PARAMETRIC STUDIES ON CELL FLOTATION OF MAZIDAĞI PHOSPHATE ROCK

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ABSTRACT

PARAMETRIC STUDIES ON CELL FLOTATION OF MAZIDAĞI PHOSPHATE ROCK

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Phosphate is one of the essential minerals for all living organisms. It has to be supplied to the soil in order for plant growth. In Turkey, most of the soils lack phosphate mineral. Although this can be overcome by the use of phosphate fertilizers, in Turkey there are no phosphate mines being utilized; and this brings about the need to import phosphate rock and phosphate fertilizers. The estimated phosphate rock reserve of Turkey is around 300 million tons, but it cannot be utilized since no economical method of upgrading has been proved to work yet.

The aim of this study has been two-fold; to determine the effects of several parameters on the cell flotation of Mardin-Mazıdağı phosphate rock and to increase the grade of the product above 30% P_2O_5 content with a reasonable recovery rate, so that it could be used commercially.

Phosphate rock upgrading was made by using flotation in a cell. There are many factors affecting the recovery and grade of the product such as, particle size, pulp pH, collector volume, acid and collector conditioning times and temperature.

Phosphate rock samples used contained 14% P_2O_5, 43% $CaCO_3$ and 1% SiO_2 with a CaO/P_2O_5 ratio of 3.1. Due to the low silica content, one-stage flotation was made.

In the experiments, effects of the important parameters were tested at constant pulp density (10% solids by weight). Particle sizes were between 53 μ and 150 μ, while the pH values were kept between 5,0 - 6,5 using amounts of acid within the range of 6 - 19 kg H_3PO_4/ton of rock. The collector (mixture of kerosene and oleic acid in 1:3 volumetric ratio) was used in the range of 0,6 ml (0,96 kg collector/ton rock) and 5,4 ml (8,64 kg collector/ton rock). Acid and collector conditioning times were changed between 10-110 s and 10-80 s, respectively. The temperature range was between 15-35 °C.

At the end of the parametric studies a grade of 36% P_2O_5 with a recovery of 93% could be obtained.

Keywords: Cell Flotation, Parametric Study, Phosphate Rock

ÖZ

FLOTASYON HÜCRESİNDE MAZIDAĞI FOSFAT KAYASI İLE YAPILAN PARAMETRİK ÇALIŞMALAR

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Fosfat tüm canlılar için gerekli olan minerallerdendir. Türkiye'deki toprakların çoğu fosfat bakımından fakir olduğu için, bitkilerin gelişimi için toprağa fosfat gübresi eklenmelidir. Ancak, Türkiye'de işletilen fosfat yatakları olmadığı için, fosfat kayası ve fosfat gübresi ithal edilmektedir. Ülkemizin tahmini fosfat kayası rezervi 300 milyon ton olarak bilinmektedir, fakat, ekonomik bir zenginleştirme yöntemi bulunamadığından işlenememektedir.

Bu tez çalışmasının amacı iki yönlüdür; Mardin-Mazıdağı fosfat kayasının hücre flotasyonuna etkiyen çeşitli parametreleri incelemek ve kayanın tenörünü %30 P_2O_5 seviyesi üzerine çıkararak ticari kullanım için yeterliliğini sağlamaktır.

Fosfat kayası zenginleştirmesi flotasyon yöntemiyle, flotasyon hücresinde yapılmıştır. Flotasyona etki eden birçok faktör vardır. Bunların arasında parçacık boyutu, palp pH, asit ve kollektör şartlandırma zamanları ve sıcaklık sayılabilir.

Bu çalışmada kullanılan fosfat kayasının içeriğinde %15 P_2O_5, %43 CaO ve %1 SiO_2 bulunmaktadır ve CaO/P_2O_5 oranı 3.1dir. Silis miktarının düşük olması nedeniyle tek aşamalı flotasyon yapılmıştır.

Bu çalışmada yapılan deneylerde önemli parametreler, ağırlıkça %10 katı madde içeren palp kullanılarak incelenmiştir. Parçacık boyutu 53 μ ve 150 μ, arasında değiştirilmiştir. Palp pH seviyesi 5,0 - 6,5 arasında değiştirilmiştir ve bunun için kullanılan asit miktarı 6-19 kg H_3PO_4/ton kaya arasındadır. Kollektör (kerosen ve oleik asitin hacimce 1:3 karışımı) ise 0,6 ml (0,96 kg kollektör/ton kaya) ve 5,4 ml (8,64 kg kollektör/ton kaya) arasında değişen miktarlarda kullanılmıştır. Asit ve kollektör şartlandırma zamanları sırasıyla 10-110 sn ve 10-80 sn arasında değiştirilmiştir. Palpın sıcaklığı ise 15-35 °C arasında değiştirilmiştir.

Parametrik çalışmalar sonucunda %36 P_2O_5 içeren fosfat kayası %93 geri dönüşümle elde edilebilmiştir.

Anahtar Kelimeler: Hücre Flotasyonu, Parametrik Çalışma, Fosfat Kayası

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Elif ÖZTİN

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A.I.	Acid insoluble
K_{SP}	Solubility product
EDL	Electrical double layer
IEP	Isoelectric point
LOI	Loss on ignition
PZC	Point of zero charge
W_A	Work of adhesion (dynes/cm)
W_B	Work of cohesion (dynes/cm)
θ	Three-phase contact angle (degrees)
γ_{ma}	Interfacial tension between mineral and air bubble(dynes/cm)
γ_{mw}	Interfacial tension between mineral and water (dynes/cm)
γ_{wa}	Interfacial tension between water and air bubble (dynes/cm)
ΔG	Free energy change per unit area (dynes/cm)
ξ	Surface potential (mV)
ζ	Zeta potential (mV)

CHAPTER 1

INTRODUCTION

Phosphorous is an important element for all living organisms since it takes part in energy storage and in transmission of genetic characteristics in animals and plants. Phosphorous is found in complex forms in nature; it combines with other elements to form phosphate rock. Depending on its geological origin, there exist various types of phosphate rock in the earth's crust. Apatite form is the major polar salt-type mineral of phosphorous in phosphate rock, which has a general formula of $CaX_2.3Ca_3(PO_4)_2$ (X being either OH^-, F^-, Cl^-, CO_3^{2-}). In igneous deposits, there are three species of apatite: chlorapatite, hydroxyapatite, and fluorapatite. In sedimentary rocks, the species are, francolite and hydroxy-fluor-carbonate. Phosphate in these rocks is built around a calcium (Ca) and phosphate (PO_4) structure with varying degrees of Ca substitution by other elements (e.g. Na, Mg, Pb, Cd, Cr, As). [1] As a result of this substitution, P_2O_5 content of the rock may change between 42% and 28% [2].

The phosphate deposits of Turkey are mainly in the Southeastern Anatolia, namely in, Mardin (Mazıdağı), Bingöl, Bitlis, and lower Fırat region. In Turkey, the estimated phosphate rock reserves which can be mined economically (bed thickness of which is about 70 cm with at least 8% P_2O_5 content) is around 300-400 million tons.

Approximately, 300 million tons of these deposits are found in Mardin-Mazıdağı with a phosphate grade ranging between 8% and 25% P_2O_5. Except for the Northeastern part of Turkey, soils are rich in calcium content and every year phosphate fertilizers must be used. As a result, phosphate rock and phosphate-rich fertilizers are imported each year, which rank the second or the third among the annual import items. The commercial phosphate rock contains at least 30% P_2O_5. Therefore, Mazıdağı phosphate rock must be concentrated up to that level and this upgrading can be made by flotation [3].

Flotation has been used in the minerals processing industry since the mid-1800s with many applications to mineral recovery extensively developed between 1900 and 1925. Today, including almost all of the world’s important minerals copper, lead, zinc, nickel, silver, molybdenum, manganese, chromium, cobalt, tungsten, and titanium, are processed using flotation. Recovery of minerals for production of base metals, like copper, zinc, lead, nickel, etc. was the first potential use of flotation. Very rapidly this method showed its capability in recovering coal, phosphates, carbonates, oxides, metallic gold, etc. [2]. Flotation has permitted the mining of low grade and complex ores that would have been counted as waste. Flotation technology converted the tailings dumps into mines in other words. Another major usage of flotation is by the coal industry for desulfurization and the recovery of fine coal, once discarded as waste. Flotation has also been applied outside the mining industry, particularly in the chemical, paper, and food processing industries.

The development of flotation continues today with the need to recover minerals from increasingly poorer grades of ores, as well as its non-traditional application to other types of materials.

The major development in flotation technology is the invention of flotation columns. Flotation columns have simpler operation and provide greater grade/recovery performance and for these reasons flotation columns are gaining an increasing acceptance in mineral processing industry. Flotation can be made in either cells or in columns. The two differ from each other in both design and operation. [4]

The aim of this study has been to investigate the effects of the parameters of flotation process, namely, particle size, pH, acid conditioning time, collector conditioning time, collector quantity and temperature on the flotation of Mardin-Mazıdağı phosphate rock in a flotation cell. Also, it was aimed to obtain a rock grade, which would make it possible to utilize the reserves commercially.

CHAPTER 2

THEORY OF FLOTATION

2.1.Theory of Flotation

Flotation is a process for separating finely divided species of solids from each other. It is a physico-chemical process where the difference in hydrophobicity of the minerals is used to separate one mineral from another. In other words, it takes advantage of the differences in wettability of solid particle surfaces. When flotation is used as a process of separation, two streams are produced, one of them is known as tailing, and it usually contains the worthless substances and is discarded. The second stream, known as concentrates, usually contains the valuable substances in a concentrated form. [5]

Solid surfaces naturally wettable by water are termed *hydrophilic*. A surface that is non-wettable is water repelling and termed hydrophobic. Most minerals adhere to water in preference to air; only a few minerals like talc and graphite are naturally hydrophobic. If a surface is hydrophobic, it is also typically air attracting, termed *aerophilic*, and is strongly attracted to an air interface, which readily displaces water at the solid surface. In most mineral flotation, the hydrophobicity of the valuable minerals is induced by the addition of chemical reagents called collectors and activators. These reagents are capable of coating a particular mineral selectively, thereby increasing its hydrophobicity. This hydrophobicity allows the treated particles to attach on to the bubbles. In flotation, separation of a binary solids mixture may be accomplished by the selective attachment of hydrophobic solid particles to gas bubbles that is typically air. Hydrophilic solid particles remain in the liquid that is typically water. The difference between the density of the air bubbles and water provides buoyancy that preferentially lifts the hydrophobic solid particles to the surface, affecting the separation. For solids of similar densities and sizes, separation methods based upon gravity may fail to work, however, flotation can often be used in separating such solids. [5]

As is well known, flotation involves the capture of small solid particles by bubbles in slurry followed by their attachment and transportation into the froth zone. The success of flotation separations depends on the interactions among the physical, chemical and mechanical factors involved in the system. The figure below represents schematically the interactions between the physics of flotation, chemical factors and mechanical design of flotation system. [6]

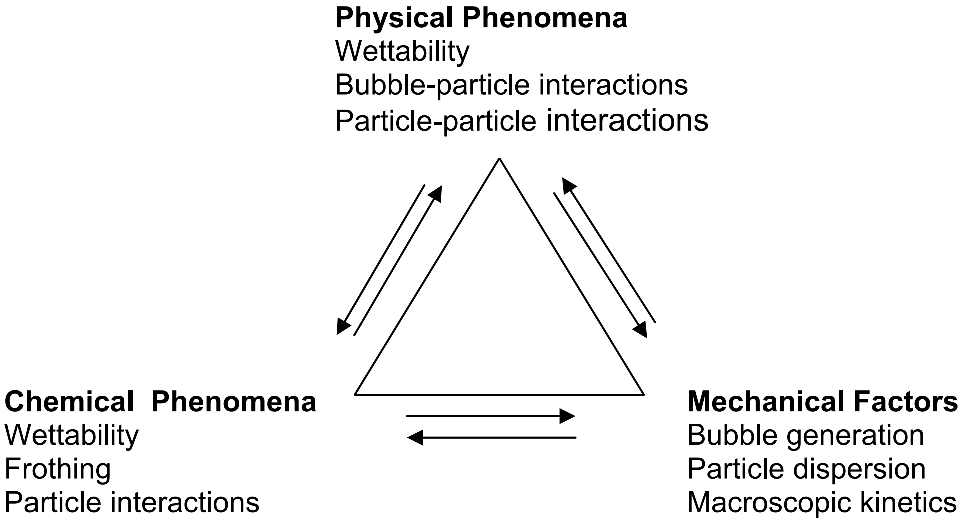

Figure 1. Schematic Representation of the Three Elements Of Flotation. [6]

The very basis of flotation involves the relative interaction of three phases: one solid and two fluids. The triangular relationship shown in Figure 1 summarizes this. These interactions control which of the two fluids will wet the solid phase (wettability) preferentially. Physical phenomena control bubble-particle interactions (microscopic flotation kinetics) and particle-particle interactions (dispersion, slime coating).

The chemical phenomena corner of the triangle is the key of flotation process. Flotation is achieved by modifying the interaction between water molecules and solid surface. The successful results rely on the use of a wide variety of chemical reagents because their adsorption at the solid-liquid, solid-gas, liquid-gas interfaces determine the physical and chemical characteristics of the system.

The third corner of the triangle involves the mechanical factors which control bubble generation, dispersion and as a result of these the macroscopic kinetics of flotation. [6]

Flotation can be made in cells or in columns. Flotation studies are carried in cells before testing in the continuous mode (columns). Cells are used especially in the separation of very fine particles. On the other hand, columns have better separation efficiencies compared to the cells. The main features that distinguish a flotation column from a cell are summarized in Table 1. [7]

Table1. Comparison of Flotation Cells and Flotation Columns [7]

Feature	Flotation Columns	Mechanical Flotation Cells
Bubble-particle attachment mechanism	Collision	Collision and entrainment
Flow of pulp-air	Counter-current	Differs according to the design of rotor system and feeding
Flow conditions	No turbulence, mostly plug flow	Turbulent flow (Re= 10^5), well-mixed
Froth layer	Deep; removed with wash water	Not deep; no wash water used
Supply of air	By sparger	By the impeller
Air rate	0,8-3 cm/s	0,3-1 cm/s
Quantity of gas hold-up	15-30 %	15 %
Bubble diameter	Easy to control bubble size	Hard to control the size

2.2. Phosphate Rock, Its Use and Beneficiation

The properties of phosphorous chemicals are unique because of the important role of phosphorous in many biochemical processes, the ability of polyphosphates to complex many metal cations, and versatility in forming various types of organic and inorganic polymers. The most important use of phosphate rock is in fertilizers.[8] More than 75% of apatite mined is converted to phosphoric acid.[9] The major end-uses of phosphoric acid are fertilizers (85%), detergent materials (5%), animal feed (5%) and food, beverages and dentifrices (5%).[8] Phosphoric acid is utilized principally to produce major fertilizer products such as ammonium phosphates (made by the controlled addition of ammonia to phosphoric acid) and triple superphosphates (produced by phosphoric acid acidification of phosphate rock).[3]

Phosphate rock deposits being beneficiated in the world are calcium, aluminum and iron phosphates of marine origin (75%), magmatic origin (20%) and "guano" origin (5%).[10] In nature, phosphate rock can be found as igneous or sedimentary rock with an abundance ratio of 13:87.[1] Igneous rock phosphate deposits have the characteristic of well-crystallized and nonporous surfaces, which after grinding, give particles of low specific surface and roughness. Consequently, igneous rock phosphates show high amenability to concentrate by flotation. In the case of sedimentary rocks, larger specific surfaces of phosphate particles are encountered because of the porous/microporous and irregular texture, resulting in high reagent consumption during concentration process and reduced adsorption selectivity of the collector. Also due to their friable nature, sedimentary phosphate rocks produce more slime (particles of size smaller than 20μm) during grinding. Therefore, processing of igneous rocks is much easier than that of sedimentary rocks. [11]

The major commercial phosphate rock deposits are in the United States of America (Florida, North Carolina), North Africa (Morocco), the former Soviet Union (Kola), South Africa (Phalaborwa), China, Finland, Middle East and some Pacific islands.[1] The first three mentioned have 77% share of the world phosphate rock production. Morocco has the largest phosphate rock deposits in the world and governs one-third of the world phosphate rock export. [10]

In industry, there are several ways to express the calcium content of the phosphate rock. [10]

BPL: Bone Phosphate of Lime
TPL: Triphosphate of Lime
P_2O_5: Phosphorus Pentaoxide
P: Phosphorus (not used widely)

The relationships among these are:
P_2O_5/ BPL = 2.18
BPL / P = 5

Most often, industrial terminology uses the term P_2O_5. Phosphate rock is a very general term; it is used widely in industrial applications, and it does not have a certain chemical composition.

2.2.1. Mazıdağı Phosphate Rock

In Turkey, there have been some attempts to beneficiate phosphate rock. These can be classified as (a) milling and screening [12,13], (b) calcination and slaking [12,14], (c) flotation [12,13,14,15]. Eti Holding had started a plant for Mazıdağı phosphate rock beneficiation in 1977 with a capacity of 125,000 ton/yr, and in 1989 the plant started operating with a capacity of 750,000 ton/yr. The phosphate rock enriched in this plant has the chemical composition as given in Table 2, and after a complete processing of the rock, concentrate P_2O_5 content can be increased from 18% to 30.5%. [10]

Table2. Comparison of the Chemical Compositions of the Industrial and Mazıdağı Phosphate Rocks. [10]

Chemical Composition	Industrial Phosphate Rock Min.-Max. %	Mazıdağı Concentrate %
P_2O_5	29 - 38	30.5
CaO	46 - 54	51.27
SiO_2	0.2 - 8.7	3.55
Al_2O_3	0.4 - 3.4	0.29
MgO	0.1 - 0.8	0.27
Na_2O	0.1 - 0.8	0.53
CO_2	0.2 - 7.5	6.00
F	2.2 - 4.0	2.05
Cl	0.0 - 0.5	0.01
SO_3	0.0 - 2.9	1.15
CaO / P_2O_5	1.35 - 1.70	1.70

2.2.2. Phosphate Ore Processing

There are more than 200 minerals existing in the earth's crust with P_2O_5 content greater than 1% [10]. The depletion of high-grade phosphate ores is bringing about a search for a suitable and economically viable technique that can process the abundant low-grade phosphate reserves. Most phosphate rock is processed through a concentration stage that removes the bulk of the inert materials that may be bound up with the phosphate substrate or that may be around the phosphate rock. This step is known as beneficiation. Main impurities in sedimentary rocks depend on the location. They can be silicates, carbonates, a range of clays, organics, iron oxides, heavy metals, iron-aluminum phosphates and radionucleides. This variable composition and structure defines a wide range of processing methods ranging from little more than simple grinding and screening for the easily separable concentrates, to extensive washing (clays), flotation (silicates and carbonates), calcination (organics and carbonates), and magnetic separation (iron) for the tightly bound structures [2].

About 75% to 80% of the world's low-grade phosphate reserves are associated with carbonate gangue that is not amenable to treatment by the simple techniques of physical separation. The processing of sedimentary dolomitic/calcareous phosphate ore has numerous problems, the major of which is the similar surface properties of the carbonate and phosphate.[11] Carbonates are one of the undesired ingredients that are chiefly associated with sedimentary as well as igneous phosphate deposits. Although to varying degrees, carbonate is part of the crystal structure of the apatite found in sedimentary phosphate ores (francolite) and it is imperative to reduce the free carbonate contents of phosphate ores as much as possible. [11,21]

High carbonate content in phosphate rock increases sulphuric acid consumption during acidulation in the wet process for phosphoric acid production. Table 3 shows sulphuric acid requirement depending on CaO/P_2O_5 ratio.

Table 3. Sulphuric Acid Requirement versus CaO/P_2O_5 ratio. [16]

Grade of Rock	Low	Medium	High
CaO/P_2O_5 Ratio	1.70	1.50	1.35
Sulfuric Acid Requirement, ton/ton P_2O_5*	3.15	2.78	2.50

* *Assuming 94% recovery*

A wide variety of techniques have been proposed for the removal of carbonates from phosphate rocks. These techniques are briefly discussed next [11].

Attrition–acid scrubbing: This technique is generally recommended with or without dilute acids for igneous phosphates to remove free carbonates (dolomite/calcite) and iron mineral coatings, which are associated with both igneous and sedimentary phosphates as an epigangue. This is taken into consideration with desliming as a preliminary step for the flotation process. Attrition-acid scrubbing process may not be useful for low-grade ores containing endogangue, which is usually liberated at very fine grinding.

Gravity Separation: This method of concentration is employed profitably where predominant gangue minerals have comparatively higher or lower specific gravities differing at least by 1.0 from the phosphate mineral. In sedimentary carbonate phosphate ores, this may not be effective because of similar specific gravities (2.8 and 2.9) of both calcite/dolomite and apatite.

Heavy Media Separation: The preponderance of effort has been concentrated on the use of a heavy media cyclone. The heavy media technique provides an effective way for separating particles of differing specific gravities. However, the occurrence of a range of both dolomite/calcite (specific gravity = 2.8 to 2.9) and francolite (specific gravity = 2.8) in sedimentary phosphate ores contribute to a fuzzy separation.

Magnetic Separation: High-intensity or high-gradient magnetic separation can remove some of the Fe_2O_3 and Al_2O_3 from phosphate ores, although this also inevitably causes losses in P_2O_5, reducing the yield of the concentration processes. Magnetic separation can be very energy consuming and expensive. Therefore, cheaper and technically efficient alternatives, such as flotation, are preferred.

Calcination: Calcination is a rather mature and technically sound pyrometallurgical unit operation that is used industrially for the complete removal of carbonates from rock phosphate, particularly those that are high in calcareous gangues. Despite the high-energy consumption, calcination is recommended and practiced in countries where water is expensive in comparison to energy. Calcination is generally carried out around 750-900°C. After calcination of phosphorites, for decarbonization, with preservation of calcium and magnesium oxides formed in a free form, the oxides are removed by quenching and desliming of the solids using water.[17,18]

Froth Flotation: Phosphate ore is one of the most important minerals processed by flotation techniques. Flotation is efficient for the beneficiation of phosphate ores with silica gangues, but those with carbonaceous gangues are difficult to separate by flotation techniques due to the similarities in the surface properties of phosphatic and calcareous/dolomitic components. These properties are affected by the water chemistry of the surfactant-mineral. The removal of silica from igneous and sedimentary phosphate rocks is rather successful and well established due to the different surface properties of silicate and phosphate minerals.

All these techniques/processes, except for flotation, have limited applications for reasons including texture, crystallinity and contamination of phosphate ores, as well as high-energy consumption. To date, flotation has appeared to be an efficient and economical separation technique for the removal of carbonates. Flotation separation of the phosphate from a carbonate gangue has been performed successfully on igneous phosphate minerals. However, it cannot easily be applied to the sedimentary phosphates due to:

- their structural complexity and the simultaneous presence of different amorphous and porous phosphate types,
- their inability to liberate carbonaceous materials from phosphate in the flotation size range and
- very similar physico-chemical properties of carbonate and phosphate minerals.

Direct Flotation: Carbonate-phosphate separation can be affected by the direct flotation of phosphate. This becomes relatively complex in combination with reverse flotation because of the necessity for at least two distinct stages to separate carbonate and silica. Therefore, this process is best applied to feeds with low silica content or feeds from which silica has been removed by prior beneficiation processes.

Reverse Flotation: The development of the beneficiation methods of phosphate with carbonaceous gangue using reverse flotation involves carbonate recovery in froth and phosphate recovery in the residue. [11]

2.3. Physical Chemistry of Flotation

The basic phenomenon involved in flotation is that particles of an ore are carried upward and held in the froth by virtue of their being attached to an air bubble.[19] This is a dynamic process where surface reactions, collector-mineral interactions and bubble-particle attractions occur. For flotation to occur, a mineral-air interface must be created with simultaneous destruction of the water-air and mineral-water interfaces of equal areas.

Contact angle is the most important parameter in the flotation of minerals. Hydrophobicity of the surface is another phenomenon, which is important for separation of particles [20].

2.3.1. Surface Properties of Minerals

The basis of flotation process is the interfacial chemistry at the mineral surface. Generally, ore particles are impure and mineralogical heterogeneity can affect the surface properties of the particle. Particle shape and surface topography of the ore also affect surface properties [20]. Separation by flotation depends on the differences in the surface properties of the minerals. The floatability of a mineral is greatly affected by the change in the character of the surface of the mineral. Separation can be achieved by making some mineral surface hydrophobic and leaving some hydrophilic. In this process, bubble attachment can occur on hydrophobic surfaces where water wetting does not happen. Hydrophobicity can be obtained mostly by adding some collectors [21].

If a solid is brought into contact with an aqueous solution, the solid surface acquires a surface charge (a potential with respect to the solution) in one of the three ways, namely, ionization, lattice substitution or by ion dissolution. Then on the surface of the mineral, an unequal distribution of charges occurs. The interfacial system as a whole is electrically neutral because the surface charge is compensated by an equal charge distribution in the aqueous phase. The charge in solution together with the charge on the solid surface is referred to as electrical double layer (EDL). It consists of the so called Stern layer, which is thought as a fixed charge or surface charge attached to the particle or solid surface, and the diffuse Gouy layer, which is distributed more or less diffusely in the liquid in contact. [22] The detailed structure of the EDL can be seen in Figure 2.

The chemical compositions, stoichiometry and crystal structures of the solids in contact with water also play important roles in the degree of hydration that occurs at the solid-liquid interface and adsorption phenomenon that affects the flotation process. Surface charge is established by the potential determining ions (PDI). These ions include ions of which the solid is composed of, hydrogen and hydroxyl ions, collector ions that form insoluble metal salts with ions comprising the mineral surface, and ions capable of forming hydroxo-complexes with surface species. [23]

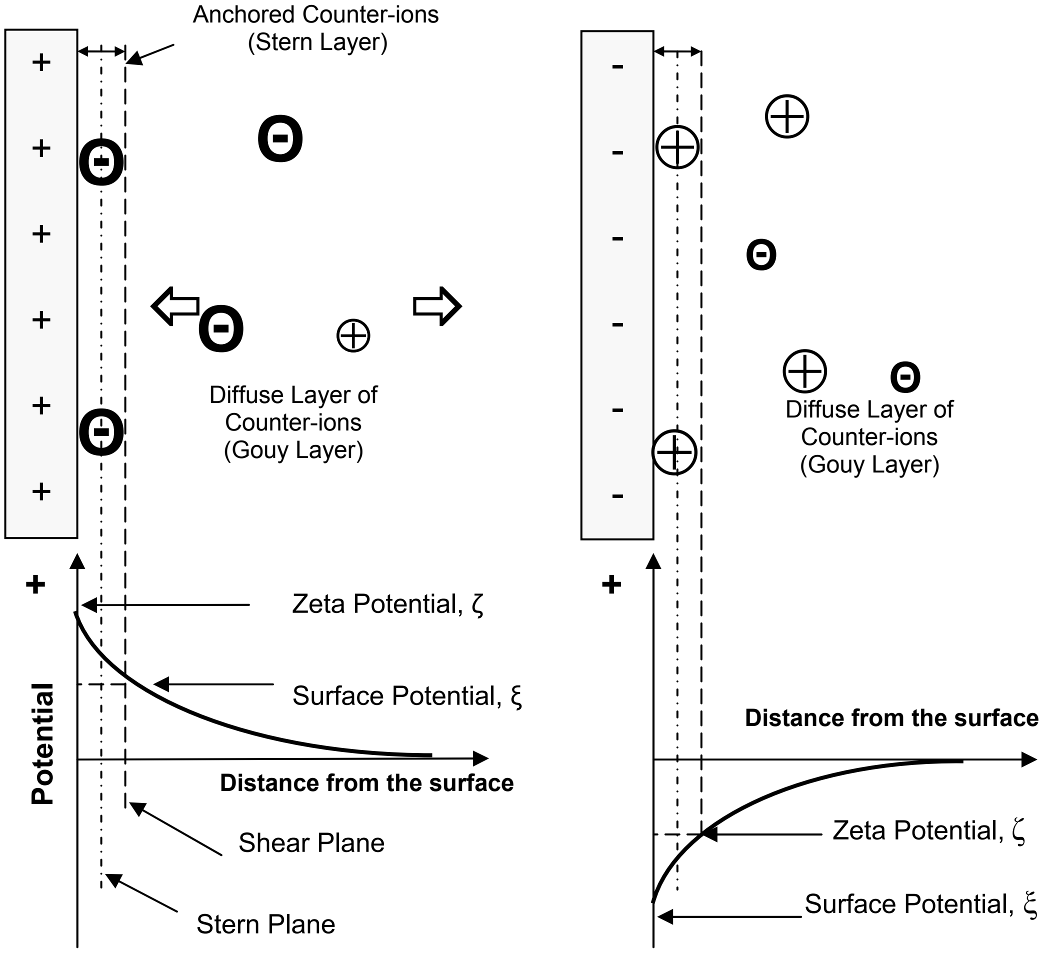

Figure 2. The Electrical Double Layer at a Mineral Surface in an Aqueous Solution. [23]

In an electric field, shear takes place between the Stern plane and the Gouy layer of a mineral. The charged particle with fixed layer will move in one direction and the diffuse layer of the counter-ions will move oppositely. The potential of the moving particle is called the zeta potential. The sign and magnitude of the zeta potential indicate the nature of the adsorbed ions and the relative magnitude of the potential in the solid phase. The magnitude of the zeta potential depends on the electrolytes in the solution. A high, positive zeta potential indicates that the mineral surface is dominated by cations. On the other hand, a high, negative zeta potential indicates that anions are dominant on the surface. A low zeta potential means that the surface is equally influenced by the cations and anions. At a certain concentration of PDI in the solution, the EDL will be absent, and the solid surface will show no net positive or negative charge and the zeta potential is zero. This point is termed as the point of zero charge (PZC), which is also known as the isoelectric point (IEP) [22].

2.3.2. Bubble Attachment Process

In order for the hydrophobic material to be carried together with the air bubbles, bubbles should attach on the surface of that mineral. Bubble attachment to a hydrophobic surface occurs when an aqueous film separating the bubble from the surface becomes unstable. Bubble starts to approach to the surface while aqueous film gets thinner, and then, it comes to a separation distance where the bubble may be distorted. The reason of thinning is the attraction forces between the particle and the bubble. The dissipation of kinetic energy of the particle on impact (dispersion forces), electrostatic interactions, capillary forces, and additional attraction forces determine the rate of thinning. If thinning comes to a critical value, rupture will happen. The interaction energy of the particle-water interphase determines the critical thickness of the film layer [23,25,26].

2.3.2.1. Contact Angle

The wetting characteristics of mineral surfaces are important in achieving selective flotation. The degree of wetting, that is the extent to which a given liquid will spontaneously wet a solid surface is important. The essential condition for froth flotation is that a particle of mineral, wetted by water, should become attached to an air bubble and be carried to the surface. The extent to which the water is displaced from the surface of the mineral, or in other words, the extent to which air/water and solid/water interfaces are replaced by an air/solid interface is characterized by the contact angle [22].

A droplet forms when a liquid is placed on a solid surface [26]. This droplet has a contact angle, θ, which describes the equilibrium state of an attached bubble where three-phase equilibrium is present [23,24]. Considering the gravity-free situation for a spherical particle, the particle may be entirely in phase A, or entirely in phase B, or it may be located in the interface, in which case both γ_{SA} and γ_{SB} (where, γ_{ij} represents the interfacial tension between phases *i* and *j*; for *i,* and *j* either of mineral, air bubble and water) contribute to the total surface energy of the system. It may be shown that if there is a finite contact angle, θ_{SAB}, the stable position of the particle is at the interface. Measured actual detachment forces are in the range of 5 to 20 dyne [19].

The restoring force stabilizing the particle at the interface varies approximately with the particle radius. For the particle to remain floating, this restoring force must be greater than or equal to that of gravity. Since gravity varies with the cube of the radius, there is a maximum size of particle that can remain at the interface. In practice, it may be possible to float somewhat larger particles than the theoretically maximum sized particles. If the particle has an irregular shape, it will tend to float such that the three-phase contact occurs at an asperity since the particle would have to be depressed considerably for the line of contact to advance further. The preceding upper limit to particle size can be exceeded if more than one bubble is attached to the particle [19].

The attachment of a bubble to a surface may be divided into steps in which the bubble is first distorted, and then allowed to adhere to the surface. The distortion step is not actually unrealistic, as a bubble impacting a surface does distort, and only after the liquid film between it and the surface has sufficiently thinned does adhesion suddenly occur [19].

The contact angle is defined by Young's equation,

$$\gamma_{ma} = \gamma_{mw} + \gamma_{wa} .\cos\theta \qquad (1)$$

However, this equation is impractical because γ_{ma} cannot be measured. The free energy change per unit area corresponding to the attachment process (displacement of water by the air bubble) is given by Dupre's equation,

$$\Delta G = (\gamma_{wa} + \gamma_{ma}) - \gamma_{mw} \qquad (2)$$

Then, combining the two equations above, a measurable equation is obtained,

$$\Delta G = \gamma_{wa} (1+\cos\theta) \qquad (3)$$

ΔG can also be described in terms of work of adhesion and work of cohesion of water,

$$\Delta G = W_A - W_C \qquad (4)$$

The work of adhesion is defined as the work required to remove liquid from the solid leaving an adsorbed water layer in equilibrium with a saturated gas phase. The work of cohesion for water is the energy to create new surface at the air/water interface.

For an effective attachment, ΔG must be positive. When the contact angle is zero, ΔG is also zero and work of adhesion is equal to the work of cohesion. This means that no work has to be done to separate the phases. In this situation, the air bubble does not displace the liquid and water spreads on the solid. A hydrophilic surface is obtained.

When the contact angle is 180°,

$$\Delta G = 2\gamma_{wa} \tag{5}$$

which means that the mineral is wetted completely by the air. There is complete displacement of water, and the solid surface is hydrophobic [19]. The three-phase equilibrium contact can be seen in Figure 3.

For effective separation, contact angles greater than 20° are needed. As the hydrophobicity of the mineral increases, contact angles also get higher. For highly water-repellent surfaces, contact angles are greater than 150° [25].

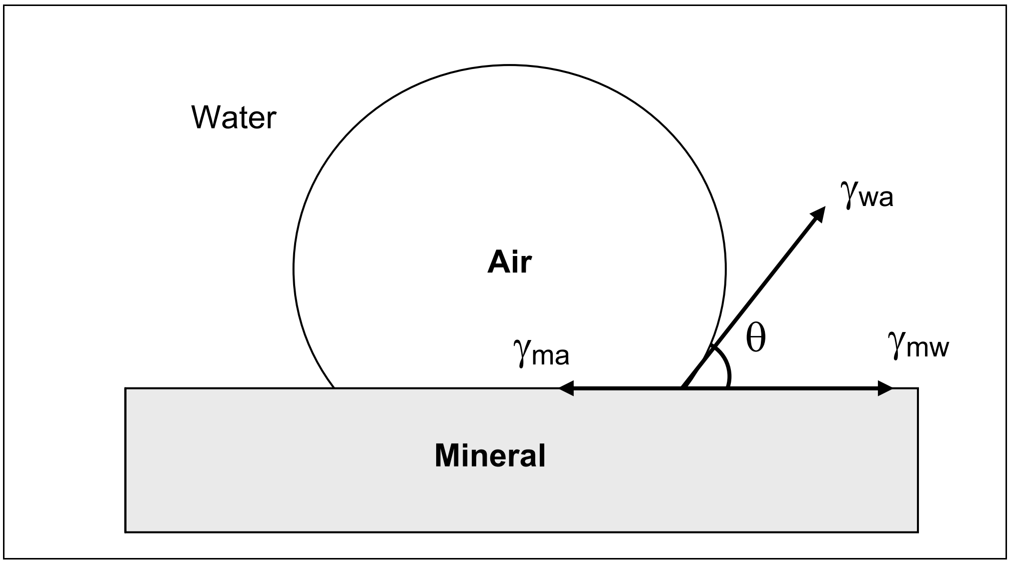

Figure 3. Representation of the Three-Phase Equilibrium Contact Between Air, Water and Mineral Surface [23,24].

2.4. Chemical Reagents Used in Flotation

There are several chemical reagents used in flotation to achieve the appropriate conditions on the surfaces of bubbles and solids. These are basically collectors, frothers, and modifiers such as, pH regulators, depressants, dispersants, activators, wetting agents, resurfacing agents.

2.4.1.Collectors

In flotation, the hydrophobicity of the solids is induced by the addition of chemical reagents called collectors. They are organic compounds that function in the solid-liquid interface. A characteristic of most collectors is that they are complex molecules, unsymmetrical in structure and consisting of two parts, one polar and one nonpolar. The nonpolar end is almost always a long-chain or cyclic hydrocarbon group that is hydrophobic [23].

The collector must be able to attach to the solid, and it is done through its polar end, which is typically an ionic group termed the solidophil group. When this group of a suitable collector contacts a mineral at a surface site that can chemically interact with the solidophil group, the collector bonds to the surface of the mineral by chemisorption or ionic bonding. The nonpolar end of the collector then orients outward from the solid surface forming a nonpolar chemical envelope surrounding the solid particle, inducing hydrophobic behavior on an otherwise hydrophilic solid surface. The solid particle can then more readily attach to an air bubble.

It should also be noted that the strength of the hydrophobicity induced by the collector is directly related to the length of the hydrocarbon group of the collector, while the strength and the type of solidophil group control selectivity of the collector’s ionic bonding. Collectors are used in small amounts just enough to form a monomolecular layer on particle surfaces. As the concentration is increased the collector tends to float other minerals reducing selectivity as well as increasing the cost. Using excessive concentrations of collectors also have an opposite effect on the recovery of valuable minerals due to the formation of possible multi-layers of collector on the mineral surface. Thus, the hydrophobicity of the surface is reduced as well as its floatability. Consequently, a key to successful flotation is to selectively induce hydrophobicity on the desired material to be recovered while retaining hydrophilicity of the non-desirable material using a suitable collector [23].

There are mainly three different types of collectors as shown in detail in Figure 4. Anionic collectors are those in which the anion renders the mineral surface water repellent. Cationic collectors are those where water repellence is ensured by the cation [22].

Anionic collectors are widely used to float metal oxides and sulfides. For example, sodium oleate, $C_{17}H_{33}COONa$, is a widely used collector for minerals separation. It is comprised of a long-chain, nonpolar hydrocarbon group, R = [$C_{17}H_{33}$], which is hydrophobic and a polar carboxyl group, [COONa], which is the solidophil group. Upon dissociation in water, the solidophil group becomes anionic. Other widely employed anionic collectors include the xanthates, containing bivalent sulfur, that are highly selective collectors in the separation of sulfide minerals. Fatty acids are used for the flotation of non-sulfide minerals such as apatite, calcite, feldspar and hematite [22].

Cationic collectors are less widely used. The most common types contain amine groups, such as aniline and pyridine. They are also typically water insoluble and require the presence of acids to induce solubility. Cationic collectors are used for silicates and other oxides, including some rare earth oxides [22].

Non-ionic collectors are largely insoluble and they are used in the flotation of coal and graphite [22].

The mechanism of mineral-collector bonding depends on the collector type and the nature and charge of the mineral surface. It can occur via physisorption or chemisorption. In the case of calcite and apatite, oleic acid is adsorbed on the surface through chemical bonding. There are several modes of chemical interaction of the collector with the mineral surface. In the case of physisorption, the collector does not interact chemically with the mineral surface. The attachment is due to van der Waals forces, and the Gibbs free energy of adsorption is relatively low. In the case of chemisorption, when the collector interacts chemically with the mineral surface without movement of the metal ions from their lattice sites, this produces monolayer coverage. When the surface chemical reactions are associated with movement of metal ions from their lattice sites, multilayers may form. If a reaction occurs in the bulk solution between dissolved ions and the collector, a hydrophobic surface will only be established if there is a bulk precipitation on the mineral surface [25].

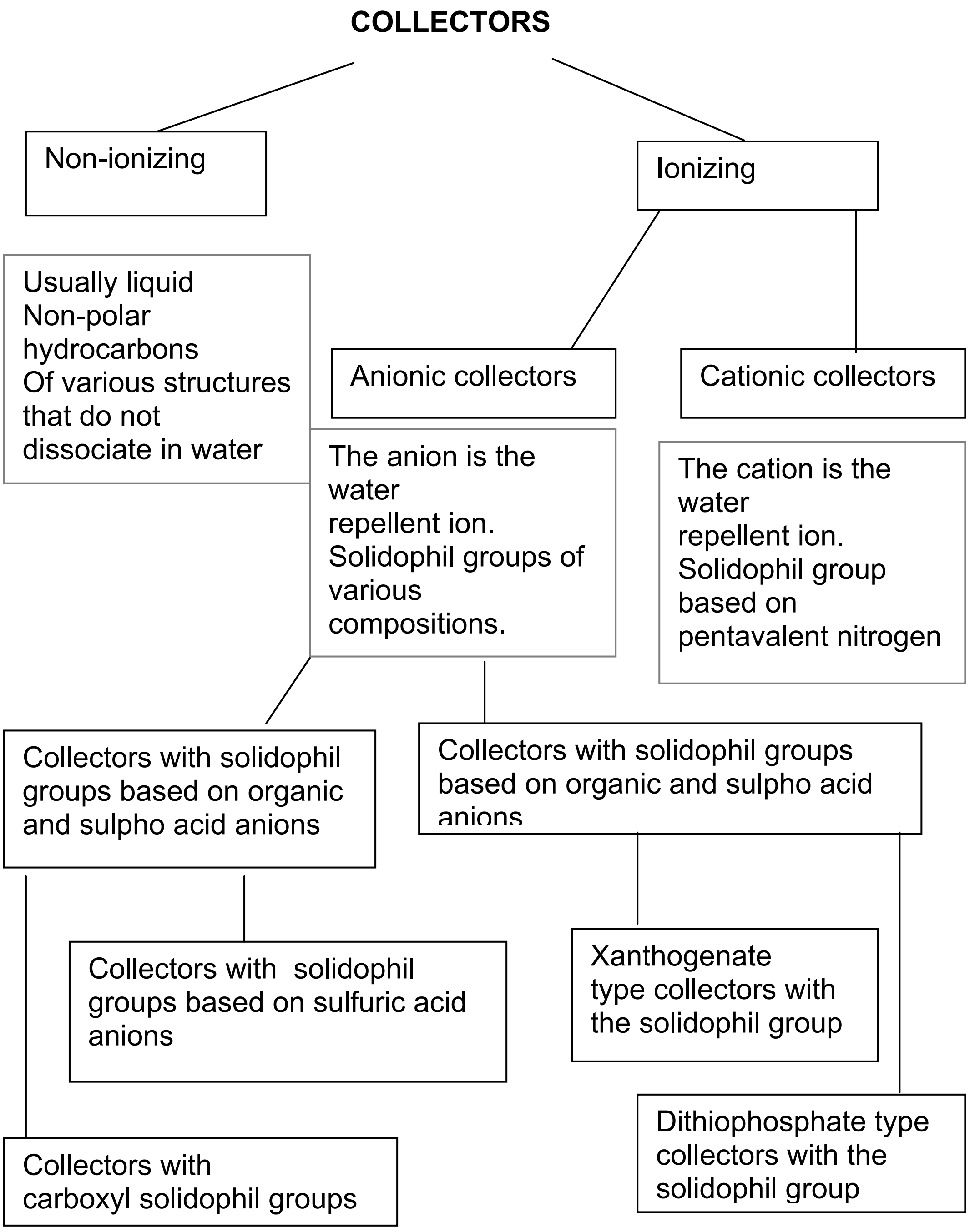

Figure 4. Classification of Collectors [23].

2.4.2.Frothers

Another important component in order to achieve a successful flotation is the frothers. A frother is a surface-active chemical whose principal function is to increase the dispersion of air significantly at a given aeration rate in the pulp phase by producing small bubbles; this is done through the reduction of the surface tension at the air-water interface [28].

Frothers, like collectors, are typically comprised of both a polar and nonpolar end. The nonpolar hydrophobic ends orient themselves into the air phase. Bubble wall strength is enhanced by simultaneous strong polar-group and water-dipole reaction (hydration) at the air-liquid interface resulting in greater bubble stability due to a localized increase in surface tension [6].

Frothers are generally classified by their polar groups, the most commons being the hydroxyl ($-OH$), carboxyl ($-COOH$), carbonyl ($=C=O$), amino ($-NH_3$), and sulfo ($-OSO_2OH$ and$-SO_2OH$) groups. However, a frother must be at least slightly soluble in the liquid medium. Increasing the straight-chain-hydrocarbon length will eventually lead to too low a solubility for effective frothing. Thus, a suitable frother must provide a balance between sufficient nonpolar interaction with air and solubility in water. With respect to the polar groups, one or two are usually sufficient to interact at the liquid-air interface to provide sufficient frothing properties, and additional polar groups provide little benefit [6]. Types and formulas of frothers are given in Table 4.

Frothers also reduce the speed of bubble. This gives a chance for a mineral particle and a bubble to contact and attach in better conditions. The reduction in the bubble speed also reduces the force of collisions between bubbles causing a stable froth. Frothers have other valuable uses in a flotation process. They result in the formation of finer bubbles improving the air dispersion in the cell, preventing coalescence of separate air bubbles, affecting collector action [23].

Table 4. Examples of Frothers and Their Formulas [6]

Frother	**Formula**
Aliphatic Alcohols MIBC (4-methyl-2-pentanol) di-acetone alcohol 2-ethyl 3-hexanol	$CH_3(CH_2)nCH_2OH$, n = 3–5 $CH_3CH(CH_3)CH_2CH(OH)CH_3$ $(CH_3)_2(OH)CH_2COCH_3$ $CH_3(CH_2)_3CH(C_2H_5)CH_2OH$
Cyclic Alcohols pine oil (terpineol)	$C_{10}H_{17}OH$ $C_{10}H_{16}O$
Phenols cresol xylenol (e.g., xylitol	$CH_3C_6H_4OH$ $HOCH(CHOH)_3CH_2OH$
Alkoxyparaffins 1,1,3-triethoxybutane	$CH_3CH_2CH(OC_2H_5)CH(OC_2H_5)_2$
Polyglycols poly(propylene glycol) monalkyl ethers poly(ethylene glycol)s	$R(OC_3H_6)nOH$, n = 2–5, R = CH_3, C_4H_9 $R(OC_2H_4)_nOC_2H_4OH$, n = 2-5
Other sulfo-cetyl alcohol sulfo-cetyl alcohol	$CH_3(CH_2)_{14}CH_2OSO_2OH$

2.4.3. Modifiers

Modifiers are chemical reagents such as activators, depressants, dispersants, wetting agents, resurfacing agents and pH regulators, which are commonly used in flotation. These additional reagents are used to achieve a more selective separation between the solid species desired and undesired to float. They modify the action of the collector either by intensifying or reducing its water-repellent effect on the mineral surface. These reagents are used to change the solid surface properties, or pulp alkalinity [22].

2.4.3.1. Activators

Activators may be added to chemically resurface the solid to increase the interaction with collectors that are otherwise ineffective alone. They change the solid surface so that they intensify the action of collector. They change the chemical composition of the solid surface either by forming a surface compound or by replacing a site in the solid lattice and by this way; they intensify the action of collector [25].

2.4.3.2. Depressants

These chemicals depress the action of collectors. The ions of depressants have the same charge as that of the collector ions and hinder the collector attachment, increase solid hydration and detach collector ions from the mineral surface. Commonly used depressants are cyanide, zincsulfate, ferrosulfate, sulfur dioxide, potassium dichromate, sodium hydrosulphide, water glass, starch, dextrin, and lime [25].

2.4.3.3. Dispersants

Dispersants act to break agglomerated particles (extremely fine slimes) apart so that single particles interact with the collectors and air bubbles. These agglomerated particles are especially the extremely fine (slimes) and these slimes will be adsorbed on the surfaces of the solid to be floated and under this condition flotation reagents will lose their effectiveness and flotation will be impaired. Dispersants commonly used are sodium silicate, starch, and polyphosphates [25].

2.4.3.4. pH Regulators

Pulp alkalinity affects the reagent concentration, surface charge, and collector adsorption on solid surface. Regulators are commonly used since the hydrophobicity of systems is often optimal within a certain pH range. Frothers also often need a certain pH range in order to form stable bubbles. Carefully controlled pH helps the selective flotation of desired solids. There is a critical pH at which the particle floats and critical pH value depends on the collector concentration, collector type and pH value. Lime, Na_2CO_3, NaOH, NH_4OH are the common pH regulators to create an alkaline medium and for acidic medium sulfuric acid, hydrochloric acid, oxalic acid etc. are used [25].

2.4.3.5. Wetting Agents

Wetting agents are used to increase the wettability of the surface that is not to be floated. Reagents that are commonly used as wetting agents are diethylhexyl sodium sulphosuccinate (aerosol), sodium silicate, and organic colloids [25].

2.4.3.6. Resurfacing Agents

Resurfacing agents resurface or plate the surface of specific minerals. Examples of these reagents are the salts of Ba, Ca, Cu, Zn, Ag. These reagents promote the adsorption of hydrophobic hydrocarbon groups to the surface to promote flotation [25].

2.5. Factors Affecting Flotation

2.5.1. Effect of Mineral Properties

Mineralogical composition, structure, and presence of impurities predetermine the required flotation conditions. The separation of mineral depends on the associated minerals. For example, phosphate-silica couple is much more easier to process than phosphate-calcite couple [29].

2.5.2. Effect of Particle Size and Shape

Particle size is one of the most important parameters affecting flotation. Flotation gives best results with fine particles of uniform size and with particle sizes smaller than 100 mesh (0.150mm). The optimum particle size depends on the surface properties, specific gravity and shape of the particles. The minerals with stronger water-repellent properties and lower specific gravity can be floated in much coarser size.

The mineral must generally be crushed, ground and de-slimed to get the maximum liberation of the valuable materials. The more the mineral is ground, the more the liberation of the valuable minerals and the higher the rock quality. However, excessive grinding results in a high amount of slime production. In order to get rid of the slimes, which may interfere with flotation, de-sliming must be made, however; this causes the loss of valuable minerals that may not be recoverable. Presence of slimes brings about a reduction in the speed and selectivity of flotation, leads to increased reagent consumption and destabilization of the froth [29].

2.5.3. Effect of Pulp Density

Pulp density is the weight percentage of solids in the pulp mixture. Increasing pulp density increases the amount of solids processed. The retention time of the pulp and volumetric reagent consumption increases with increasing pulp density. It would appear that the best results might be obtained by employing pulp of maximum density, since this will result in increased output of the flotation machine. However, excessive pulp density will result in an adverse effect such as, deterioration in pulp aeration and floatability of large particles, increased floatability of fine gangue particles, and reduced quality of concentrate [29].

2.5.4. Effect of Temperature

Pulp temperature influences the speed of reactions between reagents and phase interfaces. In general, a rise in temperature improves flotation but reduces selectivity. The effect of temperature is much less when using xanthates compared to fatty acids.

2.5.5. Effect of Pulp pH

Pulp pH is critical for separation of minerals, their optimum recovery and grade of the concentrate. Generally, there is a pH above which the mineral will not float. Change in pH indirectly affects the potential determining ions through chemical equilibria. The reactions on the surface of the minerals are controlled by the pH of the pulp [29]. The reactions taking place for both calcite and apatite have been summarized in Table 5.

At lower pH values, CO_3^{2-} ion from calcite would react with H^+ and $CaCO_3$ (s) forms, whereas, at higher pH, Ca^{2+} precipitates as hydroxide. The related reactions are as follows:

$Ca^{2+} + HCO_3^- \Leftrightarrow CaHCO_3^+$ (1)

$CaHCO_3^+ \Leftrightarrow H^+ + CaCO_3$ (aq.) (2)

$CaCO_3$ (aq.) $\Leftrightarrow$ $CaCO_3$ (s) (3)

and,

$Ca^{2+} + OH^- \Leftrightarrow CaOH^+$ (4)

$CaOH^+ + OH^- \Leftrightarrow Ca(OH)_2$ (aq.) (5)

$Ca(OH)_2$ (aq.) $\Leftrightarrow$ $Ca(OH)_2$ (s) (6)

Presence of $Ca(OH)_2$ (s) may be undesired since it forms on the apatite surface and causes phosphate depression. [29]

Table 5. Equilibria Controlling the Dissolution of Calcite and Apatite in Water [24].

		K_{sp}			**K_{sp}**
Calcite					
$CaCO_3$ (s)	$\leftrightarrows Ca^{2+} + CO_3^{2-}$	$10^{-8.4}$	$Ca^{2+} + HCO_3^-$	$\leftrightarrows CaHCO_3^+$	$10^{0.8}$
$CO_3^{2-} + H^+$	$\leftrightarrows HCO_3^-$	$10^{10.3}$	$Ca^{2+} + CO_3^{2-}$	$\leftrightarrows CaCO_3$ (aq)	$10^{3.3}$
$HCO_3^- + H^+$	$\leftrightarrows H_2CO_3$	$10^{6.3}$	$Ca^{2+} + H_2O$	$\leftrightarrows CaOH^+ + H^+$	$10^{-12.9}$
CO_2 (g) + H_2O	$\leftrightarrows H_2CO_3$	$10^{-1.5}$	$Ca^{2+} + 2H_2O$	$\leftrightarrows Ca(OH)_2 + 2H^+$	$10^{-22.8}$
Apatite					
$Ca_{10}(PO_4)_6(OH)_2$ (s)	$\leftrightarrows 10Ca^{2+} + 6PO_4^{3-} + 2(OH)^-$				10^{-118}
$PO_4^{3-} + H^+$	$\leftrightarrows HPO_4^{2-}$	$10^{12.3}$	$Ca^{2+} + HPO_4^{2-}$	$\leftrightarrows CaHPO_4$ (aq)	$10^{2.7}$
$HPO_4^{2-} + H^+$	$\leftrightarrows H_2PO_4^-$	$10^{7.2}$	$CaHPO_4$ (aq)	$\leftrightarrows CaHPO_4$ (s)	$10^{4.3}$
$HPO_4^- + H^+$	$\leftrightarrows H_3PO_4$	$10^{2.2}$	$Ca^{2+} + H_2 PO_4^-$	$\leftrightarrows CaH_2PO_4^+$	$10^{1.1}$
$Ca^{2+} + H_2O$	$\leftrightarrows CaOH^+ + H^+$	$10^{-12.9}$			
$Ca^{2+} + 2H_2O$	$\leftrightarrows Ca(OH)_2 + 2H^+$	$10^{-22.8}$			

Also, in acidic media, adsorption of $CaHPO_4$ (aq.) on the surface of phosphate particles prevents surfactant ions from approaching the surface of the particle, and again, phosphate is depressed.

Pulp pH also affects the adsorption mechanism of the fatty acid collectors. In order to achieve cationic collector adhesion on to the surface of the particle, pH value must be lower than the pH value corresponding to the isoelectric point. In anionic flotation of phosphates, Ca^{2+} present in the solution affects the grade of the concentrates by activating quartz through formation of calcium-bearing precipitates at high pH values [30].

CHAPTER 3

LITERATURE SURVEY

There is a lot of research work going on flotation technology and flotation of phosphate rock. There is an increasing demand on phosphate products as the use of fertilizers keep on increasing day by day. Until 1980’s, for about 50 years, flotation had been applied successfully to sedimentary ores with siliceous gangues. After then, the depletion of silica-rich phosphate rock deposits have led the researchers to find out methods to evaluate the carbonate-rich deposits [21].

Phosphate rocks contain silica and carbonates as the main impurities. By the help of the different surface properties of siliceous impurities and phosphate particles, it becomes easier to separate them. However, carbonates and phosphates have very similar surface properties, and this makes it hard to separate the two from each other while upgrading the phosphate rock.

Flotation is an economical and efficient separation method for carbonate removal. Separation of the phosphate from a carbonate gangue by flotation cannot be applied easily to the sedimentary phosphates because carbonate and phosphate exhibit very similar physico-chemical properties. The high degree of substitution in the crystal lattice of apatite by CO_3^{-2} and OH^- for PO_4^{-3} is the major problem in the separation of carbonates from sedimentary rocks [11]. The other problem is the friable nature of the sedimentary minerals which causes more slime production during conditioning stage. Also, the specific surface areas of phosphate particles are large due to the irregular and porous/microporous texture [30]. This results in high reagent consumption during concentration and reduces adsorption selectivity of the collector. Another reason is the inability of sedimentary phosphates to liberate carbonaceous materials from phosphate within the flotation size range [11].

Depending on the relative concentrations of the impurities, i.e. silica and carbonates, flotation can be made either in one stage or in two stages. In this study, Mazıdağı phosphate rock sample analyses for silica content revealed a concentration of 1% SiO_2, so that one-stage flotation has been made.

Anazia and Hanna developed a technique of one-stage flotation that was employed without the specific use of a phosphate depressant, and without conditioning the pulp with the collector. The rocks used were dolomitic phosphate ores from India and China, containing 18-23% P_2O_5 initially. The experiments were done with a pulp density of 18-20 w% and a pH of 4 - 4.5. The rock was upgraded to 36-38% P_2O_5 with 80% recovery in the froth [32].

Shao and Guo worked on dolomite removal from Yichang phosphate ore with 26.6% P_2O_5. They used a sulforganic depressant and Na-oleate as a collector. A concentrate with 31.59% P_2O_5 and 83.87% recovery of P_2O_5 could be obtained at pH 9 using -140/+380 mesh feed in one-stage flotation [33].

Elgillani and Abouzeid studied on depressant effect on flotation of dolomitic phosphate ores from Red Sea Coast, Egypt. The depressants tried were H_2SO_4, $H_2C_2O_4$, H_3PO_4 and KH_2PO_4. Potassium oleate was used as the collector at a pH of 5.8 with a feed of size -125 μm and grade 20% P_2O_5. The resulting concentrates were 27.6%, 30%, 31.6% and 31.8% P_2O_5 for H_2SO_4, $H_2C_2O_4$, H_3PO_4 and KH_2PO_4, respectively. It could also be achieved to concentrate the feed to 32.5% P_2O_5 concentrate with 79% recovery with a mixture of KH_2PO_4 and $H_2C_2O_4$ [34].

Shao et al. examined the effect of pH on selectivity of a specific amphoteric collector (dodecyl-N-carboxyethyl-N-hydroxyethyl-imidazoline) in the flotation of a mixture of francolite and dolomite containing 26.2% P_2O_5 and 7.21% MgO. Dolomite recovery increased to 80% in acidic medium, and to 95% in the alkaline range of pH. A concentrate with 35.2% P_2O_5 content, 2% MgO and 90% P_2O_5 recovery could be obtained by one-stage flotation at a pH of 9 with a feed of size -140/+380 mesh. In addition to this, a comparative study was carried out for the amphoteric collector and sodium oleate. It was observed that the amphoteric collector was much selective for dolomite than sodium oleate and had no sensitivity for dissolved ions in the flotation system [35].

Awadallah et al. used sedimentary siliceous West Sibaiya ores of different initial P_2O_5 contents. One-stage flotation was applied in alkaline media using rice bran oil as a collector and sodium silicate as a silicate depressor. In this work, -250/+40 micron size feeds with 30% pulp densities were used. Concentrates with P_2O_5 contents greater than 30% could be obtained, even 34.70% P_2O_5 content with 52 % recovery could be achieved with a feed of 28.20% P_2O_5 [36].

Abdulrazik tried a statistical approach to find optimum conditions for one-stage flotation of sedimentary Saudi phosphate deposits with 51% carbonate content. It was shown that P_2O_5 content could be increased from 26.6% to 36.7% with 92.1% recovery by one stage flotation employing oleic acid as collector in slightly acidic conditions. An improvement in the separation efficiency was obtained at short conditioning times when Na_2SO_4 was used as a depressor. A response surface method revealed that the most significant parameter was the pulp density (10%). This research also revealed an optimum particle size as -250/+150 microns [29].

Rao et al. used -200 mesh phosphate rock, containing 20% P_2O_5 and 44% CaO. Fluosilicilic acid and starch were employed as depressants, but no satisfactory results were obtained. On the other hand, depressing the phosphate with K_2HPO_4_by using oleic acid yielded a product with a grade of 27.6% P_2O_5 and 60% recovery [37].

Duman concentrated Mazıdağı-Taşıt phosphate ore of -149/+74 micron size, with 10.4% P_2O_5 and calcite as the main gangue mineral. P_2O_5 content was increased to 26.53 wt % P_2O_5 with a recovery of 60% by reverse flotation technique. The collector used was oleic acid and the depressant was a combination of phosphoric acid and aluminum sulphate-sodium tartrate complex. Pulp density was 20% and pH was 6.5. Direct flotation was also tried using amine types and fatty acid collectors but they did not give any satisfactory results. Moreover, other separation techniques such as gravity concentration by means of tabling and heavy media methods did not reach any success. Also, the effect of desliming on the concentrate grade and the recovery of flotation system had been investigated. However, grades above 30% P_2O_5 could not be achieved [38].

Abdel-Khalek studied flotation of sedimentary Egypt phosphate ores containing 20.9% P_2O_5 and 25.8% silica. The feed used was -150/+45 micron size. It was observed that no separation could be made with one-stage floattion. Moreover, two-stage flotation where silica is depressed floating carbonate and phosphate proved to be unsatisfactory However, anionic (oleic acid) flotation of carbonate using H_3PO_4 as a phosphate depressant, at pH 5.5 in the first stage, followed by a second stage for amine flotation of silica at pH 7, resulted in 30.7% P_2O_5 content product with 72.6% recovery. It could be concluded that better selectivity was achieved by using phosphoric acid as a phosphate depressant [30].

Henchiri et al. concentrated Tunisian dolomitic-siliceous phosphate ores by two-stage flotation. Using phosphoric esters as the collector, a product with 28.1% P_2O_5 content and 75.3% recovery was achieved. Dolomite and phosphate were floated simultaneously depressing silica in the first cell. Then, in the second stage, a selective flotation of dolomite and phosphate was attained at pH 5 [39].

Ünal has worked on Mardin - Mazıdağı phosphate rock. Particles of sizes between 210 microns and 75 microns were used for both one-stage and two- stage flotation studies. Several depressants and combinations of them were tried such as H_2SO_4, KH_2PO_4, H_3PO_4. Starting with an ore sample containing 19.4% P_2O_5, 19% SiO_2 and 41% CaO, at the end of two stage flotation, 30% P_2O_5 concentration was obtained with 47% recovery. In the first stage, calcite was floated using oleic acid as collector while phosphate mineral was depressed by phosphoric acid at pH 5.5. In the second stage, using NaOH, pH was increased to 9 and sodium silicate was used to depress silica and phosphate mineral was floated with oleic acid [21].

CHAPTER 4

EXPERIMENTAL

4.1. Materials

The chemicals used in the experiments and analyses are listed below:

- Phosphoric acid (H_3PO_4) 85%, produced by J.T. Baker
- Nitric acid (HNO_3) 65%, produced by J.T. Baker
- Hydrochloric acid (HCl) 36-38%, produced by J.T. Baker
- Perchloric acid ($HClO_4$) 60-62%, produced by J.T. Baker
- Kerosene (white spirit) obtained from Petroleum Research Center of Petroleum and Natural Gas Engineering Department, METU.
- Ammonium Molybdate crystals ($(NH_4)_6Mo_7O_{24}.4H_2O$), produced by Matheson Coleman & Bell (MCB)
- Ammonium Metavanadate powder (NH_4VO_3), produced by Sigma
- Potassium Dihydrogen Phosphate (KH_2PO_4), produced by Sigma

4.2. Experimental Set-up

In this study, there are three steps of experimental work. First stage is the crushing and grinding to achieve particle liberation. Then comes, separation of particles by froth flotation. Finally, flotation products are analyzed to obtain the P_2O_5 and $CaCO_3$ contents.

4.2.1. Crushing, Grinding and Sieving Equipment

Phosphate rock has to be crushed and ground before doing flotation experiments in order to ensure particle liberation. A jaw crusher, a rod mill, and a hammer mill were used for crushing and grinding. For the classification of the particles, ASTM standard sieves (50 cm in diameter) and a sieve shaker could be utilized. However, in this study, desliming and sieving were carried out together by using water. The sieve sizes used in the classification of the particles were: 297, 250, 210, 150, 125, 90, and 53 μm.

4.2.2. Flotation Set-up

The equipment for the flotation experiments can be listed as follows:

1) Denver D-1 type laboratory flotation machine (Fig. 5)
2) Froth collection pan
3) Froth skimmer
4) Water hose
5) Stop-watch
6) pH meter

7) Filtering flask and Buchner funnel to filtrate the flotation samples
8) Whatman 42 filter paper
9) Pipettes or syringes for reagent injection
10) Drying oven
11) Laboratory mixer

A 5-liter cell was used for flotation experiments. Denver flotation machine has a rotor-disperser assembly. Air is broken into small bubbles by the disperser. The rotor has a speed of 1200 rpm. Memmert type oven was employed in the experiments to dry the flotation product samples.

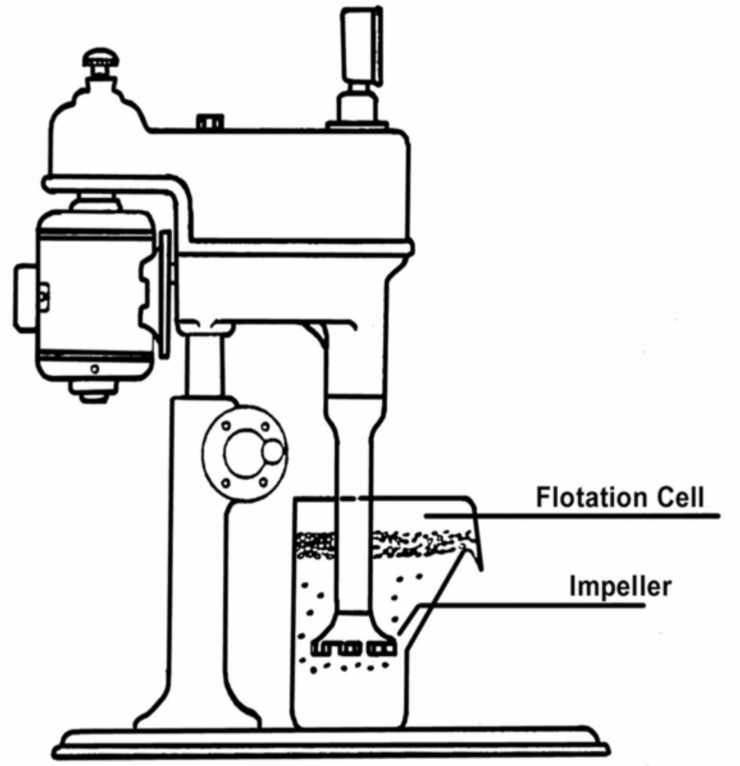

Figure 5. Denver D-1 type flotation machine.

4.2.3. Chemical Analysis Equipment

The chemical analyses of the samples were made by using two different spectrophotometers. Philips PU 9200X model atomic absorption spectrophotometer was utilized to determine the Ca content and using Hitachi U-3310 type double beam UV spectrophotometer, P_2O_5 content of the samples were determined.

4.3. Experimental Procedure

4.3.1. Grinding Experiments

Phosphate rock from Mardin-Mazıdağı was crushed and ground using a jaw crusher, a hammer, a rod mill and sieves were used to obtain classes of different particle sizes.

The following procedure was followed in the grinding experiments:

- The rock was put in the jaw crusher, and the products were sieved to separate the particles of size +297 micron.
- The upper cut (+297 micron) of the jaw crusher was fed to the hammer mill and after 45 minutes of operation, the machine was stopped.
- Then the product of hammer mill was sieved and deslimed at the same time using water by making use of a cascade of sieves of sizes 53, 90, 125, and 150 microns.
- The material left on each sieve was then dried in ovens, but the material on +150 micron sieve was taken to the rod mill for further grinding.

- Grinding was stopped when the amount of the hard material became insignificant with respect to initial amount and it seemed not to be ground further,

- After all the material had dried (including the rod mill products after desliming and sieving as mentioned above) rocks of each particle size were mixed thoroughly by coning and quartering method.[39]

Having carried out this procedure, the material is ready to be used as feed for the flotation experiments.

4. 3. 2. Flotation Experiments

The separation of apatite from calcite was done by one-stage flotation. The collector used was a mixture of oleic acid and kerosene (1:3 by volume) in acidic pH. Kerosene also helped in the frothing action. In order to regulate pH, H_3PO_4 was used which also functioned in phosphate depression.

The following experimental procedure was applied during the one-stage flotation experiments:

- Weigh the necessary amount of feed for 10% pulp density.

- Put 5 liters of water into the flotation cell. It is better to put somewhat less than 5 liters to prevent material flowing into the froth collection pan during air injection. Dump the feed sample and add measured amount of acid and start the timer. At the same time, turn on the mixer and insert the pH probe. Make sure that the pH value is constant by adding acid when necessary.

- Add measured amount of oleic acid mixed with kerosene after the acid conditioning time period has elapsed.

- Turn on the flotation machine with stopping the mixer right after the collector conditioning time ends. Use froth skimmer to remove the entire floating mineral to the pan. To maintain the pulp level constant inside the cell, add required amount of water, which would also function as wash water. Keep controlling the pH and stop the machine when the specified flotation time ends (3 minutes in our experiments).

- Filter the tail and froth using filtering flask and Buchner funnel under vacuum, and dry overnight in an oven at 70^0 C,

- Weigh the dry samples and determine their P_2O_5 and CaO contents.

4.4. Chemical Analyses

CaO and P_2O_5 analyses of feed, tail and froth samples were performed using Atomic Absorption and a Double Beam UV Spectrophotometer, respectively. The process involves digestion of the rock in a mixture of hydrochloric acid and nitric acid, and then numerous dilutions are made before analyzing. The detailed procedures of P_2O_5 and CaO analyses are given in Appendices A and B.

CHAPTER 5

RESULTS and DISCUSSION

- **Chemical Analysis of the Rock Sample**

A complete chemical analysis of the phosphate rock used is given in Table 6.

Table 6. Chemical Analysis of the Feed Material.

P_20_5 (%)	SiO_2 (%)	CaO (%)	Al_2O_3 (%)	SrO (%)	Na_2O (%)	MgO (%)	Fe_2O_3 (%)	F (%)	LOI* (%)
20.5	1.0	44.5	0.5	<0.1	0.5	0.2	0.6	1.9	30.3

** LOI: Loss on ignition*

Flotation experiments were conducted with feeds of three different particle sizes: +53/-90, +90/-125 and +125/-150 microns.

Feed was analyzed again to determine the concentrations of P_2O_5, CaO and SiO_2 at these particle sizes and they are given in Table 7.

Table 7. Assays of Feeds of Different Particle Sizes.

Feed particle size (microns)	P_20_5 (%)	CaO (%)	SiO_2 (%)	Cao/P_2O_5
+53 / -90	13.542	46.23	1.00	3.41
+90 / -125	13.906	42.85	1.00	3.08
+125 / -150	20.122	43.57	1.00	2.16

- **Experimental Parameters Studied**

The parameters tested were pulp pH, temperature, acid conditioning time, collector conditioning time, collector quantity and particle size.

The general experimental conditions were selected on the basis of the results obtained in previous studies [21,29]. The conditions were as follows:

- +90/-125 micron feed
- 3.8 ml collector/ 0.5 kg of feed (6.1 kg collector/ton of feed)
- 30 seconds each of acid conditioning and collector conditioning times
- 20°C of temperature
- pH 5.5 (14.5 kg H_3PO_4/ton of phosphate rock)
- Pulp density of 10% (wt.) solids
- 3 minutes of flotation time

This means that, for example, acid conditioning time experiments were done using +90/-125 micron feed at 20°C with 3.8 ml of collector, 30 seconds of collector conditioning time at a pH of 5.5. When collector conditioning time was the parameter, acid conditioning time was 30 seconds with all the other variables held at the values stated.

The following is a summary of the results obtained for each parameter. A detailed compilation of raw data tables can be found in Appendix D.

- **Acid conditioning time**

Acid conditioning time is the time it takes after the pulp reaches the desired pH (5.5 in this case). In the experiments, H_3PO_4 was used as a pH regulator and phosphate depressant. The effect of acid conditioning time on the grade, recovery of P_2O_5 and CaO concentration have been examined by changing the time between 10 s and 110 s. The results of the experiments are summarized in Tables 8 and 9, and Figures 6 and 7.

Table 8. Change of Grade, Recovery and CaO Content of Tail as a Function of Acid Conditioning Time.

Acid cond. Time (sec.)	**Grade (%P_20_5)**	**CaO (%)**	**Recovery (%P_2O_5)**
10	28.632	57.2	91.5
30	29.689	56.4	91.4
50	34.922	49.5	90.7
70	36.127	50.5	92.5
90	36.246	50.7	88.6
110	36.233	50.7	88.7

Table 9. Change of Grade and CaO Content of Froth as a Function of Acid Conditioning Time.

Acid cond. Time (sec.)	Grade (%P_2O_5)	CaO (%)
10	1.820	30.0
30	1.854	34.0
50	2.441	38.2
70	1.780	38.1
90	2.467	39.0
110	2.601	38.0

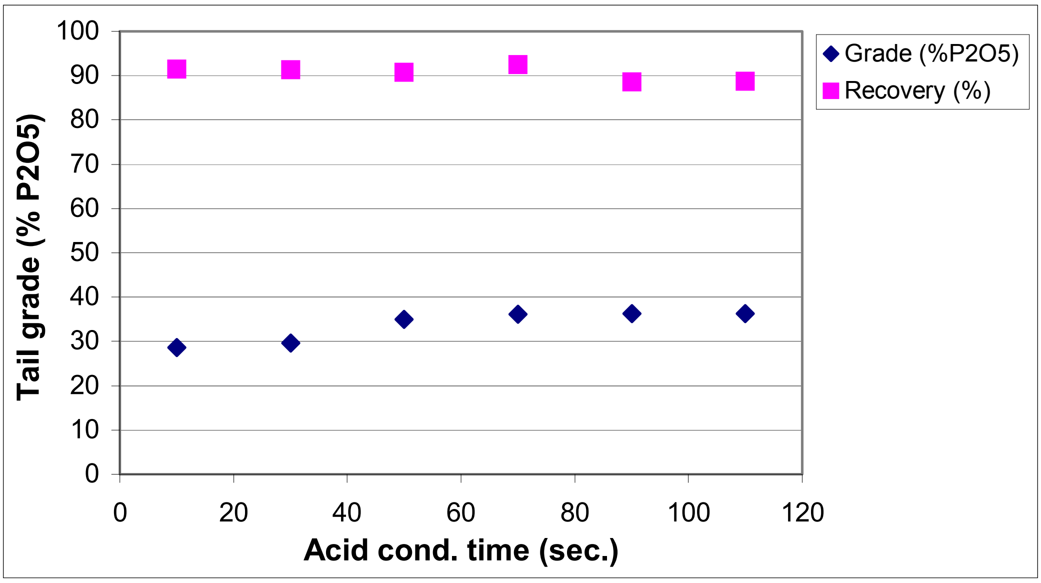

Figure 6. Change of Grade and Recovery of Tail as a Function of Acid Conditioning Time.

In the case of phosphoric acid, the following reactions take place between apatite and phosphoric acid and soluble calcium-phosphate compound forms:[33]

$$Ca_5(PO_4)_3(OH)(s) + 2PO_4^{-3} + 6H^{+} \rightleftarrows 5CaHPO_4(s) + H_2O \quad K_{sp}=10^{+52.8} \quad (1)$$

$$CaHPO_4(s) \rightleftarrows CaHPO_4(aq) \quad K_{sp}=10^{-4.16} \quad (2)$$

Phosphoric acid reacts with $CaCO_3$ to liberate Ca^{2+} ions on the calcite surface according to the following reaction:

$$2H^+ + CaCO_3 \leftrightarrows Ca^{2+} + H_2CO_3 \qquad (3)$$

and PO_4^{3-} reacts with Ca^{2+} ions to form the highly insoluble $Ca_3(PO_4)_2$ by the reaction:

$$3\,Ca^{2+} + 2\,PO_4^{3-} \leftrightarrows Ca_3(PO_4)_2\,(s) \qquad (K_{sp})^{-1} = 10^{+26,8} \qquad (4)$$

When H_3PO_4 is added to the pulp, it helps the formation of $CaHPO_4$(aq.). As the amount of $CaHPO_4$ increases in the pulp, more of the apatite is ensured to be depressed. If the time is long enough, the surface of all the apatite particles come into contact with more acid, and the maximum amount of soluble compound ($CaHPO_4$) is obtained. Therefore, waiting further does not help to increase the P_2O_5 grade. From the experiments, the time of grade stabilization was found to be 70 seconds where 36% P_2O_5 is obtained with 92% recovery in the tail.

Recovery values obtained have a general tendency of increase as acid conditioning time increases.

From Figure 7, change of CaO concentration in the froth can be seen. It can be said that its increase is an expected result since the P_2O_5 concentration also has the same trend with acid conditioning time.

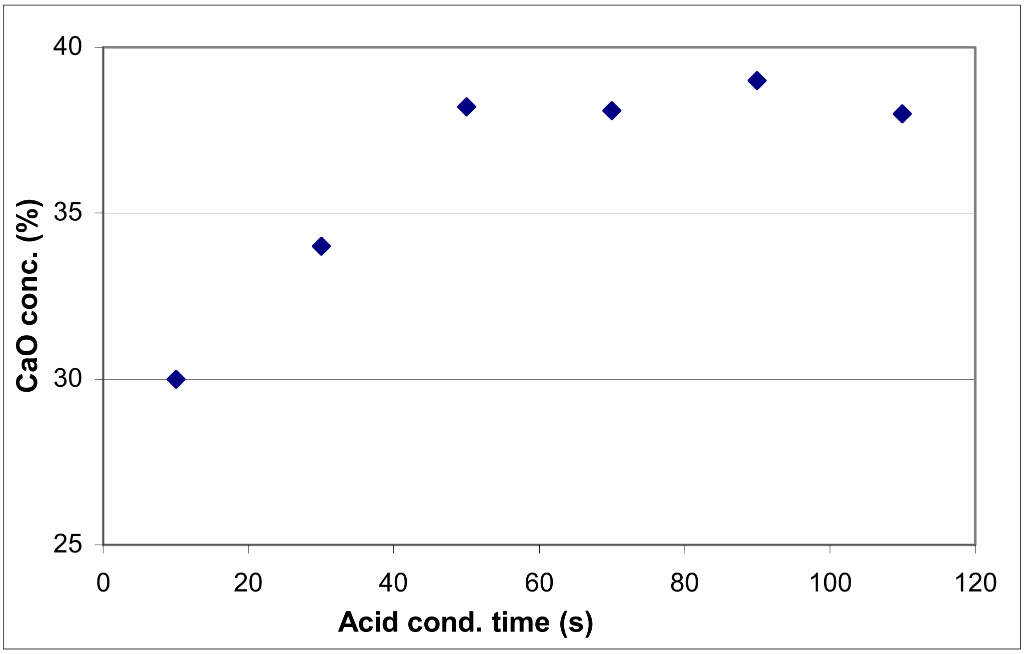

Figure 7: Change of CaO Content of Froth as a Function of Acid Conditioning Time.

- **Collector conditioning time**

Collector conditioning time must be long enough to expose all the particles to the collector molecules. From Tables 10 and 11 and Figure 8, it can be seen that grade and recovery seem to remain almost unchanged as time goes by. This is an expected result because what affects these grade, recovery and CaO concentration is the amount of collector, not the time it takes after its addition.

Table 10. Change of Grade, Recovery And CaO Content of Tail as a Function of Collector Conditioning Time.

Coll. cond. time (sec.)	Grade (%P_20_5)	CaO (%)	Recovery (%P_2O_5)
10	27.190	57.0	87.8
20	29.902	56.8	89.7
30	29.689	56.4	91.4
40	28.014	56.0	92.4
50	29.167	56.7	89.8
60	28.229	59.2	94.8
70	31.699	53.9	94.2
80	30.486	51.9	93.9

Table 11. Change of Grade and CaO Content of Froth as a Function of Collector Conditioning Time.

Coll. cond. Time (sec.)	Grade (%P_20_5)	CaO (%)
10	2.976	31.7
20	2.193	34.0
30	1.854	33.8
40	1.72	33.0
50	2.017	34.0
60	1.2	35.0
70	1.178	36.0
80	1.398	36.0

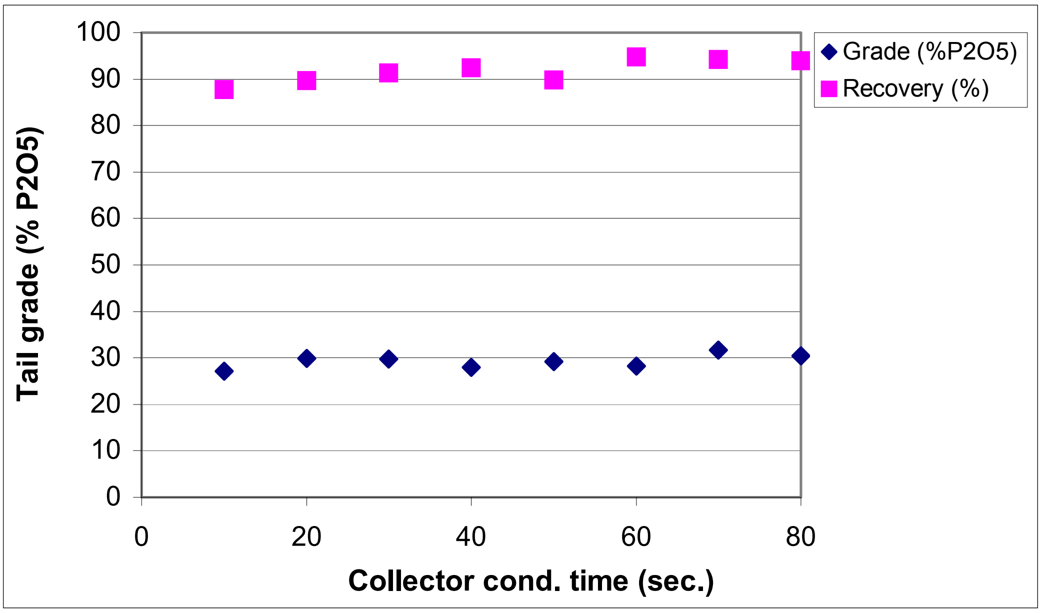

Figure 8. Change of Grade and Recovery of Tail as a Function of Collector Conditioning Time.

Change of CaO concentration in the froth is plotted in Figure 9. The increasing trend seems to stabilize after 70 seconds of collector conditioning time.

In general, in spite of the very slight increase in recovery, and a decrease in the early conditioning times, a further study of the variable may show that it has no effect on P_2O_5 and CaO concentrations and recovery. This would be due to both of the facts that the rate of increase is very small and there is a tendency of the data to remain constant.

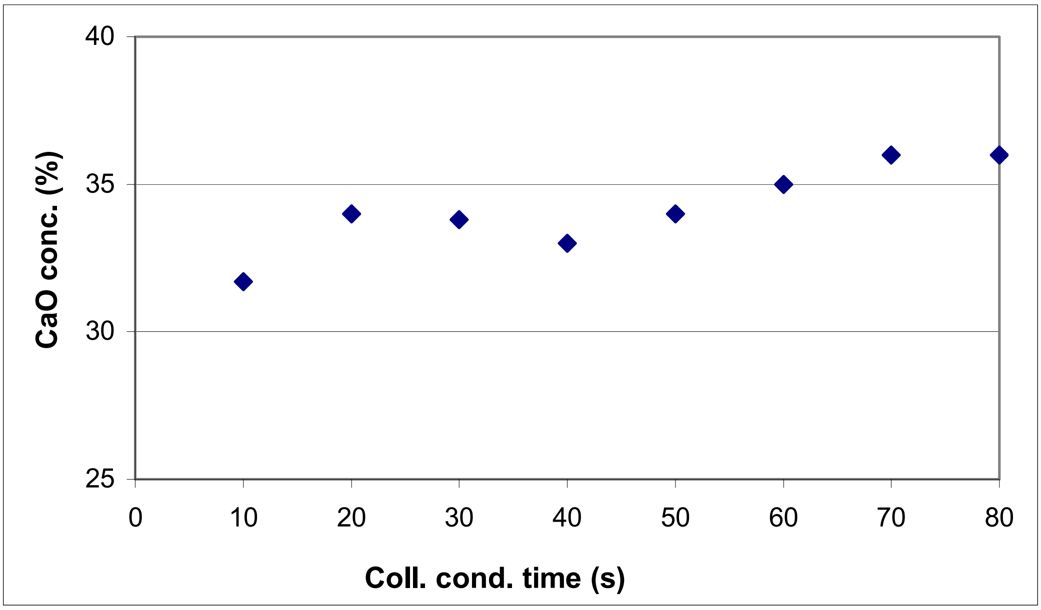

Figure 9: Change of CaO Content of Froth as a Function of Collector Conditioning Time.

- **Collector quantity**

Collector quantity is an effective parameter in flotation. The results of the experiments are given in Tables 12 and 13 and Figure 10. Depending on the amount of the collector, rock grade ranging between 19.7% P_2O_5 and 34.5% P_2O_5 can be obtained. After the value of 34% P_2O_5, grade stayed constant, so further addition of collector didnot affect. This result is because, as more collector is added, more of the calcite mineral will react to form Ca-oleate (an insoluble compound, $K_{sp}=3*10^{-15}$), but after the surface of all the calcite minerals is covered with collector molecules, adding more collector to the pulp will not change anything. [41]

Table 12. Change of Grade, Recovery And CaO Content of Tail as a Function of Collector Quantity.

Collector volume (ml.)	Grade (%P_20_5)	CaO (%)	Recovery (%P_2O_5)
0.6	19.717	45.3	99.8
1.0	20.760	43.7	98.2
1.8	24.096	53.0	96.0
2.2	26.036	54.6	96.2
2.6	25.590	55.0	92.4
3.0	28.479	57.0	94.9
3.4	31.048	52.7	92.9
3.8	29.689	56.4	91.4
4.2	31.436	53.4	91.8
4.6	33.006	51.2	85.1
5.0	34.431	51.6	86.9
5.4	34.102	51.1	89.8

Table 13. Change of Grade and CaO Content of Froth as a Function of Collector Quantity.

Collector volume (ml.)	Grade (%P_20_5)	CaO (%)
0.6	0.074	37.9
1.0	0.586	37.0
1.8	1.023	32.7
2.2	1.042	33.0
2.6	1.810	34.0
3.0	1.156	35.0
3.4	1.634	36.4
3.8	1.854	36.0
4.2	1.631	37.0
4.6	3.645	38.0
5.0	2.742	38.0
5.4	1.901	40.0

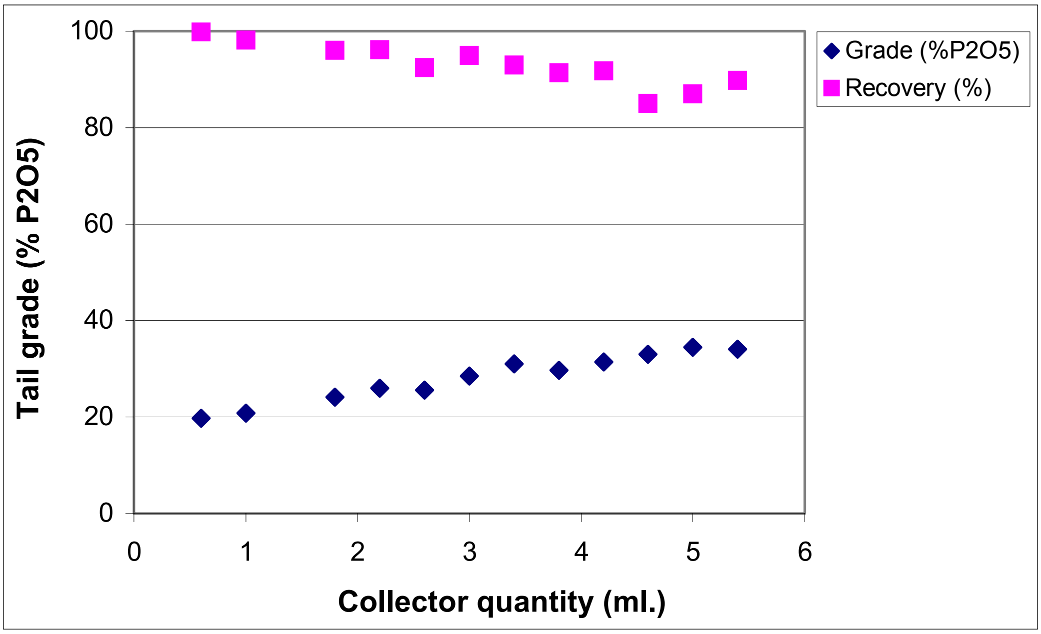

Figure 10. Change of Grade and Recovery of Tail as a Function of Collector Quantity.

In Figure 11, $CaCO_3$ concentration in the froth is plotted against collector quantity. The similar increasing trend as in P_2O_5 concentration is observed for $CaCO_3$ concentration if the first two data are to be discarded.

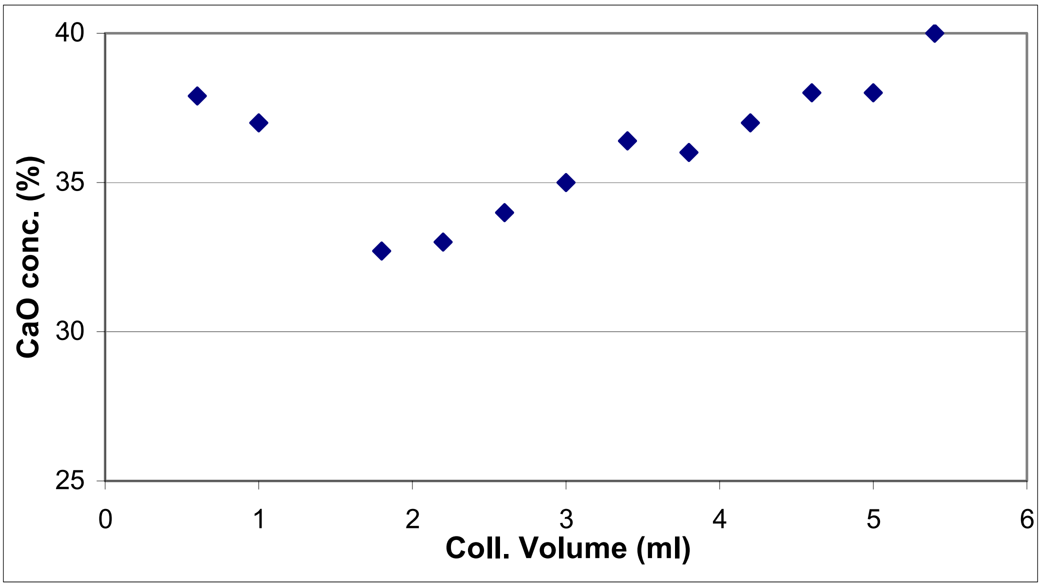

Figure 11: Change of CaO Content of Froth as a Function of Collector Quantity.

- **Pulp pH**

Pulp pH is an important factor in flotation because it controls the reaction mechanisms. It has been found that at pH 5.5-6.5, apatite is depressed and calcium carbonate is floated with oleic acid (anionic collector) [11, 25, 30]. The reason for this can be explained as follows: formation of soluble $CaHPO_4$ on apatite surface prevents collector ions from attaching the surface of the apatite particles. The reactions mentioned in the discussion of acid conditioning time prevail. [34]

While these reactions are taking place on apatite surface, Ca^{+2} in the pulp react with PO_4^{-3} according to the following reaction:

$$3Ca^{+2} + 2PO_4^{-3} \leftrightarrows Ca_3(PO_4)_2(s) \qquad (K_{sp})^{-1} = 10^{+26.8} \qquad (5)$$

By this way, thus, the calcite surface is converted to more stable phases that lead to the formation of Ca-oleate ($K_{sp} = 3x10^{-15}$) on the surface. On the other hand, apatite surface has more soluble phase ($CaHPO_4(aq)$, $K_{SP} = 10^{-2.7}$) than that of calcite, which may reduce the oleic acid adsorption [41].

The reactions given so far mean that addition of soluble phosphate salt or acid will result in increasing concentration of aqueous $CaHPO_4$ and therefore apatite would be depressed.

The experimental results for pH dependence are summarized in Tables 14 and 15. From Figure 12, it can be seen that both grade and recovery decrease as pH is increased. The reasoning for this decrease is given in the previous paragraphs. The increase in $CaCO_3$ concentration shown in Figure 13 is in expected since the grade decreases meaning that less separation is being realized as pH increases. Therefore, $CaCO_3$ in the apatite matrix is also taken out with the froth.

Table 14. Change of Grade, Recovery and CaO Content Of Tail as a Function of Pulp pH.

pH	$\frac{\text{kg of } H_3PO_4}{\text{ton of rock}}$	Grade (%P_20_5)	CaO (%)	Recovery (%)
5.0	19.0	30.902	55.6	92.3
5.5	14.5	29.689	56.4	91.4
6.0	10.2	23.848	58.7	67.4
6.5	6.0	18.317	47.6	18.0

Table 15. Change of Grade and CaO Content of Froth as a Function of Pulp pH.

pH	Grade (%P_20_5)	CaO (%)
5.0	1.731	34.6
5.5	1.854	34.1
6.0	5.390	36.1
6.5	9.527	43.0

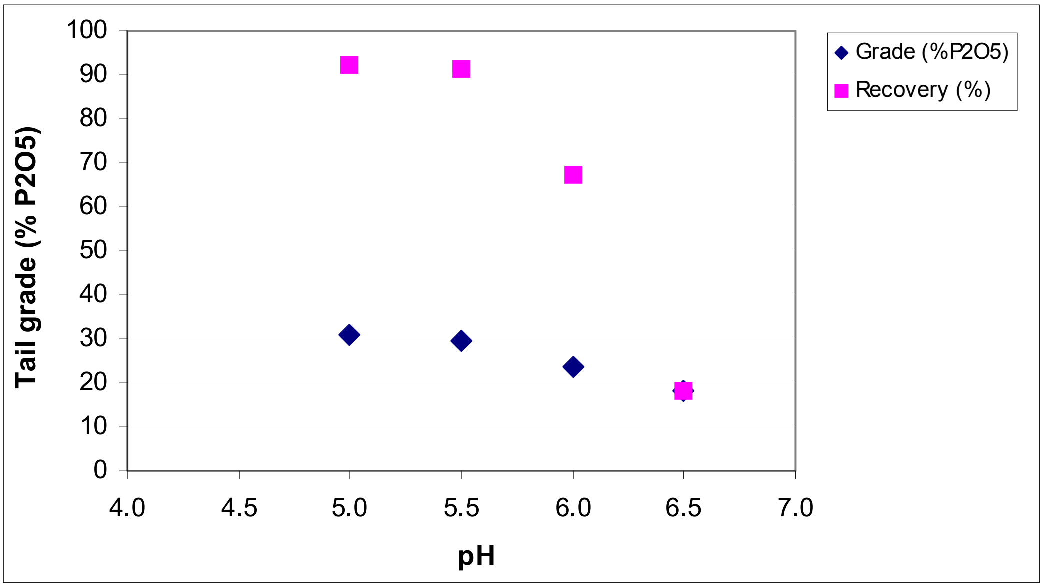

Figure 12. Change of Grade and Recovery of Tail as a Function of Pulp pH.

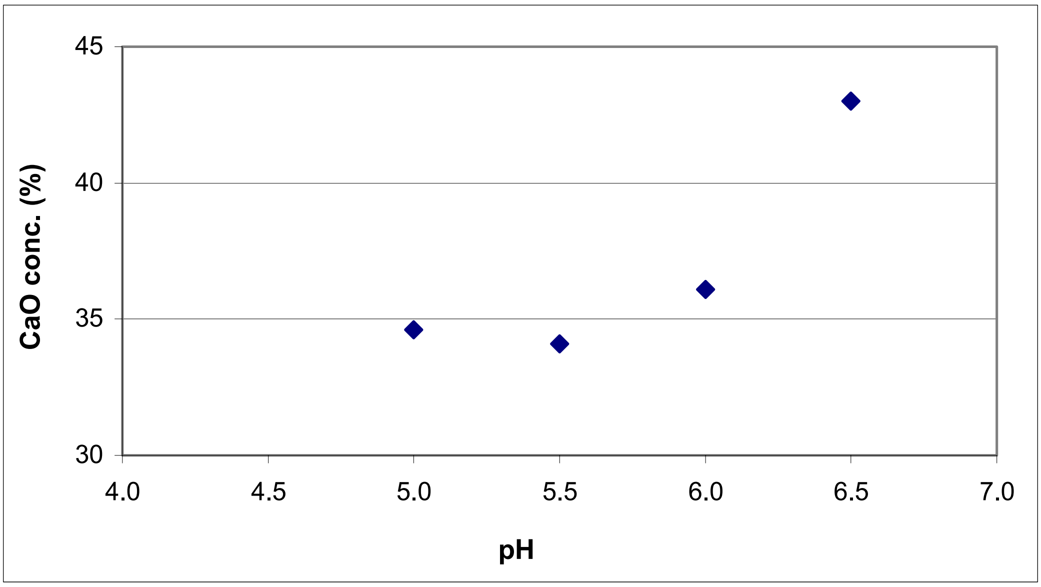

Figure 13. Change of CaO Content of Froth as a Function of Pulp pH.

- **Particle size**

Effect of particle size on flotation becomes insignificant as long as particle liberation is ensured. Liberation of calcite from the phosphate matrix is very important. Unless it is not ground properly (i.e., when particle size is above 150 microns), calcite particles will be trapped in the matrix and that will result either in the flotation of apatite attached to calcite, or calcite surface will be obscured by apatite. Also these large size particles cannot be lifted by air bubbles, which will have an adverse effect on separation.

On the other hand, excessive grinding results in particles of large surface area per unit mass. These very fine particles are called slime, and slimes interfere with flotation and cause more reagent consumption. For Mazıdağı phosphate rock, liberation of particles has been achieved below 150-micron particle size.[21] Therefore, in this study, particles of size smaller than 150 microns have been used, and the lower limit was 53 microns, since further grinding would cause excessive slime production. In addition, every fraction of particles has been deslimed with water.

From Tables 16 and 17 and Figure 14, it can be seen that particle size has almost no effect on the grade and recovery seems to increase as the particle size is increased. When particles of sizes below the critical size (150 microns) are used, grade is not affected. In Figure 15, $CaCO_3$ concentration increases as particle size increases due to the fact that at higher sizes, calcite is trapped more in the phosphate matrix at higher particle sizes, therefore it seems as though more of the calcite has been floated.

Table 16. Change of Grade, Recovery and CaO Content of Tail as a Function of Particle Size.

Particle size (microns)	**Grade ($\%P_20_5$)**	**CaO (%)**	**Recovery (%)**
+53/-90	31.816	54.1	83.4
+90/-125	30.292	49.9	87.0
+125/-150	29.134	48.1	90.4

Table 17. Change of Grade and CaO Content of Froth as a Function of Particle Size.

Particle size (microns)	**Grade ($\%P_20_5$)**	**CaO (%)**
+53/-90	3.112	27.0
+90/-125	2.904	38.0
+125/-150	1.899	40.0

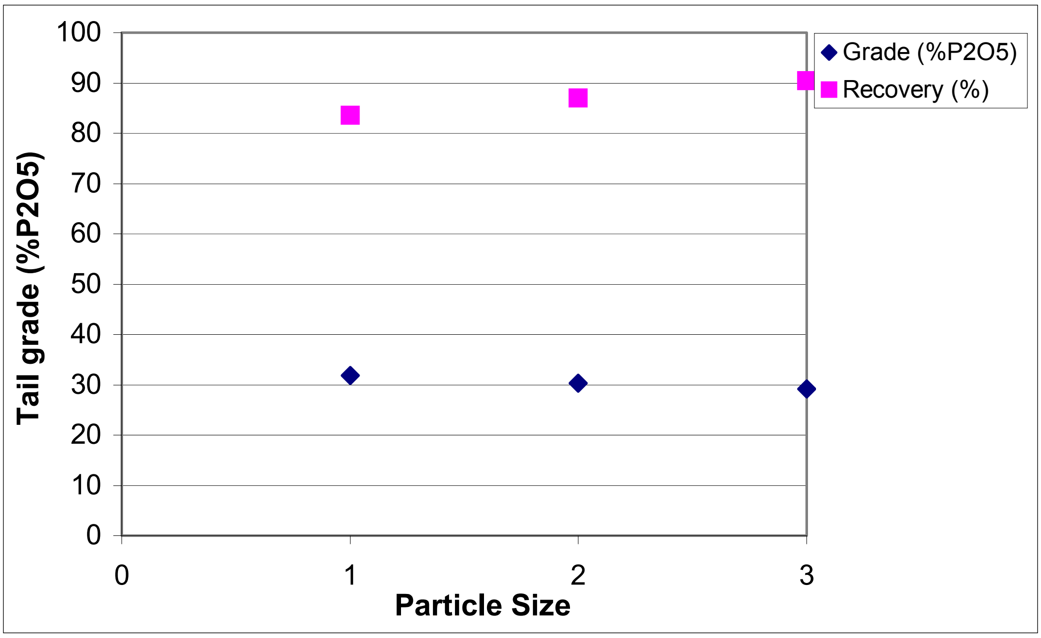

Figure 14. Change of Grade and Recovery of Tail as a Function of Particle Size.

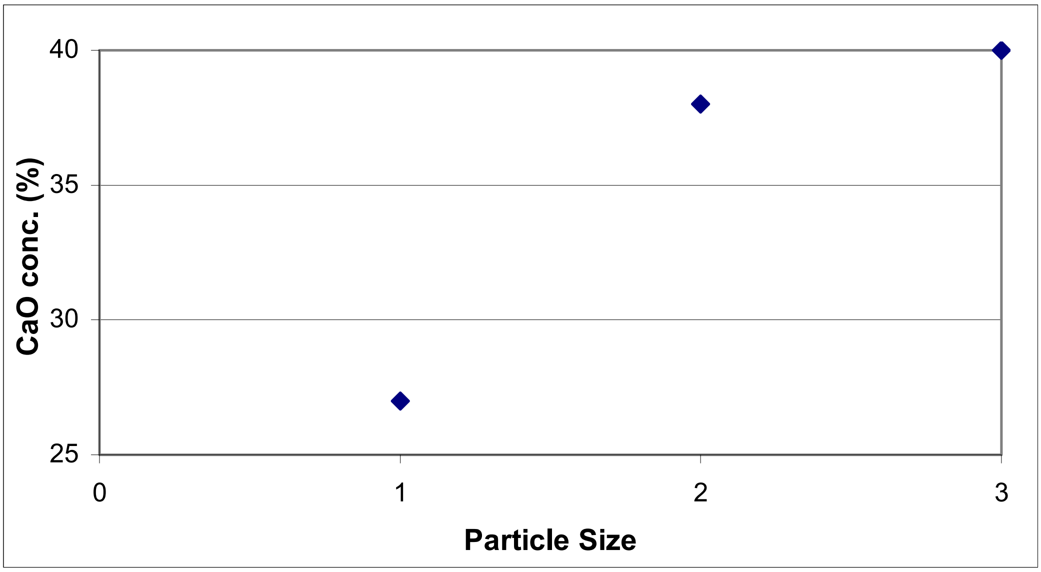

Figure 15. Change of CaO Content of Froth as a Function of Particle Size

(Note: The numbers 1, 2 and 3 in Figures 14 and 15 refer to the particle sizes in ascending order.)

- **Temperature**

The effect of temperature on flotation of phosphate rock has been given in Tables 18 and 19, and Figures 16 and 17. This subject has not been studied very intensively in literature but it is known that temperature changes affect particle attachment-detachment processes [43].

Experimental results obtained show that grade, $CaCO_3$ concentration and recovery decrease as temperature rises. These may be explained by the fact that at higher temperatures bonds between the stable compounds may be breaking down and this would adversely affect flotation.

Table 18. Change of Grade, Recovery and CaO Content of Tail as a Function of Temperature.

Temperature (°C)	**Grade ($\%P_20_5$)**	**CaO (%)**	**Recovery (%)**
15	33.949	54.2	91.6
20	30.577	55.1	94.8
25	30.165	54.2	89.2
30	28.800	57.6	78.6
35	28.160	56.3	77.0

Table 19. Change of Grade and CaO Content of Froth as a Function of Temperature.

Temperature (°C)	**Grade ($\%P_20_5$)**	**CaO (%)**
15	2.058	35.6
20	1.117	35.0
25	2.562	35.0
30	4.76	34.0
35	3.709	34.0

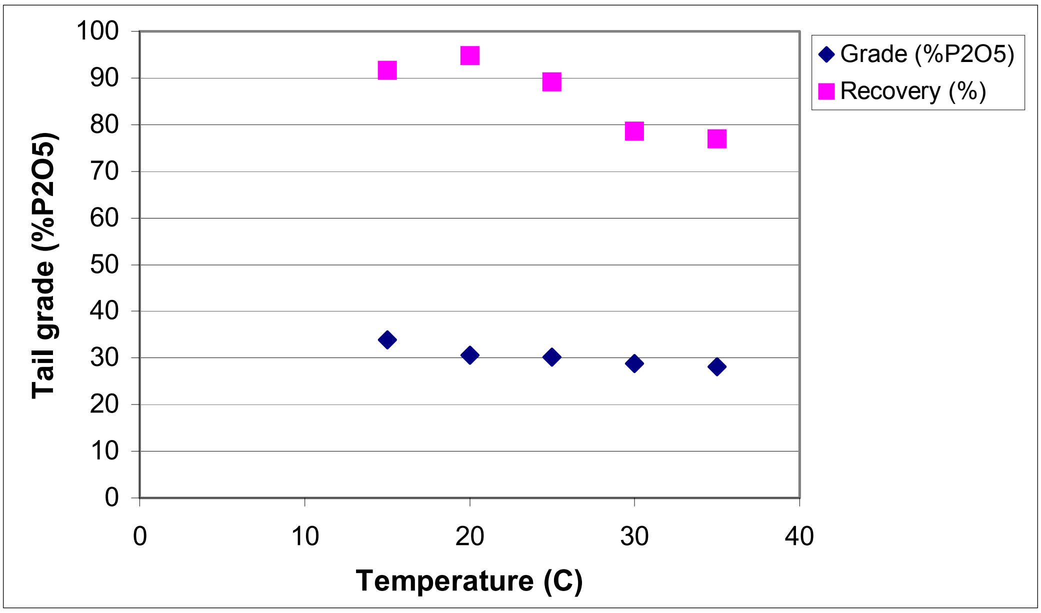

Figure 16. Change of Grade and Recovery of Tail as a Function of Temperature.

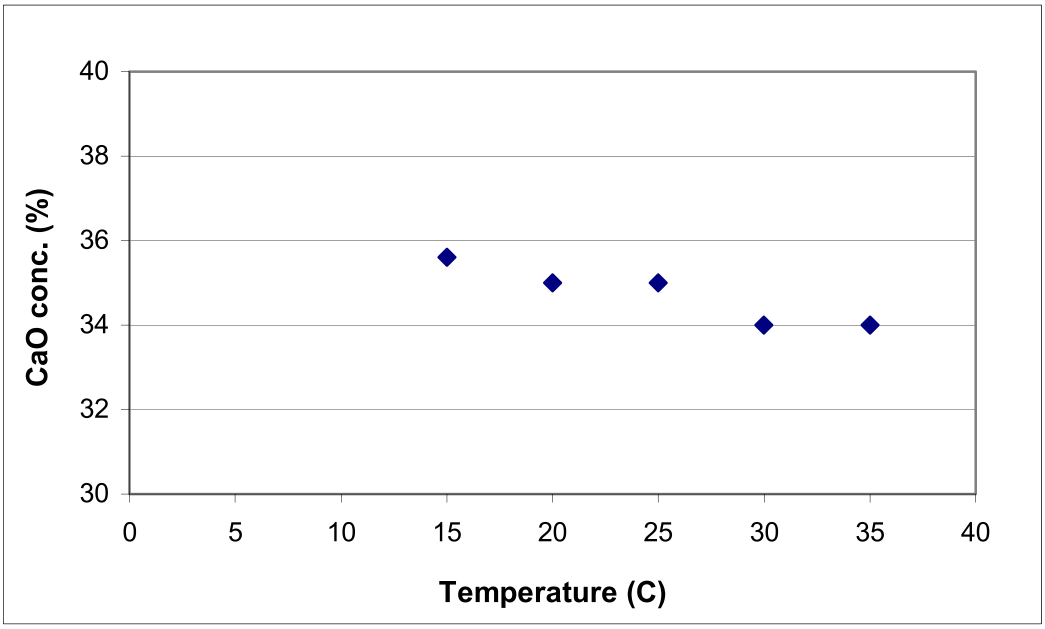

Figure 17. Change of CaO Content of Froth as a Function of Temperature.

CHAPTER 6

CONCLUSIONS

Conclusions of this work can be summarized as follows:

- As the acid conditioning time was increased, grade and recovery increased and grade was stabilized at 36% P_2O_5. A product with tail containing 36% P_2O_5 with 92% recovery and a froth with 50% CaO could be obtained. The highest recovery obtained was 92% with a grade of 36% P_2O_5 and 50% CaO concentration.

- Collector conditioning time seemed to have no effect on both the grade and the recovery. The highest recovery attained was 95% and a grade of 31.7% and 59% CaO concentration could be obtained as the maximums.

- Collector quantity showed to have a decreasing affect on recovery, however, grade yielded an increasing pattern until 34% P_2O_5 was obtained and then stayed constant around 34% P_2O_5 value. It was observed that even with the minimum amount of collector, a slight upgrading could be made. Grade increased to 20% P_2O_5 from 14% in the feed sample. CaO concentration was observed to increase as the collector quantity was increased and the highest value obtained was 40% CaO.

- As the pulp pH increased by 1.5 units, recovery decreased drastically from a maximum of 92% to 18%. Grade also decreased, the highest value of it was obtained at pH 5.0 as 31% P_2O_5 with 55% CaO concentration and 92% recovery.

- Increasing particle size increased recovery slightly, however it did not show a significant effect on the grade. It can be said that grade does not change with particle size as long as the critical particle size is used that ensures particle liberation. CaO concentration increased with particle size.

- All the experiments were done at 20°C; however, temperature experiments have shown that a higher grade and recovery could be obtained at 15°C. As the temperature increased, recovery, grade and CaO concentration decreased.

As a final conclusion, it can be said that the results of the experiments have shown that it is possible to upgrade Mazıdağı phosphate rock by one-stage flotation in acidic medium. Commercial grades (greater than 30% P_2O_5) can be obtained with high recovery.

CHAPTER 7

RECOMMENDATIONS

- Grinding is an important stage of experimental procedure in this study. Particles should be small enough for particle liberation but not as small as to produce undesired slimes. Even if the particle size is not so small, desliming must be made for every fraction of particles generated after crushing and grinding of the ore. In this study, desliming and sieving were carried out at the same time by putting the necessary sieves on top of each other and washing the rock with water until the water becomes clear. This method is effective and less time-consuming compared to separate sieving and desliming procedures.

- Performing the flotation experiments and the chemical analyses with two persons would give better results in a shorter time, especially during the experiments where one has to check the pH value and add acid if necessary, check the time, add the collector, stop the impeller and turn on the disperser; some of which have to be done instantaneously.

- Maybe the most tedious and long procedure is the chemical analysis of the products of the experiments. Before taking samples from the froth and tail, perfect mixing of them should be ensured because otherwise, analysis reveals very different concentration results. Two sub-samples should be made out of every tail/froth to ensure reproducibility.

- Future work on this subject can be made in the flotation column to test continuous operation.

- Knowing that Mazıdağı phosphate rock contains silica more than 1%, cell flotation can be repeated as two-stage flotation to remove silica as well. By this way one should have also checked the behavior in the alkaline region.

- Collector quantity and acid conditioning time can be studied for values greater than the ones tried in this study to see if a collector amount can be reached where grade decreases significantly; and if the grade is still constant after 5 more iterations of the acid conditioning time.

- Also, temperature effect should be examined in a more detailed manner.

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APPENDIX A

PHOSPHATE ANALYSIS METHODS [44]

A.1. VOLUMETRIC METHOD

Reagents: (Refer to Material Safety Data Sheets for proper handling)

a. Digestion acid solution: Four parts $HNO_3$1:1, one part HCl
b. Ammonium nitrate, 10% aqueous solution
c. Ammonium molybdate solution

Add 489 mL to HNO_3 1148 mL H_2O. Cool before using. Dissolve 100 grams molybdic acid 85% in dilute NH_4OH (144 mL NH_4OH and 275 mL H_2O). Do not allow to stand over one hour before using. Pour molybdic acid solution slowly into HNO_3 solution with constant stirring. Add 100 mL more HNO_3 and allow to stand at least 24 hours. Filter immediately before using.

d. Phenolphthalein: 1% in 95% ethyl alcohol

e. Filter medium: Blue band filter.

f. Standard NaOH, 0.3240 N

Prepare a stock solution of 50% NaOH. Allow to settle to remove carbonates. Store in an airtight container. Aliquot 17 mL or weigh 26 grams of the stock standard solution into a liter flask. Dilute to volume with CO_2 free H_2O and standardize with National Institute of Standards and Technology (NIST) potassium acid phthalate. Weigh 2.1800 grams potassium acid phthalate (dried at 120^0 C for two hours) into a 400 mL beaker. Add 100 mL CO_2 free H_2O and titrate with NaOH to a phenolphthalein end point.

$$N = \frac{\%\, Purity\, of\ KHP\ x\ Weight\ of\ KHP}{ml\ NaOH\ x\ (\ 204.23/1000\ )\, x100} \tag{8}$$

One mL of titrant is equivalent to 1% P_2O_5 based on 0.1 gram aliquot (25 mL aliquot of a gram sample diluted to 250 mL).

g. Standard HNO_3 solution, 0.3240 N

Add 20.5 mL of HNO_3 into a liter flask containing 500 mL of H_2O. Mix and dilute to one liter. Adjust normality of HNO_3 solution to equal NaOH normality using a phenolphthalein end point.

Determination:

Transfer one-gram sample into either a 250 mL Erlenmeyer flask or a 400 mL tall form beaker. Add 20 mL digestion acid. Insert a short stem glass funnel in the neck of the flask or cover beaker with a watch glass. Heat to boiling and simmer at slow boil for fifteen minutes or until red fumes disappear. Cool, dilute to approximately 50 mL with H_2O and transfer quantitatively into a 250 mL volumetric flask. Dilute to volume and mix thoroughly. Pipet a 25 mL aliquot into a suitable pr3cipitation vessel (minimum 250 mL volume) and add 50 mL of ammonium nitrate reagent solution. Add 50 mL H_2O and adjust temperature to 40^0 C.

Add slowly 50 mL ammonium molybdate solution and stir for fifteen minutes on stirring machine or magnetic stirrer. Prepare a filter pad by adding paper pulp slurry, or equivalent, to a three inch ID smooth wall glass funnel fitted with a beveled-edge perforated disc, Coors No. 3 or No. 4, or equivalent. Remove sample from stirrer, allow to settle, decent onto filter pad with suction and wash precipitate onto filter with a small stream of H_2O. Wash precipitation vessel down three times with a stream of H_2O and transfer washing to filter. Wash precipitate six times, and then transfer precipitate, disc and pad to original precipitation vessel keeping volume of H_2O to 25 mL +/- 5. Add from buret sufficient standard NaOH solution to completely dissolve the yellow precipitate plus 1-3 mL in excess (avoid large excesses). Add 0.5 mL of phenolphthalein at end or near end of NaOH titration, only when all yellow precipitate is dissolved or nearly so. Rinse down sides of beaker and dilute to 100 Ml with H_2O. Titrate excess NaOH with standard HNO_3 to a faint pink end point. Verify end point by means of a pH meter at 7.85 ± 0.05.

$$\% P_2O_5\ (N.B.) = \frac{ml\, 0.3240\, N\ NaOH - ml\, 0.3240\, N\ HNO_3}{Weight\, of\ Sample} \qquad (9)$$

$$\% P_2O_5\ (D.B.) = \frac{\% P_2O_5\ (N.B.)\, x\, 100}{100 - \ \% moisture}$$

(10)

A.2. GRAVIMETRIC QUIMOCIAC METHOD

Reagents: (Refer to Material Safety Data Sheets for proper Handling)

a. Digestion acid solution: Four parts $HNO_3$1:1, one part HCl
b. Quimociac reagent

Dissolve 70 grams of sodium molybdate dihydrate in 150 mL of H_2O. Dissolve 60 grams of citric acid monohydrate in 150 mL of H_2O, add 85 mL concentrated HNO_3, and allow solution to cool. Add the molybdate solution to the citric-nitric solution when stirring add five mL synthetic quinoline to a mixture of 100 mL H_2O and 35 mL concentrated HNO_3. Slowly add the quinoline solution to the molybdate-citric-nitric solution, mixing well during addition. Let the resultant solution stand overnight. Filter through blueband filter paper. Add 280 mL C.P. acetone and dilute to one liter. Mix and store in polyethylene bottle.

Determination:

Transfer one-gram sample into a 250 mL volumetric flask. Add 20 mL digestion acid and heat to boiling. Simmer at a slow boil for fifteen minutes or until red fumes disappear. Cool, dilute to volume and mix thoroughly. Filter sample through a dry filter to remove insoluble material. Pipet a suitable aliquot containing 25 mg or less of P_2O_5 into a 500 mL Erlenmeyer flask. Dilute to 100 Ml with H_2O and add 50 mL of quimoaciac reagent. Place on a hot plate in a well-ventilated hood and boil gently for one minute. DO NOT USE OPEN FLAME AND AVOID VIGOROUS BOILING AS THIS WILL CAUSE THE PRECIPITATE TO BE LUMPY AND DIFFICULT TO FILTER. After one minute, remove from hot plate and allow to cool to room temperature. Swirl carefully three-four times during cooling. Filter through a tared gooch crucible which has been prepared with glass fiber filter paper and dried at 200^0 C. after quantitative transfer, police the flask and wash five times with 25 mL portions of H_2O, allowing the precipitate to pull dry between washings. Dry crucible and contents at

200^0 C for one hour or 250^0C for thirty minutes. Cool in desiccator to constant weight, and weigh as $(C_9H_7N)_3H_3[PO_4.12MoO_3]$. A blank should be run through the entire procedure and its weight subtracted from the sample weight.

$$\% P_2O_5\ (N.B.) = \frac{(Weight\ of\ \mathrm{Re}sidue - Weight\ of\ Blank)\ x\ 3.2073\ x\ 250}{ml\ of\ Aliquot\ x\ Weight\ of\ Sample}$$

(11)

$$\% P_2O_5\ (D.B.) = \frac{\% P_2O_5\ (N.B.)\ x\ 100}{100\ -\ \% moisture}$$

(12)

A.3. SPECTROPHOTOMETRIC METHOD

Apparatus:

A UV spectrophotometer

Reagents: (Refer to Material Safety Data Sheets for proper Handling)

a. Digestion acid solution: Four parts $HNO_3$1:1, one part HCl
b. Molybdovanadate reagent

Dissolve 1 gram ammonium metavanadate in 125 mL hot H_2O, cool, add 125 mL $HClO_4$ and cool again. In another vessel, dissolve 20 grams ammonium molybdate tetrahydrate in H_2O. Slowly add this solution with stirring to the metavanadate solution and then add 100 mL more $HClO_4$. Allow to stand overnight and dilute to 2 liters.

c. P_2O_5 stock solution, 1000 ppm P_2O_5

Weigh 1.9155 g KH_2PO_4 and check sample adjusted for moisture, which will provide a solution containing one mg P_2O_5 per mL. Place this weighed sample into a one liter tall form beaker and add 80 mL of digestion acid. Heat to boiling and continue to slowly digest sample for fifteen minutes or until red fumes are disappear. Cool, transfer to liter flask, dilute to volume and mix thoroughly.

d. Working standard solutions

Pipet 100 mL of the 1,000 ppm P_2O_5 stock solution and transfer to a one liter volumetric flask. Dilute to volume and shake (100 ppm P_2O_5 standard). Transfer a series of aliquots (10, 20, 30, and 40 mL from the 100 ppm P_2O_5 standard) to 100 mL volumetric flask. These standards will contain 0.010, 0.020, 0.030 and 0.040 mg P_2O_5 per mL. They will be equivalent to 10.00, 20.00, 30.00 and 40.00 % P_2O_5. Add 20 mL molybdovandate reagent, dilute to volume, mix thoroughly and let stand ten minutes.

Determination:

Transfer 0.5-gram sample into either a 250 mL Erlenmeyer flask or a 400 mL tall form beaker. Add 20 mL digestion acid. Insert a short stem glass funnel in the neck of the flask or cover beaker with a watch glass. Heat to boiling and simmer at slow boil for fifteen minutes and until red fumes disappear. Cool, dilute to approximately 50 mL with H_2O and transfer quantitatively into a 250 mL volumetric flask. Dilute to volume and mix thoroughly. Pipet 5 mL aliquot into a 100 mL volumetric flask, add 50 mL H_2O, 20 mL molybdovanadate reagent, dilute to volume, mix thoroughly and let stand ten minutes. Standards should be prepared so that the sample or samples fall between two that are 10% P_2O_5 apart. When a number of samples are being run, standards to bracket all of them will have to be prepared, including a zero standard if the sample should be below 10% P_2O_5. It is essential that the Molybdovanadate reagent be added to all standards and samples in rapid succession. Read absorbance of samples immediately after calibration with blank and standards. With wavelength set at 400 nm, calibrate the spectrophotometer to read zero with a standard whose value is just below the value of the samples. Take absorbance reading of a higher standard whose value is 10% P_2O_5 greater than the low standard used to zero the instrument. Take absorbance readings of all samples whose values fall between the two standards. With a precision spectrophotometer, the absorbance values over a 10 % range can be assumed to be straight line function and the % P_2O_5 can be calculated.

$$\% P_2O_5 = \left[\% P_2O_5 \, of \;\; low \; Std. + \left[\frac{Absorbance \, Values \, of \;\; Sample}{Absorbance \, Values \, of \;\; High \; Std} x10 \right] \right]$$

(13)

If there is any question as to the performance of the spectrophotometer or linearity of the absorbance values, a standard curve can be plotted for each 10% P_2O_5 span by preparing a series of standards at 2% P_2O_5 intervals.

Notes on this analysis method:

- Preparation of the molybdo-vanadate complex for analyses is a very critical step. As mentioned in Appendix A.3, any undissolved material left inside the solution causes immediate precipitation by crystallization, which means the deterioration of the complex. There are two types of the ammonium molybdate tetrahydrate reagent: amorphous and crystal. Crystal type does not dissolve completely in water even after extensive mixing periods; therefore it needs to be filtered before mixing with the metavanadate solution (if filtration is necessary, it should be made by using Blueband filter paper). If possible, it is better to use the amorphous type.

- While preparing the digestion acid solution, one has to be careful not to inhale the acid vapors, which causes continuous coughing and irritation in the throat. Also after preparing the acid one should take care of the NO_x gases produced after mixing. When it comes to adding acid to the rock samples, it should be made very slowly (i.e., pouring 3 ml. at a time every 2-3 minutes). If the acid is added all at once, especially in the tail sample, there will be large bubbles occupying the beaker, which, when burst, may lead to loss of sample. As for the boiling of the samples, 15 minutes of boiling would be enough..

- While filtering the samples, one should be careful not to let any solution flow directly into the tall form beaker from between the filter paper and the glass.

- While making the necessary dilutions water and the solution should be completely mixed in order to get good analysis results.

- When the samples are ready to be analyzed for P_2O_5 and CaO, they should be analyzed immediately. Allowing them to stand more than overnight would cause interference with the analyses due to the samples being sensitive to light and probable evaporation that may change the concentrations.

APPENDIX B

METHOD USED for ANALYSIS of CaO [44]

<u>Apparatus</u>:

An atomic adsorption spectrophotometer

<u>Reagents:</u> (Refer to Material Safety Data Sheets for proper Handling)

Digestion acid solution: Four parts $HNO_3$1:1, one part HCl

<u>Determination:</u>

Transfer 0.5-gram sample into either a 250 mL Erlenmeyer flask or a 400 mL tall form beaker. Add 20 mL digestion acid. Insert a short stem glass funnel in the neck of the flask or cover beaker with a watch glass. Heat to boiling and simmer at slow boil for fifteen minutes and until red fumes disappear. Cool, dilute to approximately 50 mL with H_2O and transfer quantitatively into a 250 mL volumetric flask. Dilute to volume and mix thoroughly. Pipet 1 mL aliquot into a 100 mL volumetric flask and dilute to volume, mix thoroughly and let stand ten minutes. Standards should be prepared so that the sample or samples fall between two that are 2 ppm Ca^{2+} apart. When a number of samples are being run, standards to bracket all of them will have to be prepared, including a zero standard.

APPENDIX C

METHOD USED for ANALYSIS of ACID INSOLUBLE [44]

Reagent:

Digestion acid solution: Four parts $HNO_3$1:1, one part HCl

Determination:

Weigh a one gram or two gram sample and transfer to a 250 ml beaker, add 20 ml of digestion acid and cover with a watch glass. Digest until most of the NO_2 fumes disappear. Remove from hot plate. Rinse watch glass and sides of beaker with 25 ml H_2O. Filter through blue band filter paper and wash residue a minimum of five times with H_2O. Place the filter paper and its contents in tared crucible, dry and ignite for 15 minutes at temperature of 700 to 800 ^{0}C. Allow crucible to cool to room temperature and weigh.

APPENDIX D

RAW DATA TABLES

Table D.1. Raw data for froth and tail streams for acid conditioning time as the parameter.

Exp. Code	Grade (%P_20_5)	Avg. %P_20_5	Ca (ppm)	Wt. (gr.)
AT1F1	1.838	1.820	7.21	295.48
AT1F2	1.801		7.07	
AT2F1	1.877	1.854	6.94	296.56
AT2F2	1.830		6.81	
AT3F1	2.492	2.441	6.70	272.92
AT3F2	2.390		6.96	
AT4F1	2.076	1.780	7.47	284.96
AT4F2	1.485		6.59	
AT5F1	2.415	2.467	6.08	317.83
AT5F2	2.520		8.88	
AT6F1	3.110	2.601	5.82	315.57
AT6F2	2.091		7.22	
AT1T1	27.224	28.632	5.02	197.11
AT1T2	30.039		4.90	
AT2T1	26.170	29.689	4.48	196.00
AT2T2	24.416		5.14	
AT3T1	32.212	34.922	4.25	186.81
AT3T2	37.631		3.93	
AT4T1	36.421	36.127	3.82	172.75
AT4T2	35.834		4.38	
AT5T1	30.014	33.130	5.04	167.73
AT5T2	36.246		4.64	
AT6T1	36.233	34.588	3.85	177.42
AT6T2	32.944		3.40	

Table D.2. Raw data for froth and tail streams for collector conditioning time as the parameter.

Exp. Code	Grade (%P_20_5)	Avg. %P_20_5	Ca (ppm)	Wt. (gr.)
CT1F1	3.543	2.976	7.38	277.66
CT1F2	2.409		7.26	
CT2F1	2.335	2.193	6.91	301.07
CT2F2	2.050		7.31	
CT3F1	1.877	1.854	6.94	296.56
CT3F2	1.830		6.81	
CT4F1	2.269	1.720	6.70	285.19
CT4F2	1.171		6.96	
CT5F1	2.180	1.865	7.29	305.00
CT5F2	1.550		6.95	
CT6F1	1.034	1.117	7.11	269.62
CT6F2	1.200		7.21	
CT8F1	1.525	1.351	7.42	298.6
CT8F2	1.178		7.67	
CT9F1	1.398	1.641	7.08	270.35
CT9F2	1.883		7.28	
CT1T1	23.908	25.549	5.34	218.54
CT1T2	27.190		5.32	
CT2T1	27.430	29.902	4.88	192.8
CT2T2	32.375		4.67	
CT3T1	26.170	29.689	4.48	196
CT3T2	24.416		5.14	
CT4T1	28.860	28.014	4.75	211.79
CT4T2	27.168		4.53	
CT5T1	27.619	27.324	3.87	186.00
CT5T2	29.276		3.24	
CT6T1	32.925	30.577	4.14	207.18
CT6T2	28.229		4.54	
CT8T1	30.774	31.699	4.36	181.11
CT8T2	32.625		4.29	
CT9T1	30.486	31.905	4.51	193.55
CT9T2	33.324		4.76	

Table D.3. Raw data for froth and tail streams for collector quantity as the parameter.

Exp. Code	Grade (%P_20_5)	Avg. %P_20_5	Ca (ppm)	Wt. (gr.)
CQ1F1	1.807	1.810	7.30	260.78
CQ1F2	1.812		7.52	
CQ2F1	1.130	1.156	7.21	278.57
CQ2F2	1.182		7.45	
CQ3F1	1.655	1.634	6.96	288.42
CQ3F2	1.612		7.52	
CQ4F1	1.877	1.854	6.94	296.56
CQ4F2	1.830		7.05	
CQ5F1	1.252	1.442	7.76	309.48
CQ5F2	1.631		7.95	
CQ6F1	1.024	0.893	7.54	263.41
CQ6F2	0.763		7.81	
CQ7F1	1.058	1.042	7.32	248.28
CQ7F2	1.027		7.60	
CQ8F1	0.569	0.586	7.34	198.13
CQ8F2	0.604		7.62	
CQ9F1	0.094	0.074	7.37	162.96
CQ9F2	0.054		7.82	
CQ10F1	1.119	1.023	7.45	244.39
CQ10F2	0.926		7.20	
CQ11F1	3.869	3.645	6.91	305.95
CQ11F2	3.421		6.96	
CQ12F1	2.851	2.742	6.51	323.52
CQ12F2	2.633		7.19	
CQ13F1	2.127	1.852	6.99	331.00
CQ13F2	1.578		7.21	
CQ1T1	25.122	25.590	5.34	224.86
CQ1T2	26.057		5.88	
CQ2T1	28.400	28.479	4.31	212.77
CQ2T2	28.557		4.48	
CQ3T1	31.048	31.971	4.73	200.93
CQ3T2	32.893		5.05	
CQ4T1	26.170	29.689	4.48	196
CQ4T2	24.416		5.14	
CQ5T1	32.652	31.436	4.90	180.8
CQ5T2	30.220		4.69	
CQ6T1	25.674	28.002	5.79	236.11
CQ6T2	30.331		5.54	
CQ7T1	24.748	26.036	5.24	248.14
CQ7T2	27.325		5.24	
CQ8T1	21.885	20.760	5.45	299.56
CQ8T2	19.635		6.32	

Table D.3. Raw data for froth and tail streams for collector quantity as the parameter. (cont.d)

Exp. Code	Grade (%P_20_5)	Avg. %P_20_5	Ca (ppm)	Wt. (gr.)
CQ9T1	19.844	19.717	6.13	331.36
CQ9T2	19.590		6.59	
CQ10T1	23.307	24.096	5.24	249.21
CQ10T2	24.885		5.26	
CQ11T1	33.216	33.006	4.00	192.16
CQ11T2	32.796		4.25	
CQ12T1	36.507	34.431	4.68	171.48
CQ12T2	32.354		4.48	
CQ13T1	33.172	34.456	4.22	162.00
CQ13T2	35.739		4.45	

Table D.4. Raw data for froth and tail streams for pulp pH as the parameter.

Exp. Code	Grade (%P_20_5)	Avg. %P_20_5	Ca (ppm)	Wt. (gr.)
PH1F1	1.820	1.731	7.10	292.21
PH1F2	1.643		7.21	
PH2F1	8.180	8.432	6.22	345.00
PH2F2	8.684		6.33	
PH3F1	13.391	15.105	7.19	445.00
PH3F2	16.819		7.20	
PH4F1	1.877	1.854	6.94	296.56
PH4F2	1.830		6.81	
PH1T1	31.971	30.902	4.36	195.82
PH1T2	29.832		4.06	
PH2T1	35.253	33.812	3.58	160.92
PH2T2	32.372		3.83	
PH3T1	13.391	15.105	7.19	50.86
PH3T2	16.819		7.20	
PH4T1	26.170	29.689	4.48	195.67
PH4T2	24.416		5.14	

Table D.5. Raw data for froth and tail streams for particle size as the parameter.

Exp. Code	Grade (%P_20_5)	Avg. %P_20_5	Ca (ppm)	Wt. (gr.)
PS1F1	3.154	3.112	7.58	321.72
PS1F2	3.069		7.37	
PS2F1	3.041	2.904	7.55	294.19
PS2F2	2.766		7.67	
PS3F1	1.877	1.854	6.94	307.04
PS3F2	1.830		6.81	
PS1T1	33.607	31.816	4.85	160.13
PS1T2	30.026		4.80	
PS2T1	34.079	32.186	4.33	189.35
PS2T2	30.292		4.54	
PS3T1	26.170	29.689	4.48	189.59
PS3T2	24.416		5.14	

Table D.6. Raw data for froth and tail streams for temperature as the parameter.

Exp. Code	Grade (%P_20_5)	Avg. %P_20_5	Ca (ppm)	Wt. (gr.)
T15F1	2.058	2.411	7.36	93.50
T15F2	2.764		7.60	
T20F1	1.034	1.117	7.11	89.50
T20F2	1.200		7.21	
T25F1	2.309	2.562	7.06	87.19
T25F2	2.816		6.89	
T30F1	4.760	5.126	6.88	86.69
T30F2	5.492		6.99	
T35F1	3.817	3.709	7.05	85.00
T35F2	3.601		6.55	
T15T1	33.412	33.949	4.11	50.25
T15T2	34.487		3.93	
T20T1	32.925	30.577	4.14	54.25
T20T2	28.229		4.54	
T25T1	30.165	31.494	4.71	58.81
T25T2	32.823		4.70	
T30T1	26.255	27.527	4.74	58.31
T30T2	28.800		4.59	
T35T1	28.160	30.431	4.03	49.44
T35T2	32.702		3.88	