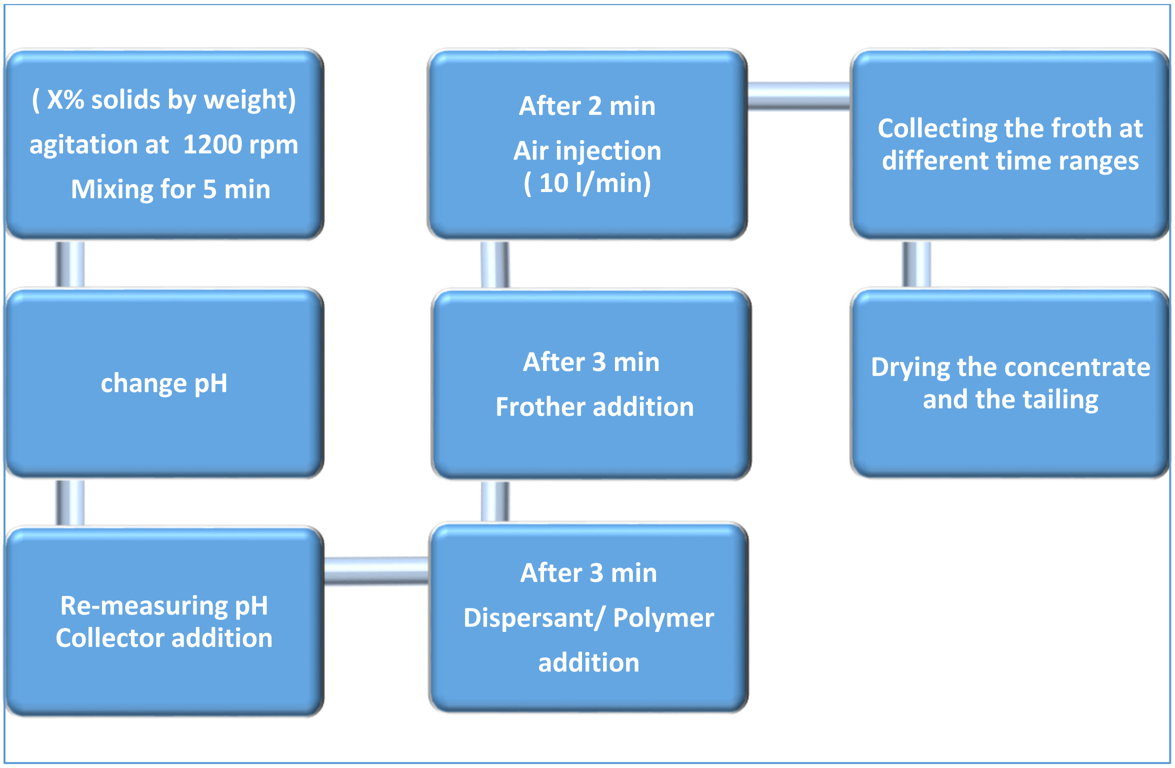


Figure 3.5. Flowchart shows the procedure used in the bench-scale flotation experiments.

The phosphate minerals recovery was calculated using dry weights of concentrates and tailing products using Equation 3.1 where C and T are dry weights of the concentrate and tailing products respectively; c and t are % of phosphate minerals in concentrates and tailings.

Recovery = $Cc/ (Cc+Tt) *100\%$......... (EQ3.1).

4. RESULT AND DISCUSSION

4.1. CHARACTERIZATION OF TAILINGS SAMPLES (FLOTATION FEED)

4.1.1. XRD Analysis. X-ray powder diffraction (XRD) was conducted on the flotation feed to identify the different minerals, as well as other possible materials present in the samples. There are two major sources of error in XRD analysis: sample preparation and instrumental errors. To reduce common errors associated with mineral identification and analysis such as orientation, specimen transparency granularity, and microabsorption, the sample size was reduced and the surface roughness of the samples was diminished by mortar and pestle before conducting XRD analysis. As shown in Figure 4.1 two major minerals were detected: phosphates and quartz. The semiquantitative result demonstrated that phosphate minerals constituent was approximately 70 percent of the sample and the rest was quartz. About 85 percent of phosphate minerals were flourapatite phases.

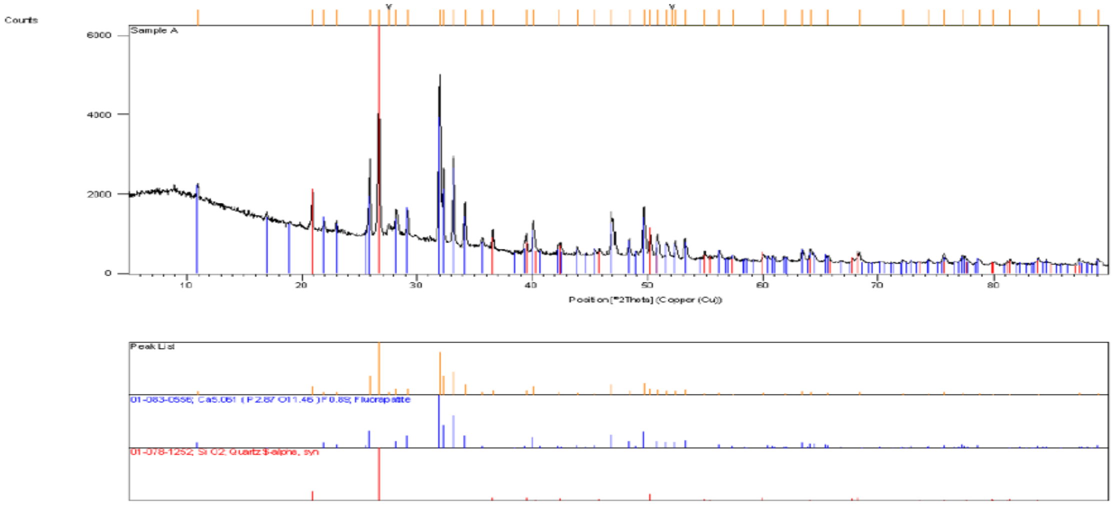


Figure 4.1. Identification and semiquantitative analysis of the crystalline phases of the tailing samples.

The distribution of phosphate minerals in different size fractions of the whole sample according to XRD is shown in Figure 4.2 and Table 4.1. For the whole sample, the majority of phosphate minerals were in the size range of 63-250 microns.

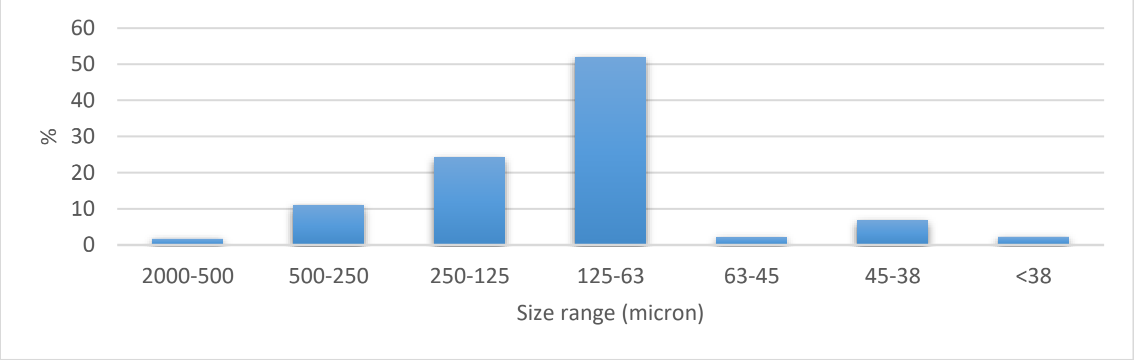


Figure 4.2. Distribution of phosphate minerals in different size fractions of the tailing samples.

Table 4.1. Distribution of phosphate minerals in different size fraction of tailing sample.

Size range (mesh)	Size range (micron)	Phosphate minerals (%)
35-60	500-250	11
60-120	250-125	24.3
120-230	125-63	52
230-325	63-45	2.1
325-400	45-38	6.8
<400	<38	2.2

4.1.2. Scanning Electron Microscopy (SEM). The SEM micrographs of the sample studied in this work are shown in (Figure 4.3). SEM images revealed that approximately 80% of the mineral grains were smaller than 100 microns, which are consistent with the results obtained from sieve analysis. Figure 4.3 also shows some particle agglomeration in the sample.

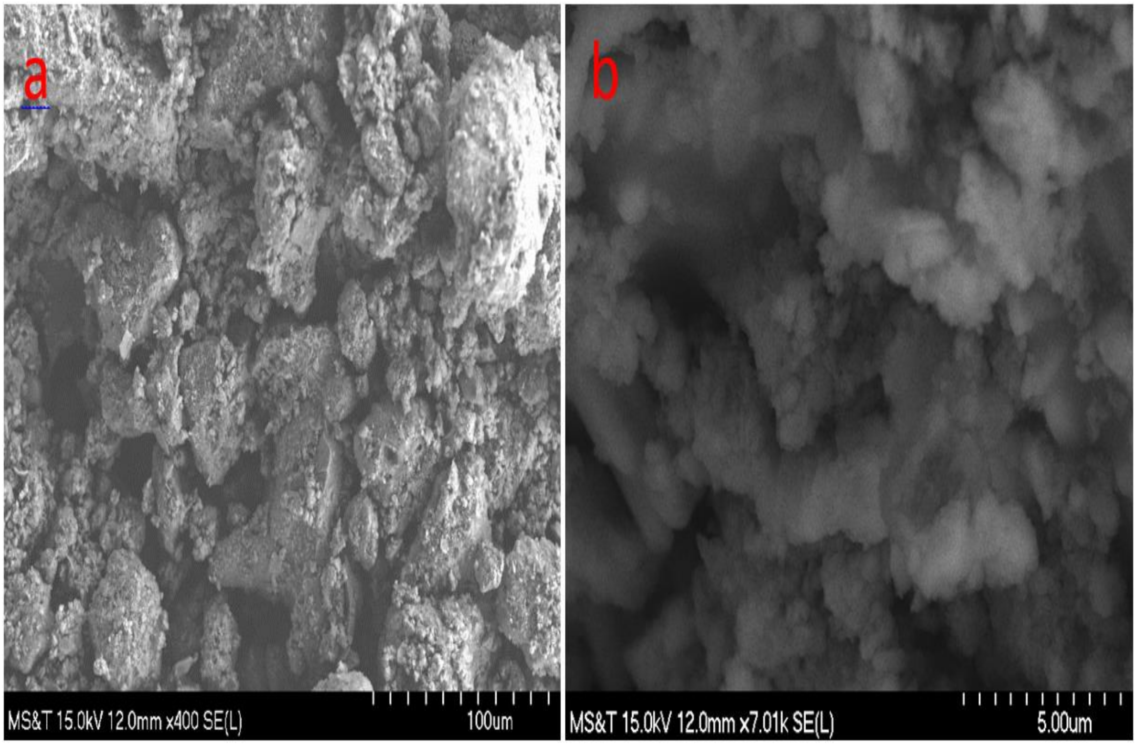


Figure 4.3. SEM micrographs of tailing samples at different scales, (a) 100 µm (b) 5 µm.

Figure 4.4 shows EDS micrographs. These EDS micrographs revealed qualitative information about the chemical composition of the sample as well as the distribution of major elements including O, P, Ca and Si that were present in the sample. Semiquantitative EDS microanalysis is presented in (Table 4.2). The mass fractions or weight percentages of the elements present in the sample were calculated. The samples were flattened and polished. Samples also needed to be homogeneous and ‘bulky’ not porous or thin films on a substrate, otherwise the matrix correction procedures would not work correctly.

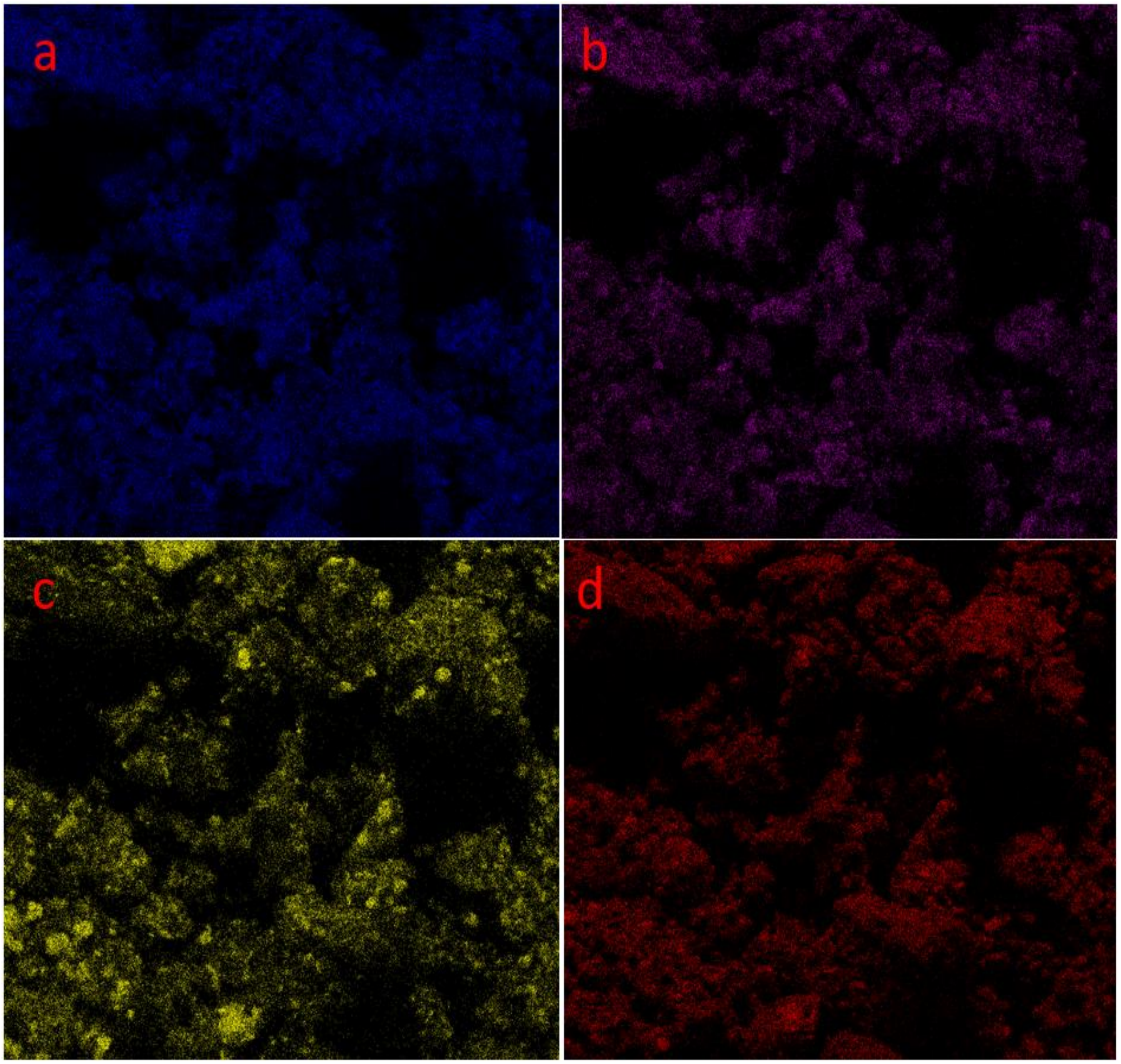


Figure 4.4. SEM-EDS images of tailings samples showing distribution of (a) Calcium (b) Phosphorous (c) Silicon (d) Oxygen.

Table 4.2. Elemental analysis (wt. %) of tailing sample calculated by SEM.

Element	Wt.%	At%	Element	Wt.%	At%
O	30.66	48.73	**Cl**	0.15	0.1
F	10.03	12.4	**Cd**	0.42	0.09
Na	4.85	4.95	**K**	1.14	0.68
Mg	1.43	1.38	**Ca**	18.73	10.98
As	0.36	0.11	**Ti**	0.2	0.1
Al	3.29	2.86	**V**	0.34	0.16
Si	11.53	8.24	**Cr**	0.36	0.16
P	7.63	5.16	**Fe**	1.9	0.8
Hg	0	0	**Zn**	5.37	1.93
S	1.61	1.18	**Total**	100	100

As revealed by the semiquantitative EDS analysis shown in Table 4.2 major elements in the sample in Wt. % and At. % were O, F, Ca, P, Si and Na, which demonstrates that apatite (Flourapatite) and quartz are the primary minerals in the sample. The result achieved by EDS analysis may deviate from the result achieved by other precise elemental detection methods since the EDS analysis was performed on selected point locations on the sample.

4.1.3. Particle Size Distribution. The composite particle size distributions as determined by mineral liberation analysis (MLA) is shown in (Figure 4.5). The P_{80} of the composite particle size distributions for the -50 mesh material was approximately 100 microns for the flotation feed.

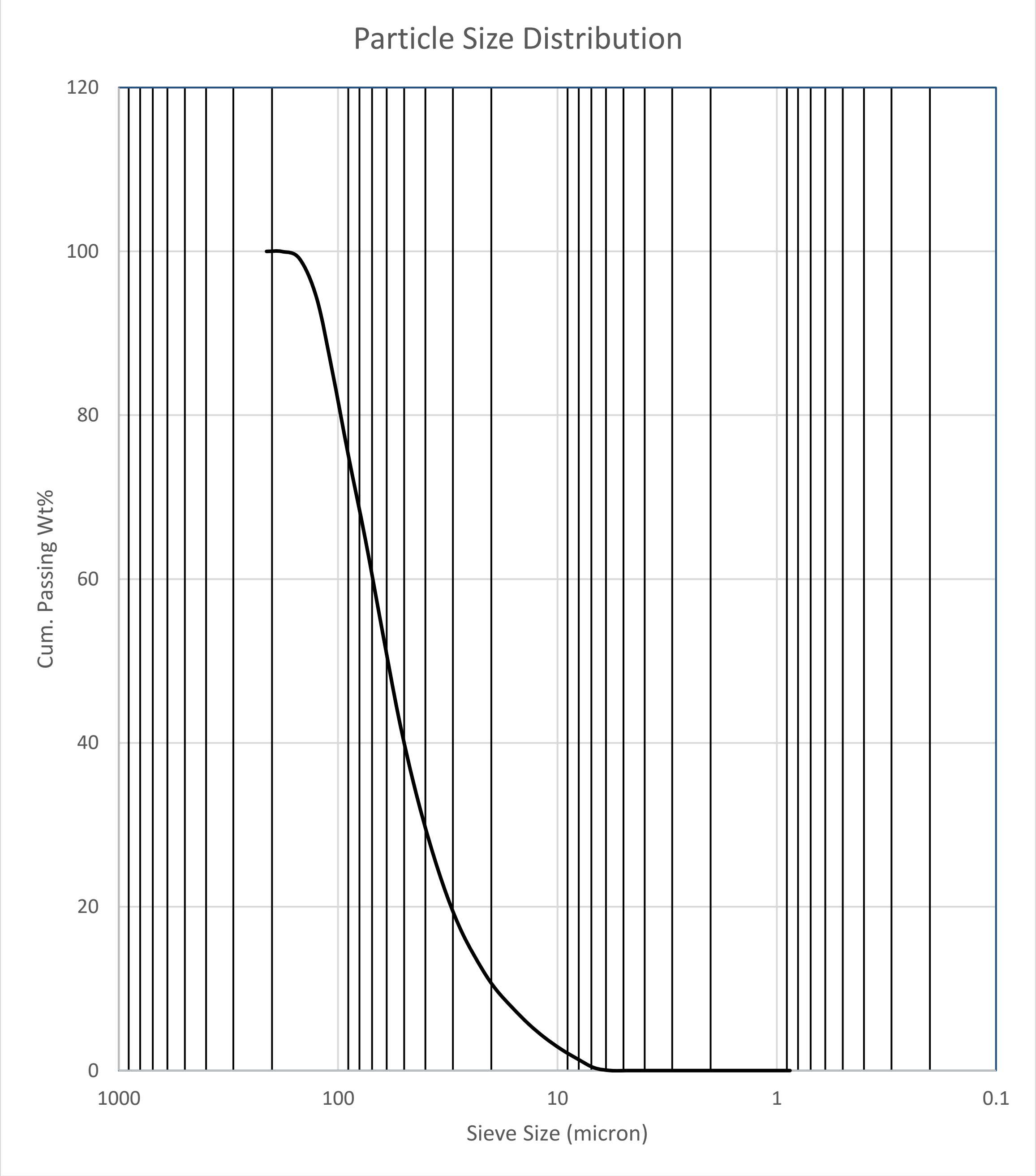


Figure 4.5. Particle size distributions of the flotation feed.

4.1.4. Modal Mineralogy. In the Figure 4.6 shows the distribution of minerals in different size fractions of the tailing samples. The primary phosphorus-containing phases were apatite and the apatite-fluorite mix. Apatite and the mixed apatite phase (apatite-fluorite mix) were found in different amounts in the tailing sample at ~50% Apatite and ~ 36% Flourapatite.

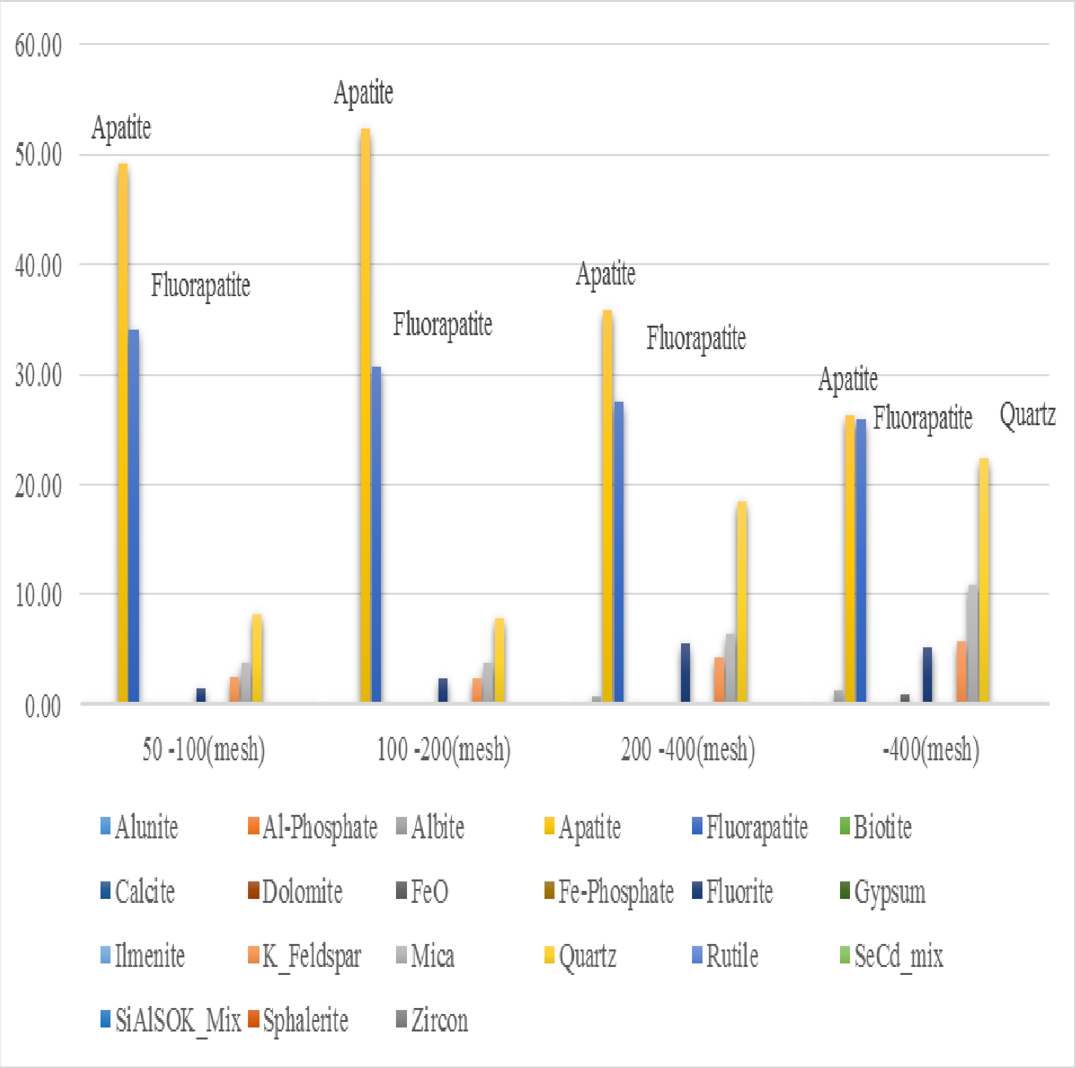


Figure 4.6. Distribution of minerals in different size fractions of the tailing samples.

The flotation feed particles presented complex textures with many of the phases displaying variable chemistry making phase assignment difficult. The primary phosphorus-containing phases were apatite and the apatite-fluorite mix. Apatite and the mixed apatite phase (apatite-fluorite mix) were found in equivalent amounts in the flotation feed at 36% each. Quartz was found to be 12%, mica (K-Al silicate) was nearly 8%, fluorite was 3.5% and K-Feldspar was just over 3%. The complete listing of the phases is shown in Table 4.3.

Table 4.3. The complete list of all minerals in the flotation feed and their wt. %.

Mineral	Formula	Feed
Apatite_Fluorite_mix	$(Ca_5(PO_4)_3F)\ (CaF_2)$	36.1
Apatite	$Ca_5(PO_4)_3F$	35.8
Quartz	SiO_2	12.1
Mica	$KAl_2(AlSi_3O_{10})\ (OH)_2$	7.94
Fluorite	CaF_2	3.49
K_Feldspar	$KAlSi_3O_8$	3.25
Albite	$NaAlSi_3O_8$	0.47
SiAlSOK_Mix	$(KAl_3(SO_4)_2(OH)_6)\ (SiO_2)$	0.30
FeO	Fe_2O_3	0.17
Calcite	$CaCO_3$	0.12
Dolomite	$CaMg(CO_3)_2$	0.09
Rutile	TiO_2	0.05

Table 4.3. The complete list of all minerals in the flotation feed and their wt. % “cont.”.

Ilmenite	$FeTiO_3$	0.02
Zircon	$ZrSiO_4$	0.02

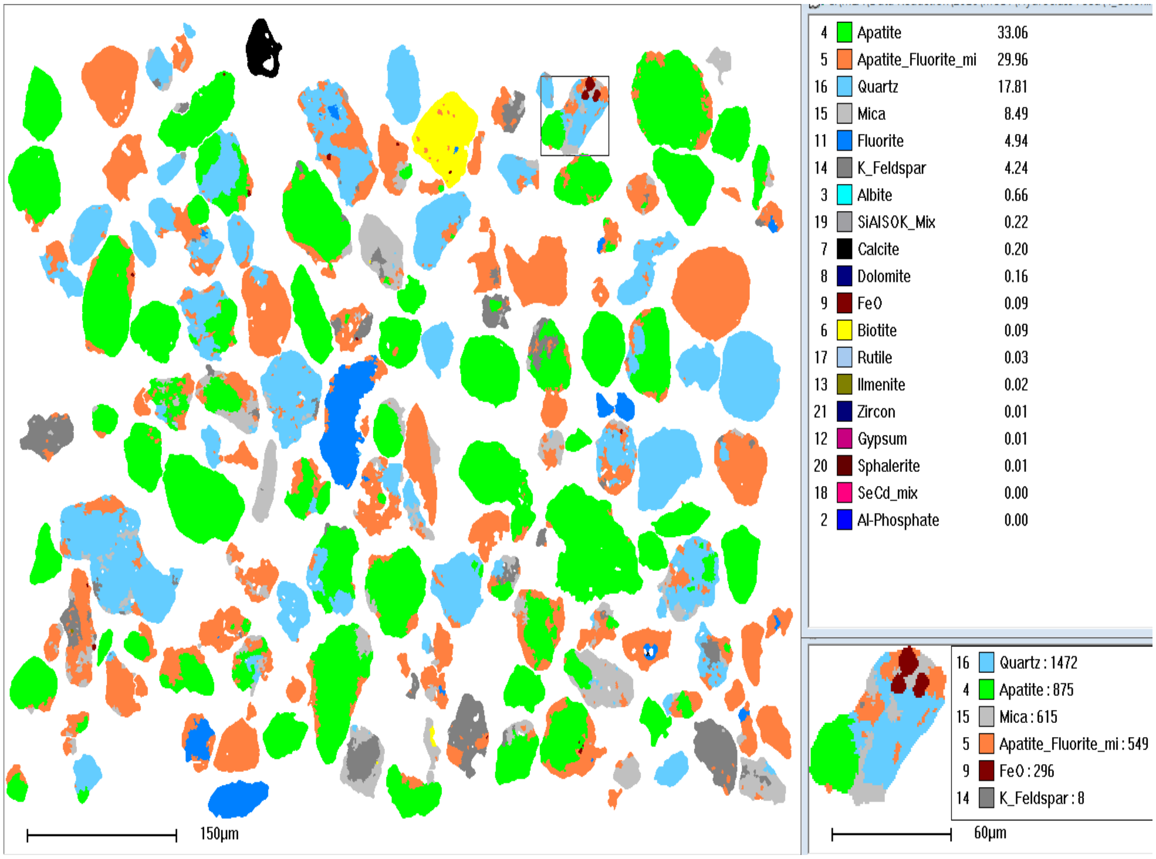
4.1.5. Elemental Distribution. Apatite was the primary phosphorus-containing phase in the feed, and it accounted for 53% of the total phosphorus content according to MLA with the balance being contained in the mixed apatite phase (Table 4.4).

Table 4.4. Phosphate-bearing minerals in the flotation feed.

Mineral	Feed
Apatite	53.4 %
Apatite-Fluorite mix	46.6%
Total	100 %

4.1.6. MLA Images. The classified false color MLA image in Figure 4.7 highlights a quartz/apatite particle with FeO inclusions. The FeO inclusions are the brightest phase in the quartz/apatite particle in the back-scattered electron (BSE) image in (Figure 4.8).

4.1.7. Mineral Liberation. Apatite was slightly better liberated than the mixed apatite/fluorite phase. The liberation for apatite by sieve fraction showed a decrease in liberation with a decrease in particle size, which is unusual, but observation of the MLA false color image (Figure 4.7) indicates that attached mixed phases were more prevalent as particle size decreased and likely the cause of this result. Liberation of the mixed apatite/fluorite phase was not clear, but it seemed to be more successful with the coarser particles.



4	🟩	Apatite	33.06
5	🟧	Apatite_Fluorite_mi	29.96
16	🟦	Quartz	17.81
15	⬜	Mica	8.49
11	🟦	Fluorite	4.94
14	⬛	K_Feldspar	4.24
3	🟦	Albite	0.66
19	⬜	SiAlSOK_Mix	0.22
7	⬛	Calcite	0.20
8	🟦	Dolomite	0.16
9	🟥	FeO	0.09
6	🟨	Biotite	0.09
17	🟦	Rutile	0.03
13	🟫	Ilmenite	0.02
21	🟦	Zircon	0.01
12	🟪	Gypsum	0.01
20	🟫	Sphalerite	0.01
18	🟥	SeCd_mix	0.00
2	🟦	Al-Phosphate	0.00

16 Quartz : 1472
4 Apatite : 875
15 Mica : 615
5 Apatite_Fluorite_mi : 549
9 FeO : 296
14 K_Feldspar : 8

Figure 4.7. Classified MLA image of flotation feed (200 X 400 mesh). Particle inset units are in pixels and concentration.

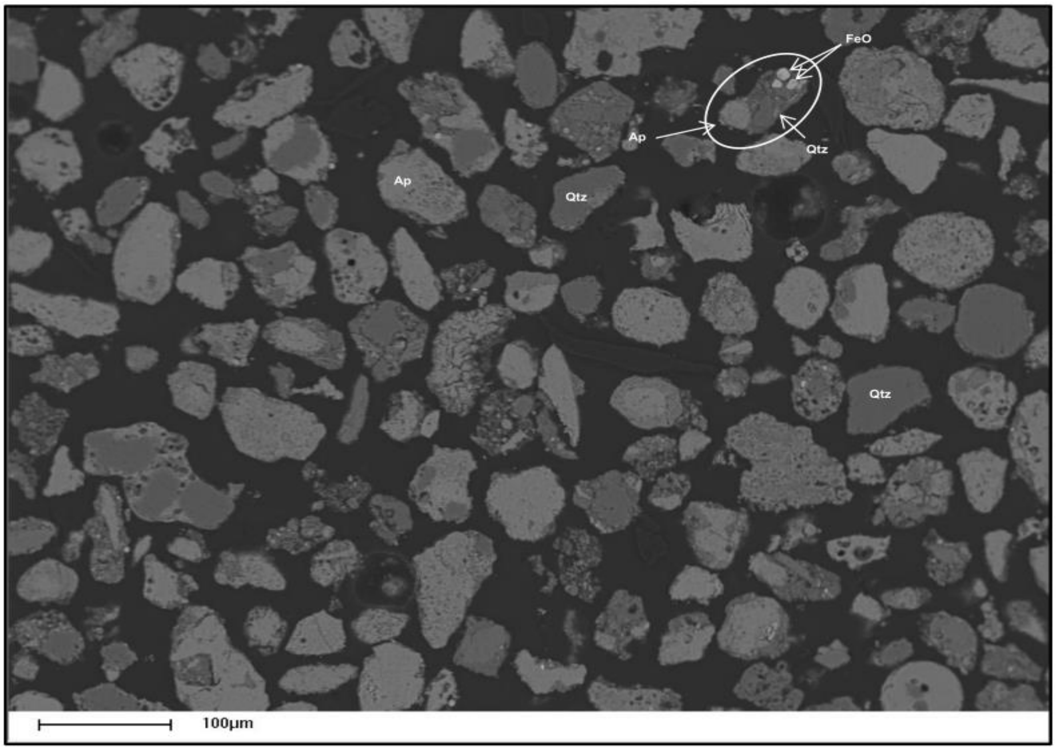


Figure 4.8. BSE image of flotation feed (200 X 400 mesh).

4.2. ZETA POTENTIAL MEASUREMENTS

Zeta potential measurements of apatite and quartz were conducted, separately, to fundamentally explore and compare the surface properties and electrical characteristics (surface charge) of mineral suspensions as well as to identify the interaction mode between the mineral and different reagents. Figure 4.9 shows the change of the surface charge (as indicated by the sign and magnitudes of zeta values) of apatite and quartz dispersions over the pH range of 2-12. The isoelectric points of apatite and quartz were at pH 4.9 and 2.8, respectively. As shown in (Figure 4.9), at natural pH of the flotation feed (pH ~ 7) the measured zeta potential values of apatite and quartz were very close to each other (~ 3 mV). The optimum pulp pH in direct flotation of phosphate minerals that is reported in literature is between 9 and 11. At that pH range, the zeta potential values of apatite and quartz were -20 and -37 mV, respectively. This difference in the electrical characteristics at that pH range makes it possible to selectively alter the surface properties of either mineral through the addition of an appropriate reagent. For example, a negatively charged reagent will preferentially adsorb on the surface of apatite particles since they are less negative while a positively charged reagent will preferentially adsorb on the surface of quartz particles due to electrostatic attractive forces that will lead to partial charge neutralization.

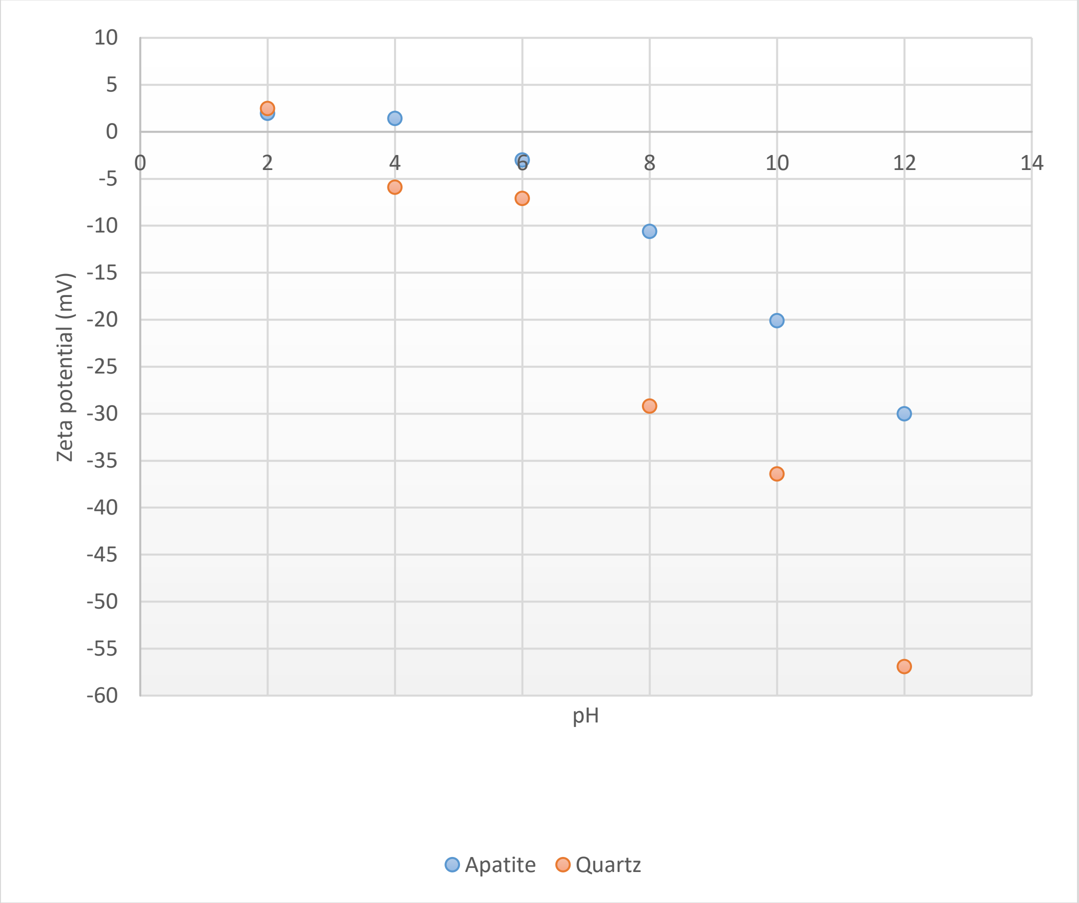


Figure 4.9. Zeta potential of pure apatite and quartz dispersions as a function of pH.

Figures 4.10 (A and B) shows the zeta potential values of quartz and apatite suspension before and after mixing with different reagents at pH 9 which will be considered the pH of the pulp in all flotation experiments unless otherwise stated. As indicated from the change of zeta values after reagent adsorption, the interaction of sodium oleate (collector) with apatite was stronger as compared to quartz. The zeta value of apatite increased from -15 mV before the addition of the collector to -3 mV (Figure 4.10-A), while it barely changed when quartz was mixed with collector. This indicates that the collector would preferentially adsorb on the surface of apatite rather than the surface of quartz. On the other hand, the interaction of quartz with polymer was stronger in comparison with apatite. As shown in Figure 4.10-B, the zeta value of quartz increased from -33 mV to -15 mV after mixing with Hy-PAM. In the case of apatite, the zeta value slightly increased when mixed with Hy-PAM polymer. This observation suggests that the polymer would preferentially adsorb on the surface of quartz and depress it. A conceptual view of the hypothesized role of the polymer is depicted in Figure 4.11. The polymer consists of positively charged Al(OH)3 colloidal particles on which organic polyacrylamide chains are grafted. The positively charged Al(OH)3 are anticipated to adsorb on the surface of quartz particles via electrostatic attraction mechanism which results in consequent charge neutralization as indicated by the increase of the zeta potential value of quartz dispersions. The charge neutralization allows the suspended quartz particle to reach close proximity so the polyacrylamide arms can flocculate them via bridging mechanism and thus depress their flotation. The change of zeta potential values of both apatite and quartz dispersions after mixing with the dispersant were quite interesting. As shown in Figure 4.10 (A and B) the dispersant adsorbed on the surface of both apatite and quartz, however, it seems that its interaction with apatite was stronger as indicated by the large shift of the zeta value (toward a more negative value). For that reason, when designing flotation experiments, the collector was added prior to dispersant addition.

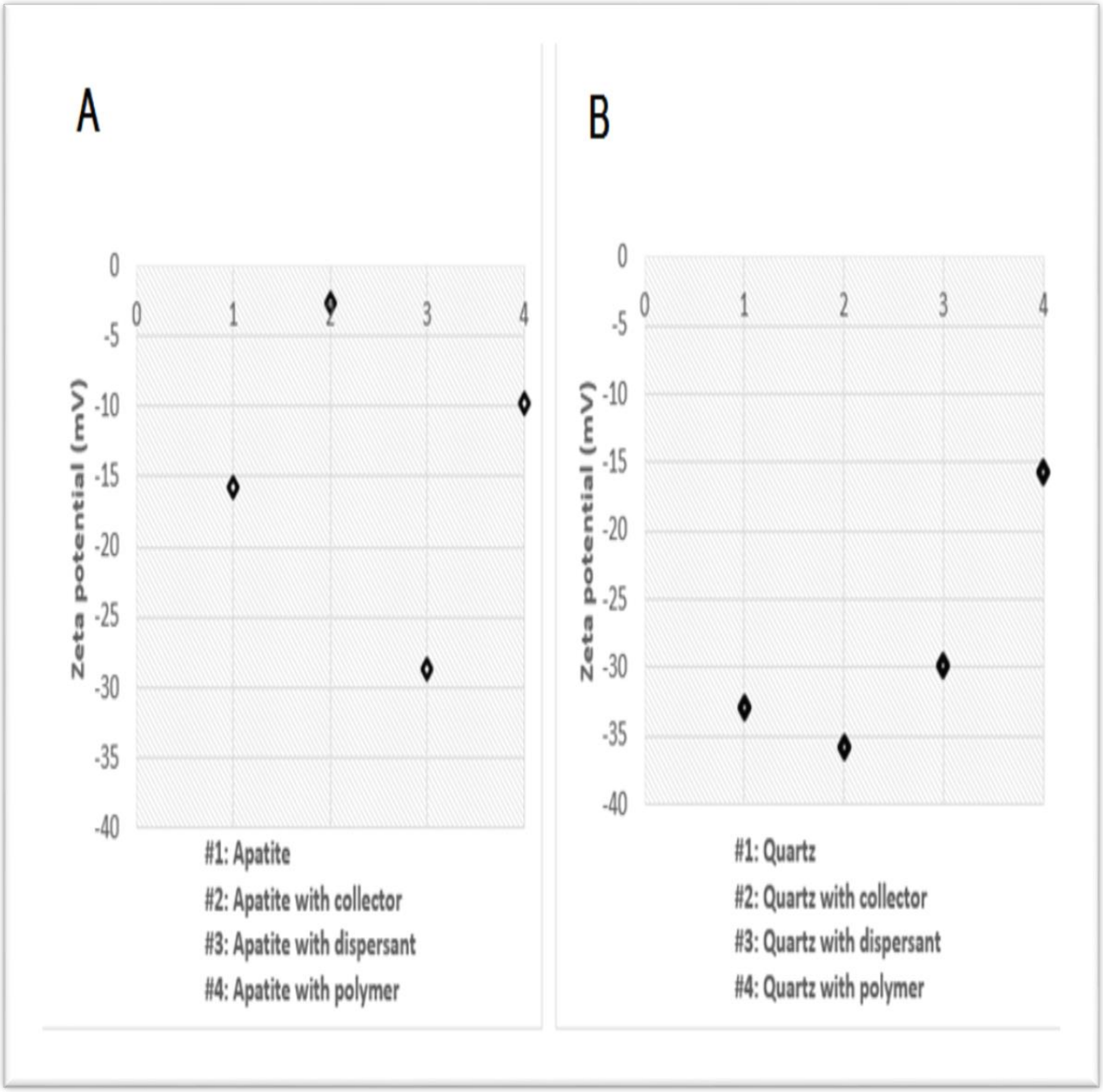


Figure 4.10. Zeta potential of A) apatite and B) quartz before and after mixing with different reagents at pH 9.

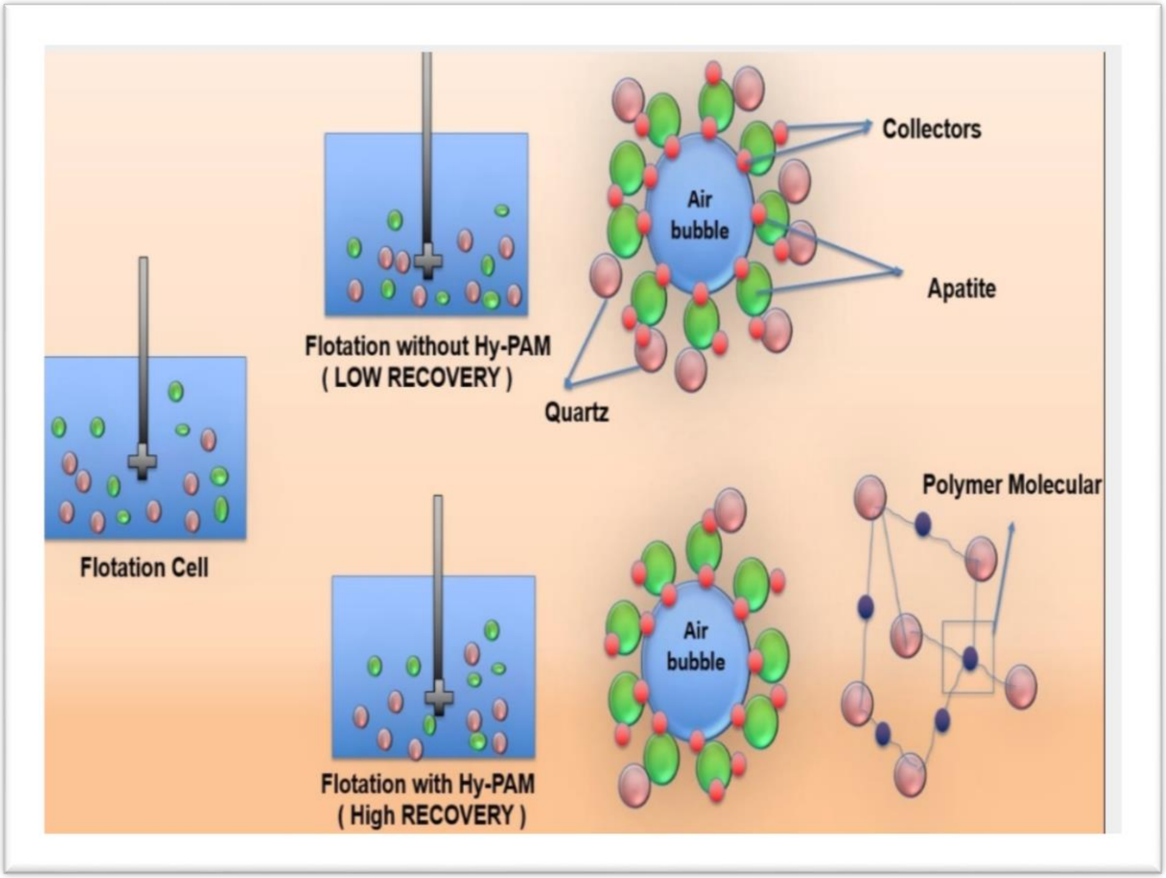


Figure 4.11. A conceptual view of the proposed role of Hy-PAM polymer as a quartz depressant.

4.3. FLOTATION EXPERIMENTS

4.3.1. Baseline Experiments. The baseline experiments were performed periodically based on conditions mentioned in Table 3.2. This was done in order to define a base recovery and to ensure the reproducibility of the results as well as a congruity of the experimental parameters. In these experiments, the solid concentration of the flotation pulp was 60% and the froth was collected over 10 min. As shown in Table 4.5 and Figure 4.12, the average recovery of phosphate minerals was ~74.6% as calculated from XRD data analysis. The phosphorus grade showed an increased by 1.49% when compared to the grade of the feed.

Table 4.5. The recovery and phosphorus grade (%) - Baseline experiment (@60% pulp solids).

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**600**	**54.1**	100	**9.42**
Concentrate	448.7	59	74.6	10.91

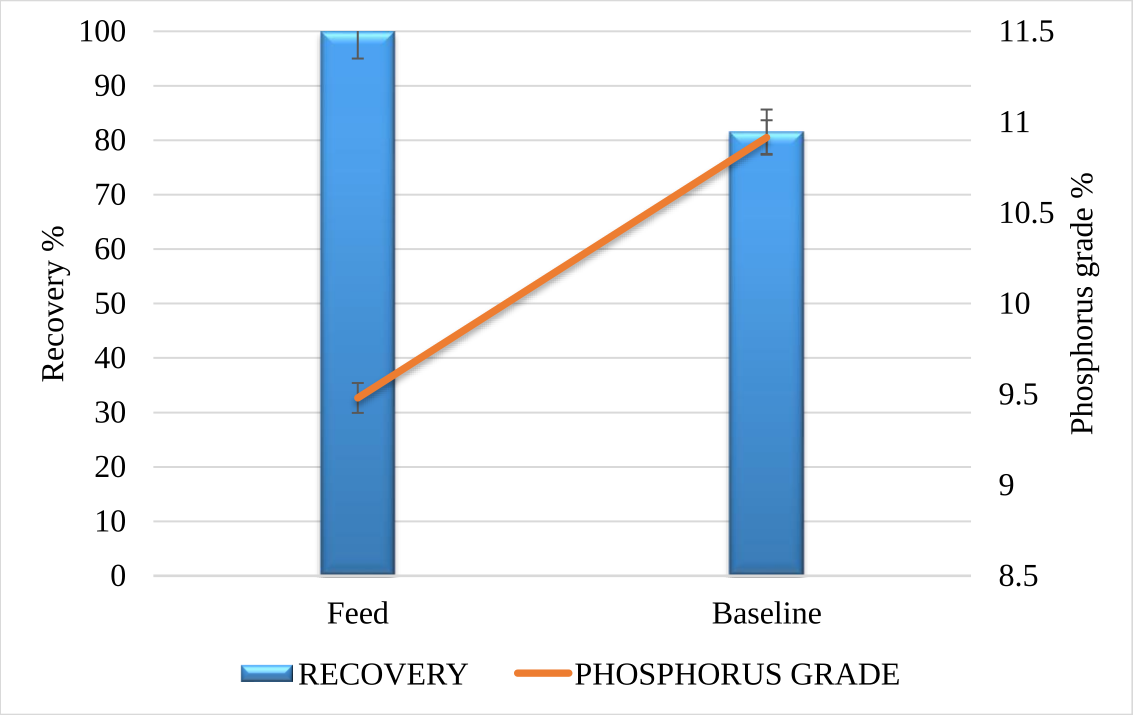


Figure 4.12. Flotation recovery and phosphorus grade (%) of concentrate products obtained from baseline experiments.

4.3.2. Flotation Experiments in the Presence of Sodium Silicate Dispersant. The function of the dispersant in any direct froth flotation process is to disperse the unwanted minerals, increase their hydrophilicity and depress their flotation. In this set of experiments, sodium silicate was chosen as a dispersant because it is considered to be one of the most effective dispersants for silicate minerals. Sodium silicate was added at a fixed dosage of 250 g/t which is reflected in (Table 3.2). Different influencing parameters were examined in an attempt to optimize the flotation process in the presence of sodium silicate dispersant. These parameters are discussed in the following sub-sections.

4.3.2.1. Effect of solid content. The effect of solid concentration of the pulp on the recovery of phosphate minerals and on the phosphorus grade of the concentrate products was examined at solid contents 20 wt. %, 40 wt. %, and 60 wt. %. In this set of experiments, the collector, the dispersant, and the frothing agent were sequentially added to the feed at the specified solid percentage value at pH 9. The froth was collected over a period of 10 minutes. The average recovery of phosphate minerals was 30.88% at 20% solid while the phosphorus grade increased by only 0.38 % compared to feed. When solid contents increased to 40 wt. %, the average recovery of phosphates increased to 51.70%, and the phosphorus grade also increased to 9.99%. The best flotation performance was observed when solid contents were increased to 60 wt. %. At which point the average recovery of phosphate minerals was 55.4% and the grade of phosphorus increased from 9.42% in the feed to 10.92% in the concentrate products. Results are shown in Tables 4.6 - 4.8 and (Figure 4.13). Compared to the results obtained from baseline experiments, the recovery was lower when sodium silicate was used which may be anticipated to the depression of phosphate minerals by sodium silicates at long residence time (10 min).

Table 4.6. The recovery and phosphorus grade (%) at 20 wt. % of pulp solids-when sodium silicate was used as a dispersant.

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**200**	**54.1**	100	**9.42**
Concentrate	63.05	53	30.88	9.8

Table 4.7. The recovery and phosphorus grade (%) at 40 wt. % of pulp solids-when sodium silicate was used as a dispersant.

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**400**	**54.1**	**100**	**9.42**
Concentrate	207.2	54	51.70	9.99

Table 4.8. The recovery and phosphorus grade (%) at 60 wt. % of pulp solids-when sodium silicate was used as a dispersant.

	Mass	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**600**	**54.1**	**100**	**9.42**
Concentrate	304.8	59	55.4	10.92

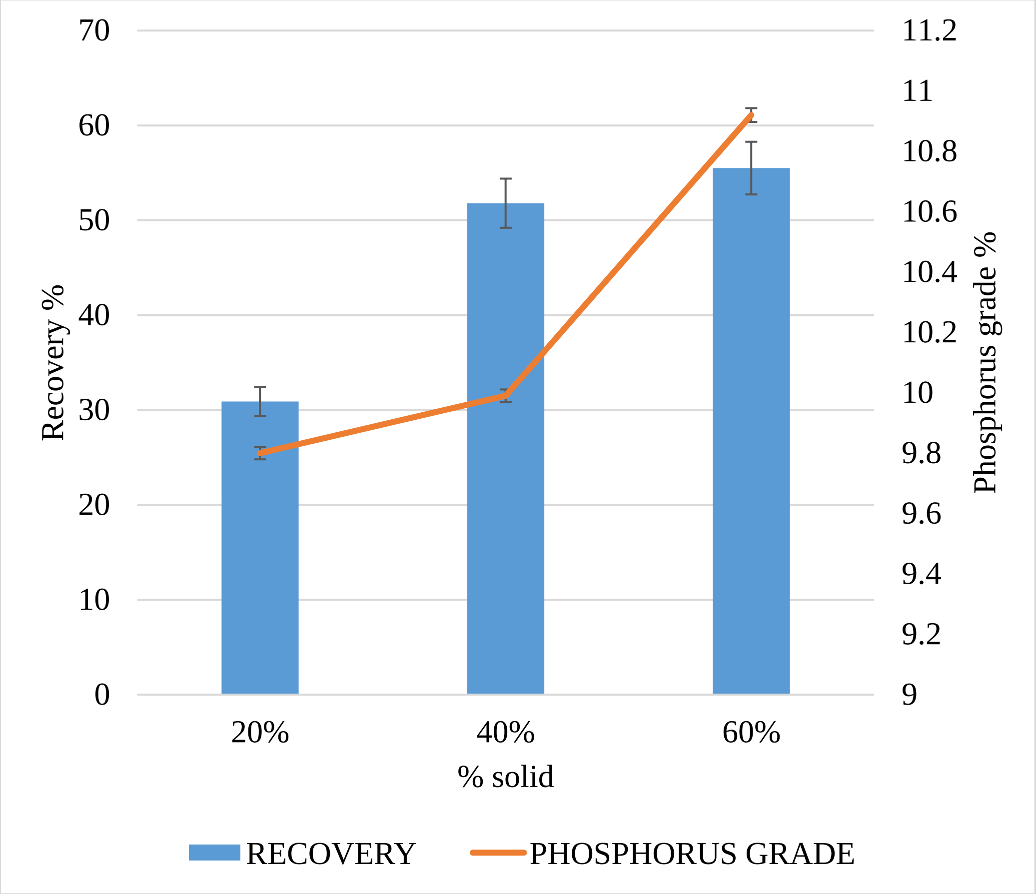


Figure 4.13. Flotation recovery and phosphorus grade (%) at different percentages of pulp solids (wt. %).

4.3.2.2. Effect of pulp pH. The pH value of the pulp plays an important role in the froth flotation process because any small change of the pH value may alter the electrical characteristics of solids and reagents at different interfaces. One of the objectives of this research was to investigate the effect of pH value and the pH modifier type on the flotation performance of phosphate-bearing samples. Flotation experiments were conducted at natural pulp pH of 6.87 and pH 9 with 60 wt. % feed solids and the froth was collected over 10 minutes. To increase the pulp pH to 9, two different reagents were used: sodium carbonate and sodium hydroxide. Results are shown in Tables (4.9 – 4.11) and (Figure

4.14). The average recovery of phosphate minerals at natural pH was 69.49% while the phosphorus grade of the concentrate increased by only 0.2% from that of the feed. However, when the pulp pH increased to 9 by using sodium carbonate, the average phosphorus grade increased by 1.5% at a 55.4% recovery. When sodium hydroxide was used as a pH modifier, the recovery of phosphate minerals dramatically increased to 84.35% while the phosphorus grade increased only by 1.3%. It was anticipated that sodium carbonate would have had a depressing effect on apatite since it could adsorb on its surface and thus render it more hydrophilic. However, the concentrate grade was slightly better in the case of Na_2CO_3. Additionally, Na_2CO_3 is a cheaper reagent compared to NaOH.

Table 4.9. The recovery and phosphorus grade (%) at natural pulp pH (6.87).

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**600**	**54.1**	**100**	**9.42**
Concentrate	433.8	52	69.49	9.62

Table 4.10. The recovery and phosphorus grade (%) when Na_2CO_3 was used as a pH modifier.

	Mass (%)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**600**	**54.1**	**100**	**9.42**
Concentrate	304.8	59	55.4	10.92

Table 4.11. The recovery and phosphorus grade (%) when NaOH was used as a pH modifier.

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**600**	**54.1**	**100**	**9.42**
Concentrate	472.1	58	84.35	10.73

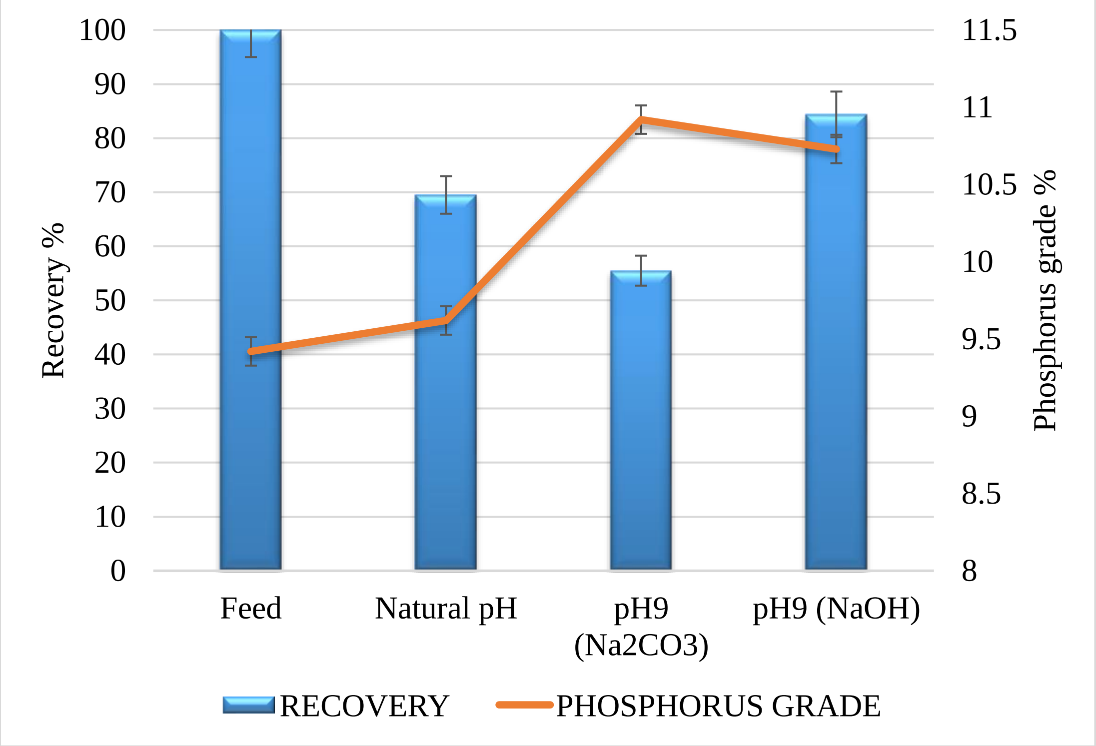


Figure 4.14. Flotation recovery and phosphorus grade (%) at different pH values with different pH modifiers.

Based on the information obtained from the previous experiments, all the following flotation experiments were conducted at 60 wt. % feed solids and a pulp pH of 9 while using sodium carbonate as a pH modifier.

4.3.2.3. Effect of residence time. The effect of froth collection time was investigated in order to determine the optimum residence time in the presence of 250 g/ton of sodium silicate dispersant at pH 9. As shown in Figure 4.15, the average recovery of phosphate minerals was 55.4% when the froth was collected within 10 minutes. At this recovery value, the phosphorus grade of the concentrate product increased by 1.5 % when compared to grade of the feed. When the froth was collected at shorter time intervals of 0-2, 2-4, and 4-6 minutes, the average recoveries of phosphate minerals were 51.19%, 22.66%, and 4.46% respectively. The phosphorus grade of concentrates collected over the first 4 minutes was 12.39 % compared to 9.42% in the flotation feed. The accumulated recovery at the first 4 minutes was 73.85%. It is concluded that shorter residence flotation time is better in the presence of sodium silicate dispersant (Table 4.12. and 4.13).

Table 4.12. The recovery and phosphorus grade (%) at longer residence time (10 min).

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**600**	**54.1**	**100**	**9.42**
Concentrate	304.8	59	55.4	10.92

Table 4.13. The recovery and phosphorus grade (%) at shorter residence time intervals.

	Mass (g)	**% Phosphate minerals**	**Recovery %**	**%P**

Table 4.13. The recovery and phosphorus grade (%) at shorter residence time intervals "cont.".

Feed	**600**	**54.1**	**100**	**9.42**
Concentrate (1) **0-2 min**	248	67	51.189	12.39
Concentrate (2) **2-4 min**	109.8	67	22.66	12.39
Concentrate (3) **4-6 min**	25	58	4.46	10.73

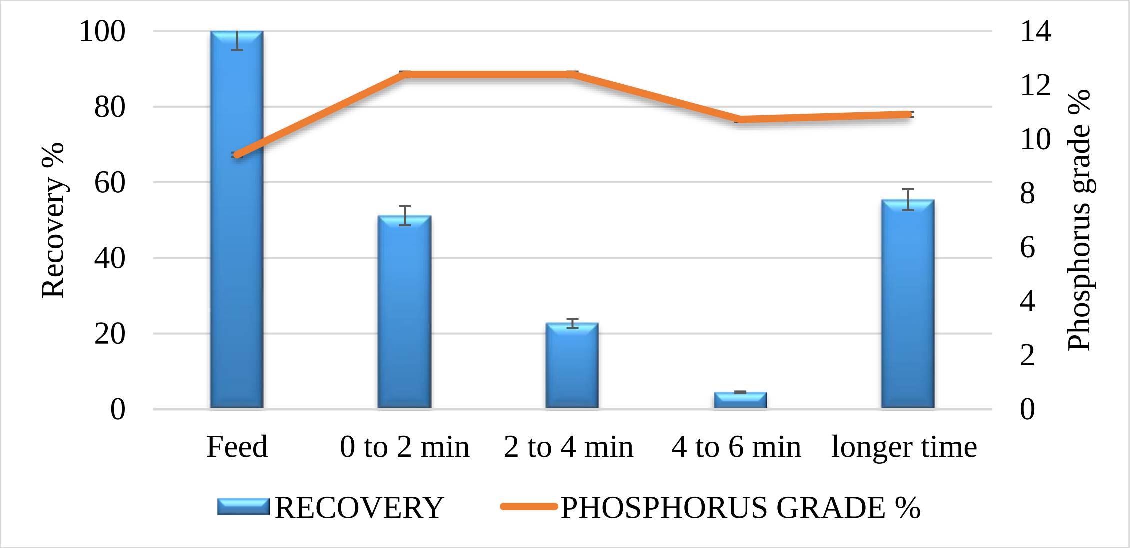


Figure 4.15. Flotation recovery and phosphorus grade (%) at different froth collection time range when sodium silicate was used as a dispersant.

In Figure 4.16 shows froth products collected at different time ranges when sodium silicate dispersant was used 1) 0 to 2 min, 2) 2 to 4 min, and 3) 4 to 6 min. And in Figure

4.17 a picture of froth products collected at longer residence time (0 to 10 min) when sodium silicate dispersant was used.

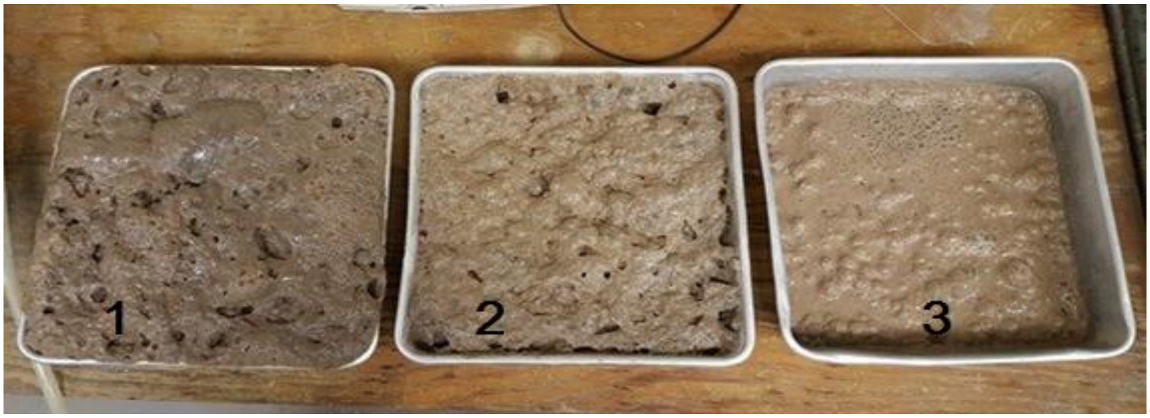


Figure 4.16. A picture of froth products collected at different time ranges when sodium silicate dispersant was used 1) 0 to 2 min, 2) 2 to 4 min, and 3) 4 to 6 min.

Figure 4.17. A picture of froth products collected at longer residence time (0 to 10 min) when sodium silicate dispersant was used.

4.3.3. Flotation Experiments in the Presence of Hy-PAM Depressant. As discussed in the previous sections, the anticipated role of Hy-PAM polymer is to preferentially adsorb on the surface of quartz particle and flocculate them so they settle on the flotation tank. Flotation experiments in the presence of Hy-PAM were conducted at solid concentration of 60 wt. % feed solids. In this set of experiments, the influence of polymer dosage and froth collection times were examined as discussed in the following sections.

4.3.3.1. Effect of polymer dosage. A series of flotation experiments were conducted to investigate the effects of Hy-PAM at various dosages (i.e., 150, 200, 250, and 300g/ton) on both the recovery of phosphate minerals and phosphorus grade of concentrate products. In this set of experiments, the collector, Hy-PAM polymer, and the frothing agent were sequentially added to feed slurries. The concentrates were collected over 10 minutes. As shown in Figure 4.18 the average recovery of phosphate minerals was 67.5% at a polymer dosage 200 g/ton. At this recovery value, the phosphorus grade of the concentrate product increased by 3.71%. Compared to grade of the feed. When Hy-PAM dosage increased to 300 g/ton, the recovery of phosphate minerals dramatically increased to 86.8%. While the phosphorus grade increase by 2.98%. Figure 4.19, compares the flotation performance at 250 g/t of Hy-PAM and 250 g/ton of dispersant when froth was collected over 10 min. The average recovery of phosphate minerals was 55.4% with dispersant compared to 71.5 % with polymer. Moreover, the grade of phosphorus in the concentrate products was 12.21% compared to 10.92% when dispersant was used.

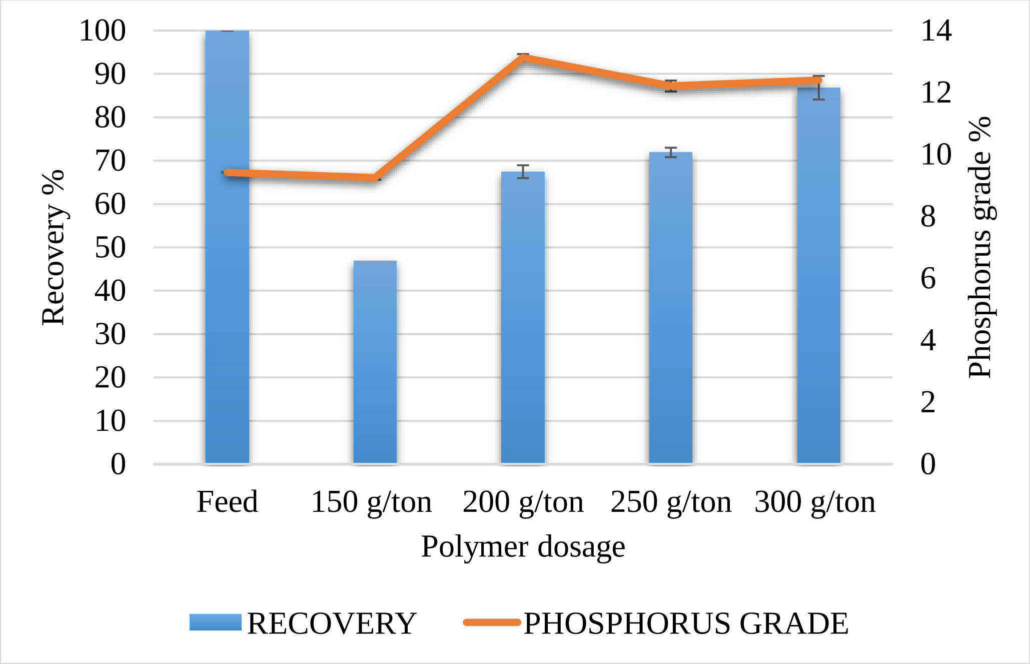


Figure 4.18. Flotation recovery and phosphorus grade (%) as a function of Hy-PAM polymer dosage.

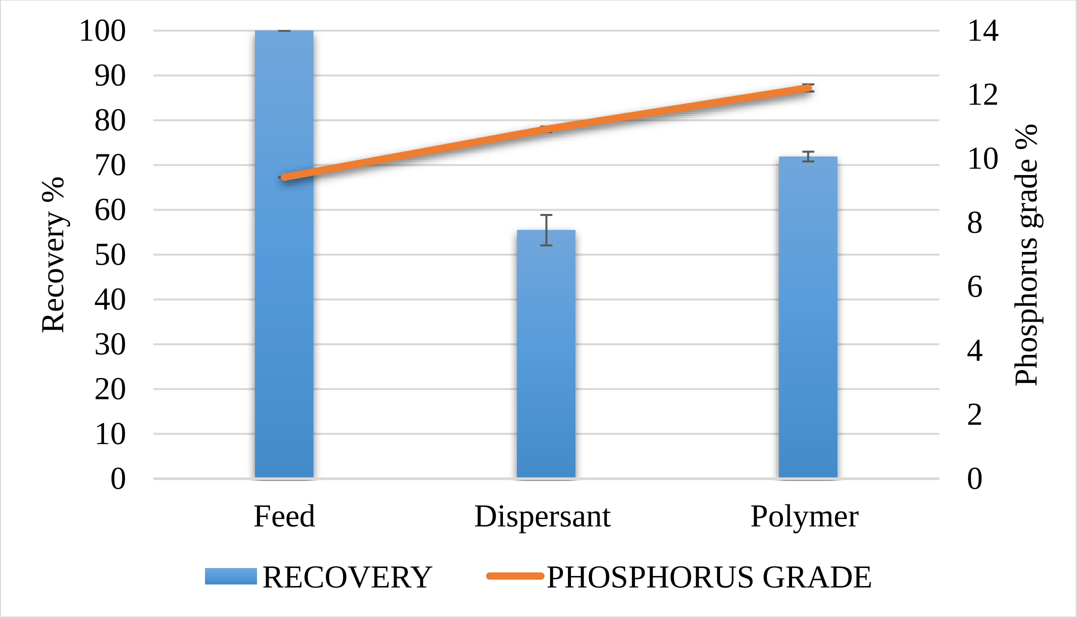


Figure 4.19. Comparison between the recoveries and phosphorus grades when flotation was conducted in the presence of either a dispersant (Sodium silicate) or a polymer (Hy-PAM) at a residence time of 10 minutes.

4.3.3.2. Effect of the residence time at pH9. Flotation performance of phosphate-bearing samples was then tested as a function of froth collection time at polymer dosage of 250 g/t. As shown in Tables (4.14. and 4.15.), the average recovery of phosphate minerals was 71.9% when froth was collected over a longer time (10 min). The phosphorus grade also increased by 2.79 % as compared to grade of the feed when froth was collected at shorter time intervals: 0-2, 2-4, and 4-6 minutes, the average recoveries of phosphate minerals were 53.18%, 12.64%, and 4.28% respectively and the phosphorus grades of the concentrate products were 12.21%, 11.47%, and 11.66%, respectively. As indicated the accumulated recovery dropped from 71.9% at longer residence time to appropriately 65.82% when froth was collected over the first 4 minutes (Figure 4.20 – 4.22).

Table 4.14. The recovery and phosphorus grade (%) at longer residence time (10 min).

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**P%**
Feed	**600**	**54.1**	**100**	**9.42**
Concentrate	354	66	71.9	12.21

Table 4.15. The recovery and phosphorus grade (%) at shorter residence time intervals.

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**P%**
Feed	**600**	**54.1**	**100**	**9.42**

Table 4.15. The recovery and phosphorus grade (%) at shorter residence time intervals "cont.".

Concentrate (1) **0-2 min**	261.58	66	53.18	12.21
Concentrate (2) **2-4 min**	66.2	62	12.64	11.47
Concentrate (3) **4-6 min**	22.1	63	4.28	11.66

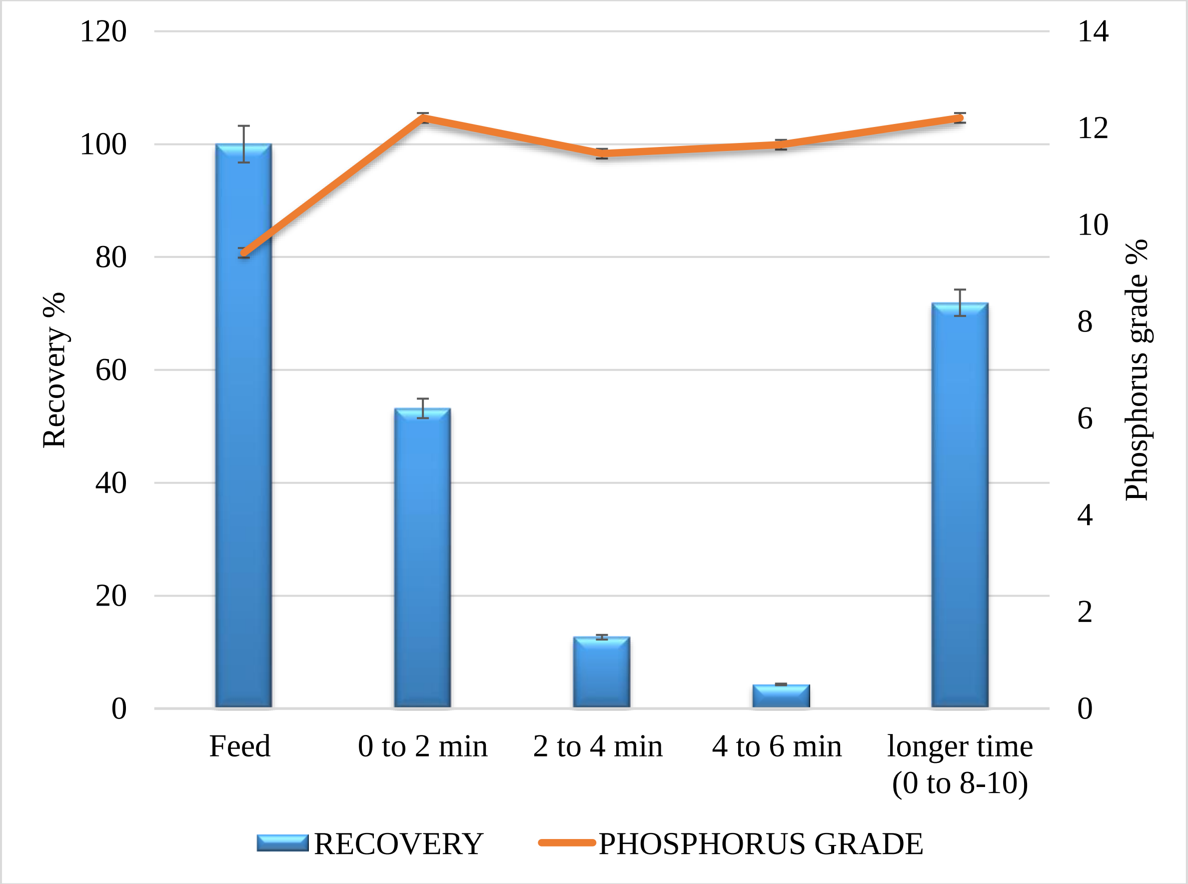


Figure 4.20 Flotation recovery and phosphorus grade (%) at different froth collection time range when Hy-PAM was used as a depressant at pH 9.

Figure 4.21. A picture of froth products collected at different time ranges when Hy-PAM dispersant was used 1) 0 to 2 min, 2) 2 to 4 min, and 3) 4 to 6 min.

Figure 4.22. A picture of froth products collected at longer residence time (0 to 10 min) when Hy-PAM was used as a quartz depressant.

4.3.3.3. Effect of pulp pH. Flotation experiments were conducted at natural pulp pH of 6.87 and compared with results obtained when pulp pH was 9, as discussed in the previous section. Test were performed at 60 wt. % feed solids and 250 g/t Hy-PAM dosage. Initially, the froth was collected over a period of 10 minutes. Results are shown in Tables (4-16 and4-17) and Figure 4.23. The average recovery of phosphate minerals at natural pH was 84.79% compared with 71.9 % recovery at pH 9. Moreover, at natural pH, the average phosphorus grade increased by 2.97% compared to an increase of 2.79% when flotation was conducted at pH 9.

Table 4.16. The recovery and phosphorus grade (%) At natural pH.

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**600**	**54.1**	**100**	**9.42**
Concentrate	410.8	67	84.79	12.39

Table 4.17. The recovery and phosphorus grade (%) when Na_2CO_3 was used as a pH modifier.

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**600**	**54.1**	**100**	**9.42**
Concentrate	354	66	71.9	12.21

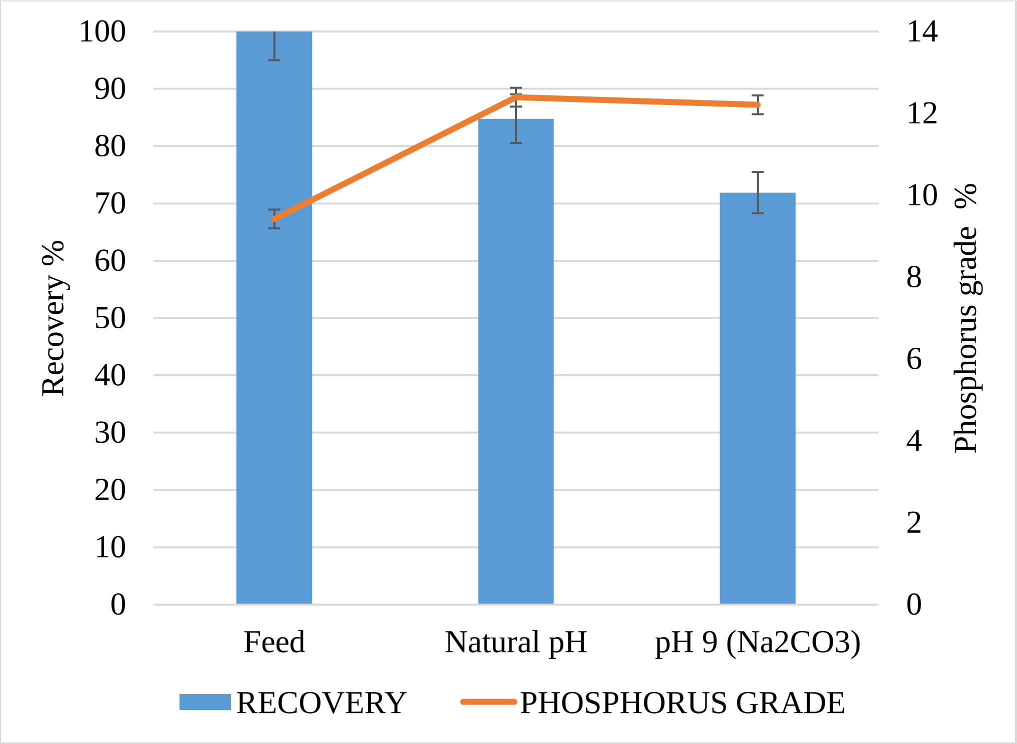


Figure 4.23. Flotation recovery and phosphorus grade (%) at different pH values with different pH modifiers.

4.3.3.4. Effect of the residence time at natural pH. The effect of froth collection time was also investigated in the presence of 250 g/ton of Hy-PAM polymer at natural pH. As shown in Table 4.18 and Figure 4.24. When the froth was collected at shorter time intervals of 0-2, 2-4, and 4-6 minutes, the average individual recoveries of phosphate minerals were 65.48%, 15.15%, and 3.79% respectively. The phosphorus grade of concentrates collected over the first 4 minutes was 12.39 % compared to 9.42% in the flotation feed. The accumulated recovery at the first 4 minutes was 80.36%. It is concluded that shorter residence flotation time is better in the presence of Hy-PAM polymer at natural pH.

Table 4.18. The recovery and phosphorus grade (%) at shorter residence time intervals.

	Mass (g)	**% Phosphate minerals**	**Recovery (%)**	**%P**
Feed	**600**	**54.1**	**100**	**9.42**
Concentrate (1) 0-2 min	317.24	67	65.48	12.39
Concentrate (2) 2-4 min	72.34	68	15.15	12.58
Concentrate (3) 4-6 min	18.36	67	3.79	12.39

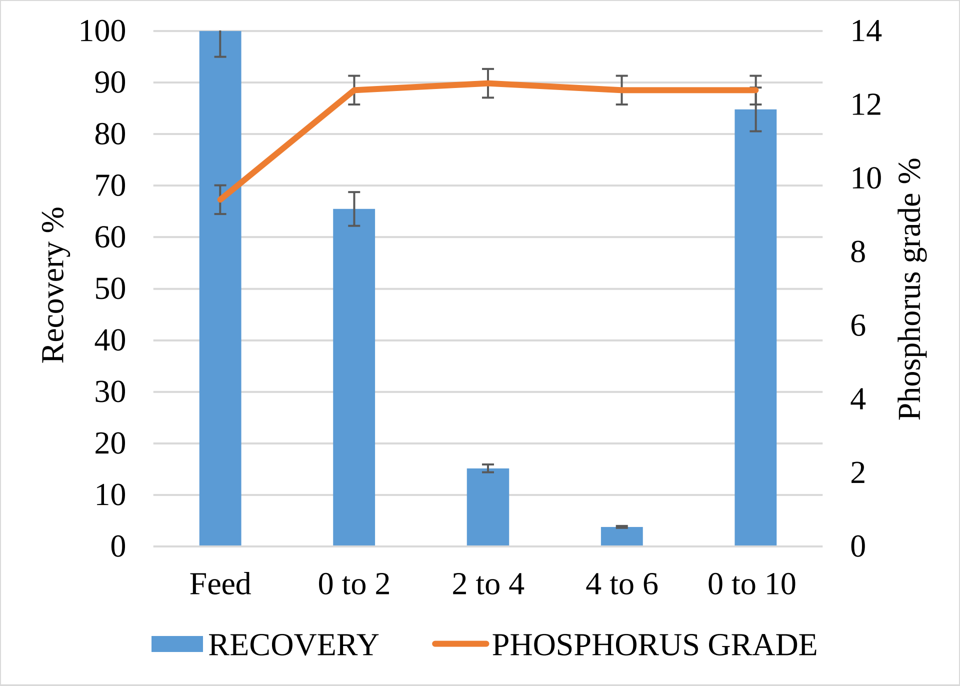


Figure 4.24 Flotation recovery and phosphorus grade (%) at different froth collection time range when Hy-PAM was used as a depressant at natural pH.

4.3.4. Flotation Experiments in the Presence of Dual Dispersant/Depressant System at Specific Mass Ratio. Flotation performance of phosphate tailing samples was tested using a mixture of sodium silicate and Hy-PAM polymer at 1:1 ratio by mass. Both the polymer and the dispersant were added at a dosage of 250 g/ton. The results are shown in (Figure 4.25.). Results demonstrated that the grade of phosphorus in the concentrate was 11.47 % compared with 12.21 % and 10.92 % when either the polymer or the dispersant was used, respectively. Furthermore, the recovery of phosphate minerals was better when the polymer was used without the addition of the dispersant.

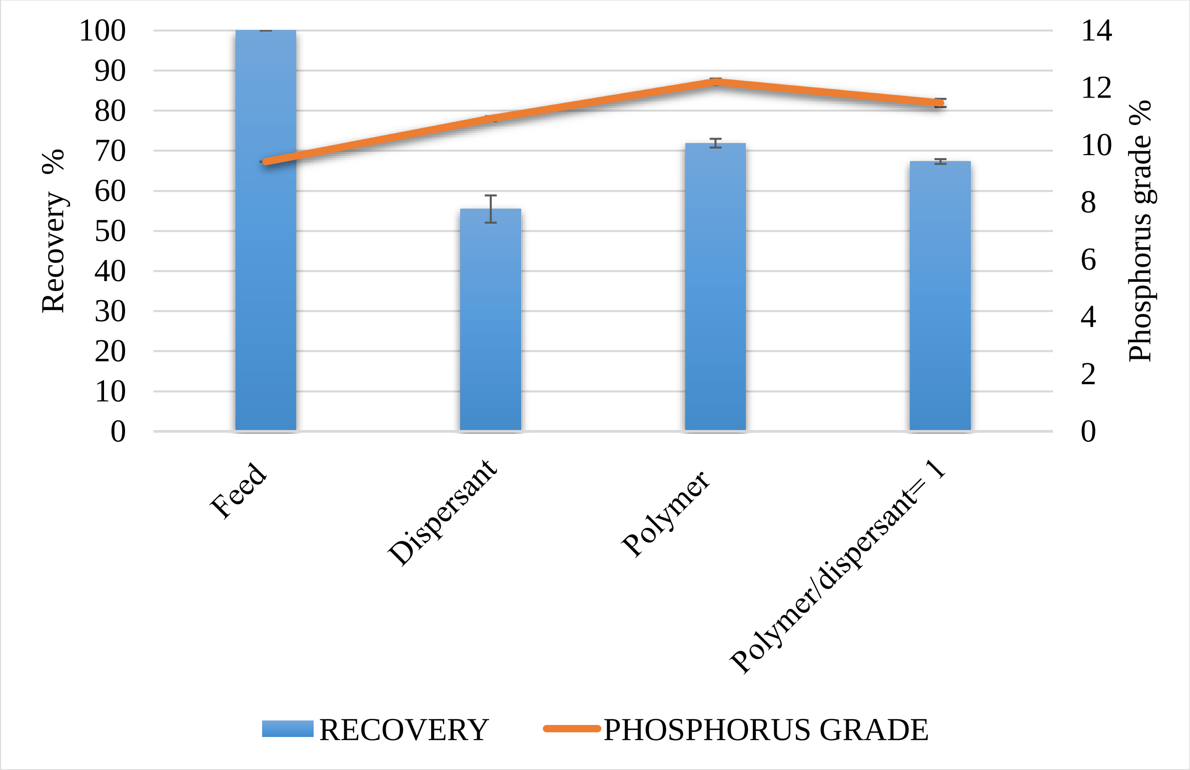


Figure 4.25. The recoveries and phosphorus grade (%) of concentrates obtained when floatation was conducted in the presence of the either sodium silicate dispersant, Hy-PAM depressant or dual dispersant/ depressant system.

5. CONCLUSIONS AND FUTURE WORK

5.1. CONCLUSION

This study investigated the potential to upgrade the phosphorus content in the tailings produced from phosphorus production plant using direct froth flotation process. Bench scale flotation tests were carried out using a Denver flotation cell in the presence of different reagents. These reagents include sodium silicate which is a commercially-used gangue dispersant and in-house synthesized novel gangue depressant, Hy-PAM. Hy-PAM is an organic-inorganic hybrid polymer which consists of polyacrylamide organic chains grafted on nano-size $Al(OH)_3$ inorganic particles. Moreover, several influencing parameters such as solid contents of the flotation pulp, pulp pH and pulp residence time were investigated to optimize the flotation outcomes in terms of froth recovery and grade. Studies using a dual dispersant/depressant system, at a specific mass ratio, were also conducted to figure out if the synergy could improve the overall flotation performance. The following conclusions may be drawn from this study:

1) Zeta potential measurement performed on pure apatite and quartz suspensions before and after mixing with different reagents indicated that the collector has a preferential adsorption on apatite surface rather than quartz. Zeta measurements also demonstrated that Hy-PAM polymer would have a preferential adsorption on the surface of quartz. It was also concluded from zeta measurements that sodium silicate has a tendency to get adsorbed on the surface of apatite particles which may result in apatite depression in flotation when pulp residence time is long.

2) In the presence of sodium silicate dispersant, the best flotation performance was observed at 60% feed solids and 4 minutes residence time when the pH of the pulp was kept at 9. Under these conditions, the average recovery of phosphate minerals was 74.6% and the grade of phosphorus increased from 9.42% in the feed to 12.39% in the concentrate products.

3) The study has proven that pH value and the pH modifier type impacted the flotation performance at longer residence time. Flotation experiments results showed that using sodium carbonate as pH modifier improved the phosphorus grade by 1.5% at 55.4% recovery. On the other hand, the phosphorus grade of the concentrate increased by 1.3% when sodium hydroxide was used as a pH modifier at 84.35% recovery.

4) Results also showed that adding Hy-PAM at 250 g/t with longer residence time of 10 min time improved the recovery of phosphate minerals compared with dispersant at same dosage and same residence time. Moreover, the grade of phosphorus in the concentrate increased to 12.21% compared to 10.92% with dispersant.

5) Flotation tests results showed that the optimum dosage of Hy-PAM was 200 g/ton. At which the phosphorus grade increased by approximately 3.8%.

6) In comparison (Figure 5.1), the phosphorus grade and recovery of the concentrate were better at shorter residence time of 4 minutes in the presence of dispersant while the phosphorus grade and recovery were better at longer residence time of 10 minutes in the presence Hy-PAM depressant

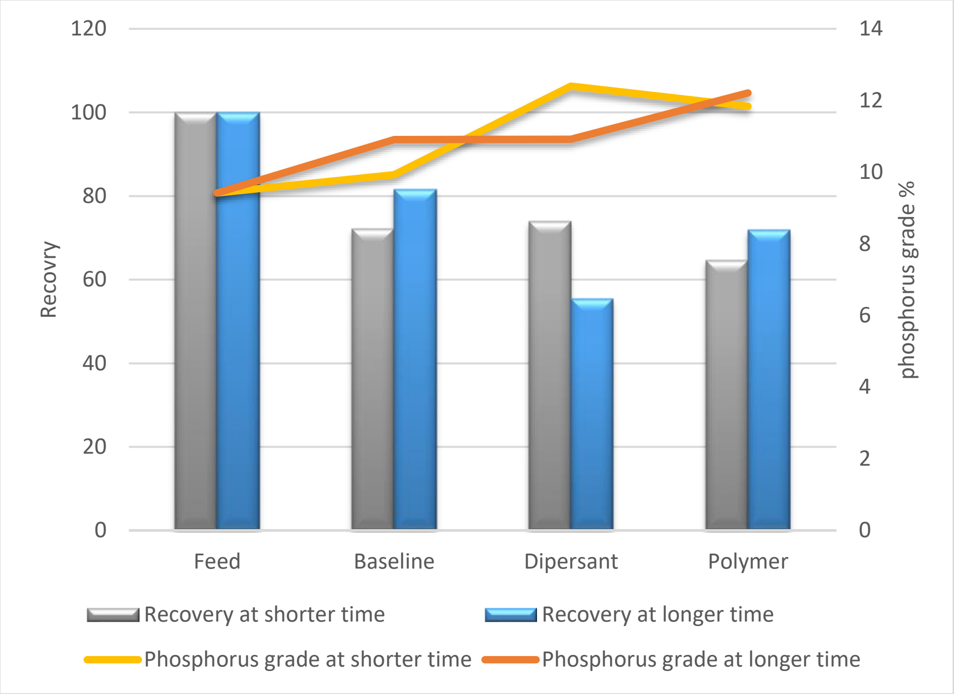


Figure 5.1. Comparison of flotation outcomes at different experimental conditions.

7) The test results indicated that the dual use of dispersant and Hy-PAM is less effective than using the polymer alone. The grade of phosphorus in the concentrate when mixed reagents were used was 11.47 % compared with 12.21 when polymer was used at same residence time.

5.2. FUTURE WORK

Findings obtained from this study show that using sodium silicate dispersant and hybrid polyacrylamide polymer (Hy-PAM) in phosphate minerals flotation has a positive impact on the phosphate recovery, phosphorus grade, and the quartz rejection. However, more studies are needed to further investigate the effects of such polymers on phosphate flotation process. The following studies are recommended for future work:

1) Studying the selectivity of Hy-PAMs adsorption on phosphate mineral particles as well as quantitative measurements of the amount adsorbed.
2) Investigating the flotation performance at different reagents types and dosage and further optimization of other parameters accordingly.
3) Conducting flotation using other flotation machines such as column flotation cell to see if this will increase the enrichment ratio.
4) Study the flotation performance in reverse flotation process.
5) Study the effect of particles size on the flotation process.

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