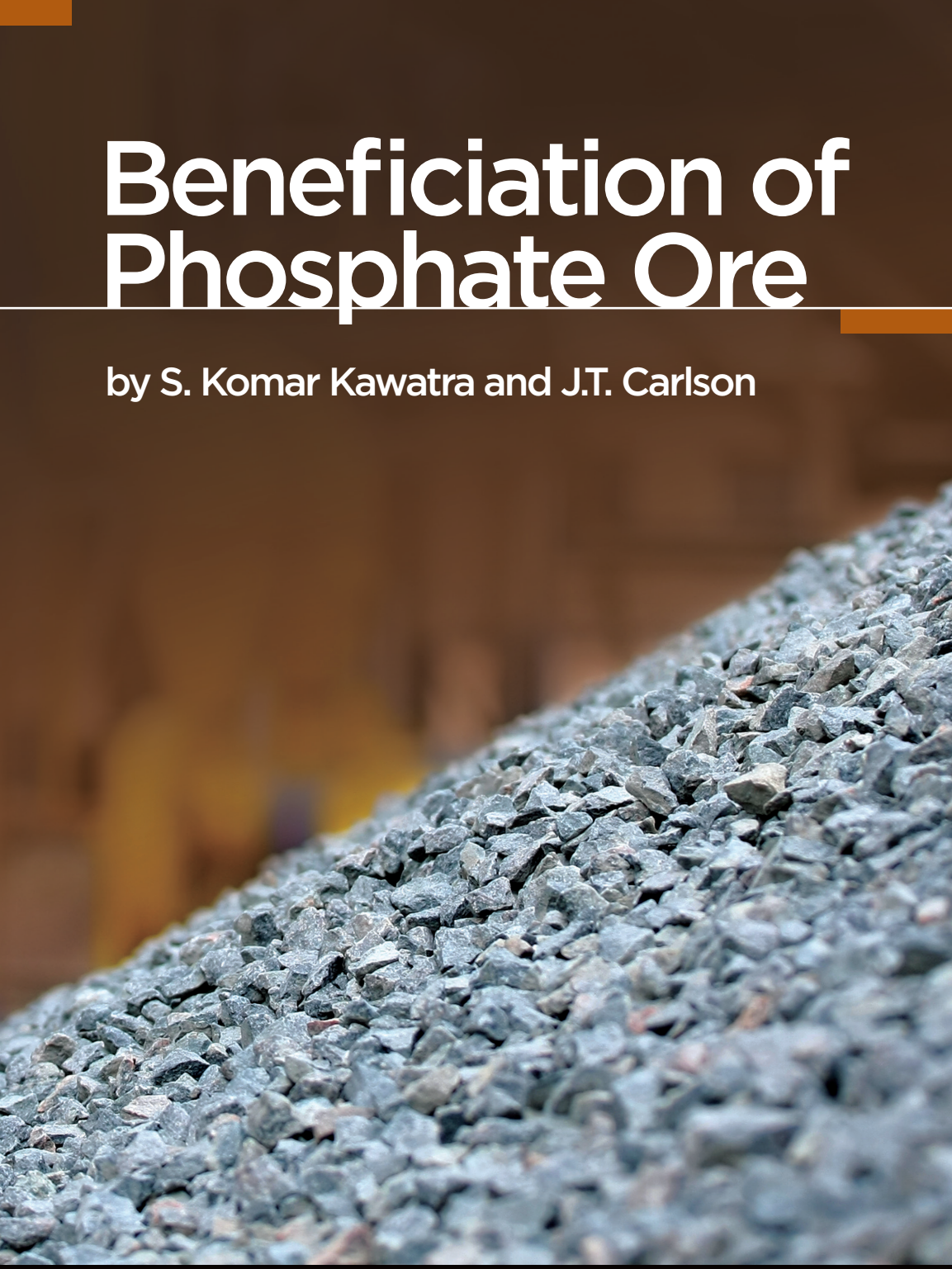
Beneficiation of Phosphate Ore

by S. Komar Kawatra and J.T. Carlson



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Preface

Advancing the minerals processing industry requires knowledge of past methods and current technology to develop new techniques and approaches. As phosphate deposits become depleted, the need for new extraction and refining methods continues to grow. Phosphate mining represents the fifth largest mining industry in the United States. The majority of this ore is used in the fertilizer industry.

In the United States from 1960 to the early 2000s, nearly 5.8 million metric tons (MMT) per year of phosphate fertilizers have been produced from phosphate rock, and this number continues to grow. In 2010, U.S. production of phosphate rock totaled 25.8 MMT. Increasing global demands for food and agriculture force a need for more fertilizer, both inside and outside of the United States. As the phosphate market expands, higher-quality mineral reserves diminish, requiring exploration and extraction of lower-grade ores. Advances in mining technology during the 20th century have allowed for higher rates of excavation. However, decreasing ore quality presents new processing challenges.

To meet new challenges, a comprehensive knowledge base must be cultivated in the minerals processing industry. *Beneficiation of Phosphate Ore* examines various methods for processing phosphate rock. Although there are many outstanding works on phosphate beneficiation, all of them are edited collections of papers. With a shortage of mineral processing engineers in the last decade, many are entering the field with no knowledge of mineral processing. This book is intended to serve as a reference and easy-to-read primer for students, engineers, and researchers, but also for the professionals who want to enter the field yet have little or no knowledge of mineral processing. The book avoids complicated equations and is intended to be very useful to a practicing engineer. Much of the information within this book is based

on experience and funded research conducted at Michigan Technological University.

Within the text, a general industry overview is followed by a lengthy discussion on raw material quality and processing implications of specific impurities. As the phosphate mining industry continues to be presented with new difficulties, information in this book provides a starting point for further process improvements and advancement. It is hoped that this book will encourage growth in phosphate processing, allowing the industry to continue to flourish.

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1
Introduction

Phosphate rock is an important mineral commodity used in the production of phosphoric acid. The majority of phosphoric acid is produced by the "wet process," in which phosphate rock is reacted with sulfuric acid to produce phosphoric acid and gypsum (calcium sulfate dihydrate). The wet process demands a phosphate rock feed that meets certain specifications in order to produce phosphoric acid efficiently and economically.

Traditionally, relatively high-grade sedimentary phosphate reserves have been mined. These reserves usually contain only clays and silica as significant gangue minerals (Lawver et al. 1978; Houot 1982; Dibble 1990; Herring and Fantel 1993; Guan 2009a). Clay slimes are removed using log washers and hydrocyclones, whereas silica is removed using the well-established Crago double float process. However, as the high-grade reserves begin to diminish, there is a need to consider processing lower-grade reserves that contain significant amounts of carbonates (Lawver et al. 1982; Llewellyn et al. 1982; Wiegel 1999). Low-grade sedimentary phosphate reserves that are high in carbonates are not isolated to Florida; they are abundant worldwide (Abouzeid et al. 1980; Vaman Rao et al. 1985; Abu-Eishah et al. 1991; Al-Fariss et al. 1991; Al-Fariss 1993; Zafar et al. 1996a; Ozer 2003; Sengul et al. 2006). These high-carbonate sedimentary phosphate reserves pose particular problems because of their dolomite ($CaMg(CO_3)_2$) content. If not removed, dolomite hinders the wet process in two ways: it increases sulfuric acid consumption, and it increases fluid viscosity, which lowers filtration rates when separating solid gypsum crystals from the valuable phosphoric acid. Removing dolomite from sedimentary phosphates has proven to be very difficult because of the mineralogical similarities between dolomite and phosphates.

Many separation methods have been investigated, but there is still no widely accepted cost-efficient method for removing dolomite from phosphate ores.

The goal of this of this book is to thoroughly explain methods used in beneficiation of different types of phosphate ores for use in the wet process. The mineralogical properties of the two major types of phosphate deposits, sedimentary and igneous, are described along with the processing methods. Benefits and disadvantages of each process are also discussed.

1.1 FEED REQUIREMENTS FOR PHOSPHORIC ACID PRODUCTION

Phosphate rock is an important mineral commodity used in the production of phosphoric acid, of which the majority goes through further processing to make fertilizers. The wet process is the most widely used method for phosphoric acid production. During the wet process (Equation 1.1), phosphate rock (i.e., fluorapatite, $Ca_5(PO_4)_3F$) is reacted with sulfuric acid (H_2SO_4) to produce phosphoric acid (H_3PO_4) and gypsum ($CaSO_4 \cdot 2H_2O$) (Chenier 2002).

$$Ca_5\left(PO_4\right)_3 F_{(s)} + 5H_2SO_{4(l)} + 10H_2O_{(l)} \rightarrow 5\left(CaSO_4 \cdot 2H_2O\right)_{(s)} + HF_{(aq)} + 3H_3PO_{4(aq)} \quad \text{EQ 1.1}$$

Filtration and washing are then used to separate the solid gypsum from the phosphoric acid. Figure 1.1 shows a simplified flow diagram for the production of phosphoric acid. This book focuses on the beneficiation of phosphate ores for use in the dihydrate wet process production of phosphoric acid. Further details on phosphoric acid production are discussed extensively throughout the literature (Noyes 1967; Slack 1968) and not discussed here.

Phosphate ores can contain many deleterious impurities of which the most common are silica, dolomite, calcite, and clays. These impurities must

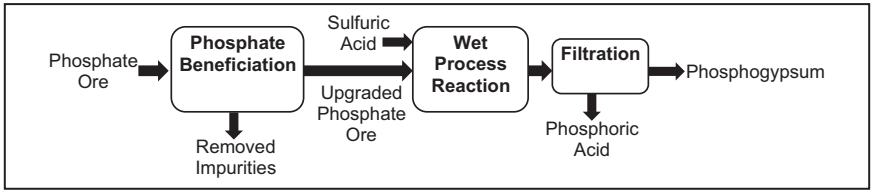


Figure 1.1 Simplified process flow diagram for production of phosphoric acid

be removed to achieve a phosphate concentrate suitable for the production of phosphoric acid by means of the wet process. Generally, for a phosphate rock concentrate to be salable, it must meet the following conditions (Sis and Chander 2003; Gharabaghi et al. 2010):

1. High P_2O_5 content (>30%),
2. Low CaO:P_2O_5 ratio (<1.6), and
3. MgO content lower than 1%.

In the phosphate industry, P_2O_5 content is often reported as bone phosphate of lime (BPL, also known as tricalcium phosphate, $Ca_3(PO_4)_2$), which can be determined by multiplying the %P_2O_5 content by 2.185. Important quality control factors for a suitable phosphate concentrate are described in Table 1.1. This review focuses on removal of dolomite, calcite, clays, silica,

Table 1.1 Important phosphate rock quality factors for production of phosphoric acid by the wet process

Quality Factor	Impact on Wet Process	Acceptable Level
P_2O_5 grade	• Lower grades increase amount of rock that must be purchased, transported, and crushed.	Phosphoric acid plants generally accept a wide range of P_2O_5 grades. BPL > 68% is desired.
CaO:P_2O_5 ratio	• Higher ratios result in an increase in sulfuric acid consumption. • The CaO level generally comes from carbonates such as calcite, dolomite, and carbonate-rich apatite.	CaO:P_2O_5 ratio less than 1.6 is desired.
Dolomite (MgO)	• Mainly used to indicate dolomite ($CaMg(CO_3)_2$) levels. • Dolomite increases sulfuric acid consumption and decreases filtration rates while filtering gypsum from the phosphoric acid product. • Some amounts of MgO are also present due to ionic substitution of Mg into the francolite (carbonate-rich apatite) lattice.	MgO < 1%

(table continues)

Table 1.1 Important phosphate rock quality factors for production of phosphoric acid by the wet process (continued)

Quality Factor	Impact on Wet Process	Acceptable Level
Fe_2O_3 and Al_2O_3	• High amounts will decrease plant capacity and decrease P_2O_5 recovery. • Small amounts are beneficial in reducing corrosiveness by complexing with F^- ions.	Less than 2–3% is desired. Up to 5% may be tolerated.
Silica (SiO_2)	• High amounts will increase erosion of equipment and may build up in vessels. • Adds to the amount that must be filtered with the solid gypsum dihydrate. • Some active silica is beneficial in reducing the formation of hydrofluoric acid by forming SiF_4 and fluosilicates instead.	Phosphate concentrates average around 2% SiO_2.
Organics	• Increases the amount and stability of foam. • Increases fluid viscosity, resulting in slower filtration rates. • Phosphate ores high in organic matter can be calcined to reach acceptable levels.	Maximum amounts vary depending on characteristics of organic matter.
Chlorides (Cl)	• High chlorine levels can increase corrosion of equipment.	Concentrations above 0.03% increase corrosion of stainless steel. Higher-quality alloys can handle concentrations around 0.10%.
Sodium and potassium (Na and K)	• Often present as fluorides. • Can cause scaling, corrosion, and precipitation of solids.	Typical phosphate concentrate contains 0.1–0.8% Na_2O.
Cadmium (Cd)	• No notable adverse effects on phosphoric acid production. • Cd is toxic and hazardous to human health. • The amount of Cd in the food chain from phosphate fertilizer is the subject of much debate, and therefore few countries have set limits.	Netherlands has Cd limit of 15 mg Cd/kg P_2O_5. Denmark has Cd limit of 22 mg Cd/kg P_2O_5 (Kossir and Maghnouj 2009).

(table continues)

Table 1.1 Important phosphate rock quality factors for production of phosphoric acid by the wet process (continued)

Quality Factor	Impact on Wet Process	Acceptable Level
Radionuclides (U and Ra)	• U and Ra do not pose problems in the production of phosphoric acid but are hazardous to human health. • Majority of U reports to phosphoric acid. • Majority of Ra reports to phosphogypsum tailings.	The U.S. Environmental Protection Agency sets radiation limits for phosphogypsum tailings at 10 pCi/g. Phosphogypsum high in Ra is stacked near plants and strictly regulated.

Source: Noyes 1967; Slack 1968; UNIDO and IFDC 1998.

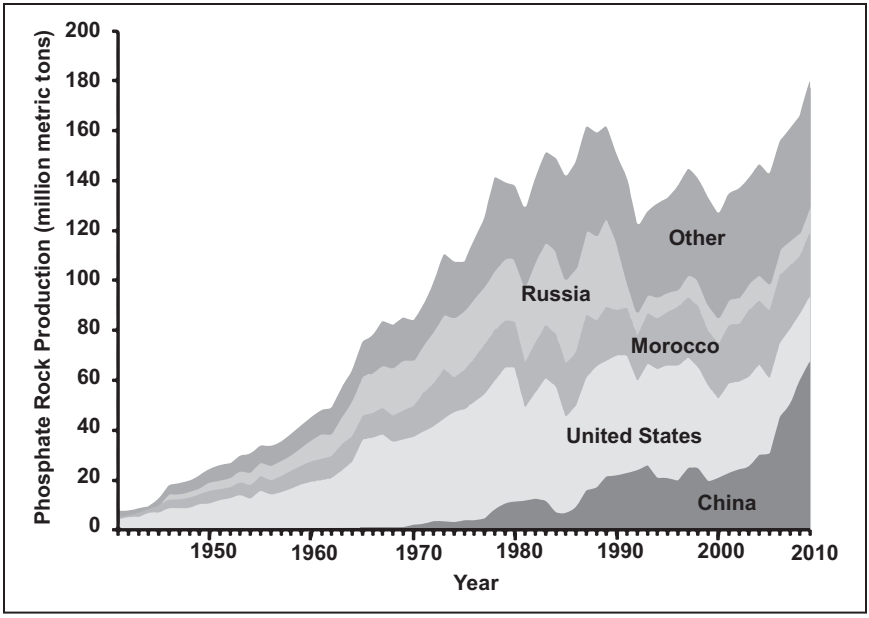
and other minerals that can be liberated and separated during phosphate ore beneficiation. Removal of cadmium, uranium, and radium are often done either during or after phosphoric acid production. The most common removal methods include precipitation, liquid–liquid extraction, and ion exchange resins (Kossir and Maghnouj 2009).

1.2 PHOSPHATE ROCK PRODUCTION STATISTICS AND RESERVES

In 2012, total world phosphate production reached approximately 181 million metric tons (MMT; Jasinski 2011). Figure 1.2 shows a steady increase in phosphate production since the 1940s. Of the total phosphate rock production in 2010, China, the United States, and Morocco produced the highest percentages of world production, at approximately 37.5% (68 MMT), 14.3% (25.8 MMT), and 14.3% (25.8 MMT), respectively. With the world's population continuing to increase, the use of fertilizers will play an important role in producing enough crops to feed everyone.

China has shown significant increases in the processing of phosphate rock over the last decade. Conversely, the United States has seen a large decrease in phosphate rock production over the same period of time. Part of the decrease in production could be attributed to diminishing high-grade reserves in Florida. Additionally, resistance from environmental groups has limited the expansions of current mines in Florida (Jasinski 2011).

The U.S. Geological Survey (Jasinski 2012) estimates current worldwide phosphate reserves at approximately 71 billion MT. Sedimentary phosphates make up the largest portion of the world phosphate reserves. Figure 1.3 shows estimated worldwide phosphate reserves. Reserves in Morocco and Western



Source: Data from USGS Mineral Commodity Summaries.

Figure 1.2 World phosphate rock production (181 MMT in 2012)

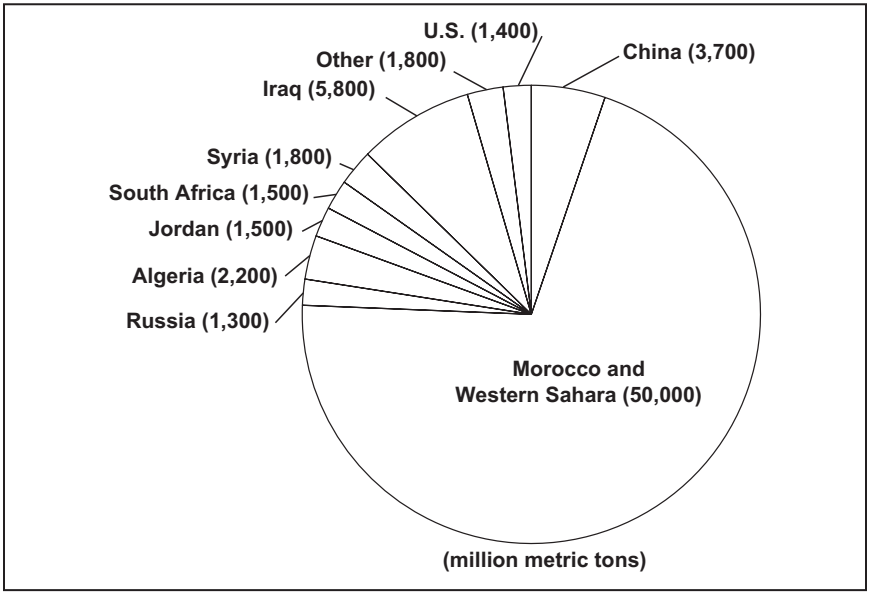


Figure 1.3 Estimated phosphate rock reserves in 2012

Sahara are generally considered to be of high quality and account for approximately 70% of the world's phosphate reserves. Other major phosphate rock sources are located in Iraq, China, Algeria, Syria, South Africa, Jordan, the United States, and Russia. The USGS defines reserves as "that part of the reserve base which could be economically extracted or produced at the time of determination" (Jasinski 2012). This means that reserve estimates can fluctuate depending on, for example, the price of phosphate rock, depletion of reserves, and technological advances in phosphate processing.

2
Sources of Phosphate Rock

Phosphate rock deposits are generally classified into three major categories based on origin and deposition (Gharabaghi et al. 2010):

1. Sedimentary deposits of marine origin
2. Igneous and metamorphic deposits
3. Biogenic deposits from bird guano

Figure 2.1 shows locations of major phosphate reserves around the world. Of the world's total phosphate rock production, approximately 80% originates from sedimentary deposits (Zapata and Roy 2004; Oelkers and Valsami-Jones 2008). Phosphate deposits can have significantly different mineralogical properties (both phosphate and gangue minerals) depending on origin and deposition, which plays a major role in determining which beneficiation methods are successful. This chapter describes the different variations of phosphate minerals, their origins, and general areas around the world in which they are found.

2.1 COMMON PHOSPHATE MINERALS

2.1.1 Apatite

Apatite is a calcium phosphate mineral group that includes chlorapatite ($Ca_{10}(PO_4)_6(Cl)_2$), hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), and fluorapatite ($Ca_{10}(PO_4)_6F$). Apatite is the basis for all major phosphate minerals. Fluorapatite is most commonly found as large, well-shaped crystals in igneous phosphate deposits. Hydroxyapatite and chlorapatite are much less common in nature (McClellan and Lehr 1969; McClellan 1980). Sedimentary phosphates (i.e., francolite,

Source: UNIDO and IFDC 1998; Zapata and Roy 2004; Abouzeid 2008.

Figure 2.1 World phosphate reserves

collophane, and dahllite) contain many different ionic substitutions into the apatite structure. Sedimentary phosphates often contain significant amounts of carbonate substituted into the apatite structure, with other ionic substitutions occurring for charge balance.

2.1.2 Francolite

Francolite is a carbonate-rich apatite mineral that is widely present in sedimentary deposits, such as the large phosphate reserves of Florida (Dibble 1990). McConnell (1938) initially defined francolite as fluorapatite that contains significant amounts of carbonate and more than 1% fluorine. Later, work by McClellan (1980) described a systematic series of anion and cation substitutions into fluorapatite, resulting in an empirical formula for francolite of $Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$. McClellan measured chemical content and unit cell values for 100 different francolites and statistically analyzed the data. Equations 2.1–2.3 are used to determine the degree of ionic substitution based on a measured unit cell *a*-value ($a_{(obs)}$), which is used to determine the composition of francolite. Knowing the exact composition of the francolite is particularly important when determining the minimum achievable levels for impurities such as MgO.

$$\frac{CO_3^{-2}}{PO_4^{-3}} = \frac{z}{6-z} = \frac{9.369 - a_{(obs)}}{0.185} \quad \text{EQ 2.1}$$

$$x = 7.173 \cdot \left(9.369 - a_{(obs)}\right) \quad \text{EQ 2.2}$$

$$y = 2.784 \cdot \left(9.369 - a_{(obs)}\right) \quad \text{EQ 2.3}$$

where

x = moles of Na^+
y = moles of Mg^{+2}
z = moles of CO_3^{-2}
$a_{(obs)}$ = determined unit cell value of a

It was also determined that carbonate (CO_3^{-2}) substitutes at a 1:1 ratio with phosphate (PO_4^{-3}) during deposition, with the net charge balanced by cationic substitutions of Na^+ and Mg^{+2} for Ca^{+2} (McClellan and Van Kauwenbergh 1991). The theoretical maximum carbonate substitution has been shown to be between 6% and 7% wt (McClellan and Van Kauwenbergh 1990).

2.1.3 Collophane

Collophane ($Ca_5(PO_4,CO_3)_3F$) is a sedimentary phosphate mineral that contains carbonate, hydroxyl, and fluorine species. It can also contain appreciable amounts of adsorbed H_2O (Frondel 1943). Collophane is also present in many phosphate reserves around the world, including Jordanian, Indian, and Chinese phosphate ores (Vaman Rao et al. 1985; Abu-Eishah et al. 1991; Shao et al. 1993; Zheng and Smith 1997).

2.1.4 Dahllite

Dahllite ($Ca_5(PO_4,CO_3)_3(OH)$) is a carbonate-rich hydroxyapatite that is mainly found in marine sedimentary ores. The most notable difference between dahllite and francolite is the fluorine content, where dahllite is generally considered to have less than 1% fluorine (McConnell 1938, 1960; Abouzeid 2008). Dahllite is also present in Jordanian phosphate ores (Abu-Eishah et al. 1991).

2.2 COMMON GANGUE MINERALS

2.1.1 Clays

Fine clays such as montmorillonite ($Si_8Al_{3.5}Mg_{0.5}O_{20}(OH)_4$), palygorskite ($(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$), and kaolinite ($Al_4(Si_4O_{10})(OH)_8$) are present in many types of sedimentary phosphates (Moudgil et al. 1995; Lowrie 2002; Guan 2009a; Barthelmy 2010). Clays are often removed from phosphate ores using washer screens and desliming hydrocyclones. If not removed, clays can significantly affect flotation processes (e.g., Crago double float) by coating the phosphate minerals, affecting interactions with reagents, and increasing reagent consumption.

2.2.2 Quartz

If not removed, large amounts of quartz (SiO_2) will increase the volume of phosphate slurry and result in increased pumping costs. Other negative effects from silica include equipment erosion and increased filtering demand. Amines are an effective collector for removal of quartz by flotation. However, some amount of reactive silica is beneficial during the phosphoric acid production process because it limits the formation of corrosive hydrofluoric acid by forming SiF_4 and fluosilicates instead (UNIDO and IFDC 1998).

2.2.3 Dolomite

Dolomite ($CaMg(CO_3)_2$) is particularly troublesome because of its Mg and carbonate content. In the phosphate industry, Mg content is usually reported as MgO. If not removed, dolomite poses two main problems during the wet process production of phosphoric acid:

1. Dolomite increases sulfuric acid consumption, resulting in increased processing costs; and
2. Dolomite increases fluid viscosity, resulting in decreased filtration rates when separating the solid gypsum from the phosphoric acid.

Separating dolomite from francolite has proven to be difficult because the minerals have very similar mineralogical properties (Somasundaran and Zhang 1999).

2.2.4 Calcite

Since calcite ($CaCO_3$) is a carbonate, it results in an undesired increase of sulfuric acid consumption during the wet process. As is the case with dolomite, calcite has similar properties to phosphate minerals, making it hard to separate with common techniques.

2.3 MINERALOGY OF SEDIMENTARY PHOSPHATES

Sedimentary phosphate ores account for approximately 80% of the world's total phosphate rock production (Oelkers and Valsami-Jones 2008). They are usually of marine origin and most likely formed by precipitation in shallow coastal waters (Dibble 1990). Figure 2.2 shows a photograph of a Florida sedimentary phosphate sample. Sedimentary phosphates usually come in the form of small pellets ranging from the size of fine sand to larger pellets. Many of the world's largest phosphate reserves, including those found in Florida, Morocco, and China, are sedimentary phosphates. These reserves typically contain some form of francolite or collophane as predominant phosphate minerals. Typical gangue minerals associated with sedimentary phosphates include clays, silica, calcite, and dolomite. Traditional high-grade reserves like the Bone Valley of Florida contain mainly clays and silica (i.e., siliceous phosphate ores). These types of ores have relatively simple and efficient processing circuits that include sizing/desliming and flotation. The beneficiation of siliceous sedimentary phosphates is discussed in detail in Chapter 3. When dealing with high-MgO sedimentary phosphate ores (MgO > 1%), where dolomite ($CaMg(CO_3)_2$) is present in significant amounts, the beneficiation process becomes more difficult because of the similar mineralogical properties between the phosphate and carbonate minerals. A thorough discussion of proposed methods for processing high-MgO phosphate ores is found in Chapter 4.

2.4 MINERALOGY OF IGNEOUS PHOSPHATES

Igneous phosphates account for around 15%–20% of the world's phosphate production and differ significantly from the more abundant sedimentary deposits. Igneous deposits usually contain well-formed apatite crystals as the predominate phosphate mineral. The majority of the igneous deposits

Figure 2.2 Florida sedimentary phosphate ore sample

around the world are found in southern Brazil, southeastern Africa, Finland, Sweden, and Russia. Igneous phosphate reserves are typically of three types: carbonatite, nephelinic-syenite, and pyroxenite (Houot 1982; UNIDO and IFDC 1998; Guimaraes and Peres 1999; Oliveira et al. 2011). Each of these types of deposits are rich in fluorapatite ($Ca_5(PO_4)_3F$) but can vary significantly in gangue minerals. Typical gangue minerals for each deposit type are shown in Table 2.1. Methods of processing igneous phosphate ores can range from a relatively simple flow sheet to a more complicated one depending on the types of impurities present. Chapter 5 describes the techniques and flow sheets for processing the most notable igneous phosphate reserves of the world. Differences between sedimentary and igneous phosphate processing are also highlighted.

2.5 MINERALOGY OF BIOGENIC (ISLAND) DEPOSITS

Biogenic phosphate deposits are typically found on islands in the Pacific and Indian oceans, and at one time accounted for significant amounts of phosphorus production. Also referred to as *insular*, or "island" deposits, biogenic deposits come from bird guano, which is high in phosphorus and nitrogen. The bird guano itself is also a source for direct application as a fertilizer (Piper et al. 1990).

Table 2.1 Typical gangue minerals associated with igneous phosphate deposits

Igneous Deposit Type	Typical Gangues	Chemical Formula
Carbonatite (Phalaborwa, Jacupiranga, Araxá, Sillinjärvi)	Barite	$BaSO_4$
	Calcite	$CaCO_3$
	Dolomite	$(CaMg)(CO_3)_2$
	Magnetite	Fe_3O_4
	Olivine	$(Mg,Fe)_2SiO_4$
	Phlogopite	$KMg_3(AlSi_3O_{10})(F,OH)_2$
	Pyrochlore	$(Na,Ca)_2Nb_2O_6(OH,F)$
	Quartz	SiO_2
	Vermiculite	$(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$
Nephelinic-syenite (Kola)	Nepheline	$(Na,K)AlSiO_4$
	Alkali feldspar	$KAlSi_3O_8$ / $NaAlSi_3O_8$
	Aegirine	$NaFe^{+3}(Si_2O_6)$
	Magnetite	Fe_3O_4
	Quartz	SiO_2
Pyroxenite (Phalaborwa)	Pyroxenes	$XY(Si,Al)_2O_6$ X=Ca,Na,Fe^{+2},Mg,Zn,Mn,Li Y=Cr,Al,Fe^{+3},Mg,Mn,Sc,Ti,V,Fe^{+2}
	Phlogopite	$KMg_3(AlSi_3O_{10})(F,OH)_2$
	Vermiculite	$(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$

Source: Houot 1982; Barros et al. 2008.

Insular deposits are typically high grade with minor quantities of quartz, clay minerals, dolomite, and other impurities sometimes present. Some of the most profitable island phosphate reserves throughout history have been (Barrett 1989; Piper et al. 1990; Walker 1990):

- Nauru Island (Pacific Ocean)
- Makatea (Pacific Ocean)
- Banaba Island (Pacific Ocean)
- Christmas Island (Indian Ocean)
- Juan de Nova Island (Indian Ocean)
- Chincha Islands (off the coast of Peru)
- Mejillones (coastal city of Chile)

Most of these island deposits have been extensively mined, depleting the majority of the reserves. In the case of Nauru Island, roughly 80% of the island's surface was strip mined, which resulted in harsh environmental consequences. Depletion of insular phosphate deposits generally makes island reserves irrelevant in today's phosphate market (Piper et al. 1990; UNIDO and IFDC 1998).

3
Beneficiation of Siliceous Sedimentary Phosphate Ores

High-grade sedimentary phosphate reserves, such as those found in the Bone Valley of Florida, typically contain quartz and clays as the main gangue minerals (Dibble 1990). Clays are removed during the sizing, scrubbing, and desliming stages, which prepares the feed for the Crago double float process (Wiegel 1999). This chapter explains the traditional processes used for the beneficiation of siliceous sedimentary phosphate ores.

3.1 FLOTATION FEED PREPARATION—WASHING, SIZING, AND DESLIMING

Sedimentary phosphate ore is typically mined using draglines, made into a slurry, and transported by pipelines to the washing plant. Washing is often accomplished using trommels, log washers, and sandwich screens (Lawver et al. 1978). Trommels are large rotating cylindrical screens that classify ore as it moves from one end to the other. A basic diagram of a trommel screen is shown in Figure 3.1. The lifting and dropping action of the rotating drum breaks up large clay balls that contain valuable phosphate pebbles. High-pressure spray nozzles are often mounted inside the drum to help break apart large balls consisting of phosphate particles agglomerated together by clay. Trommels are typically installed at a slight angle to the ground to keep the ore moving along the drum screen. The washed slurry is then sized and deslimed in preparation for the Crago double float process. The Crago process is described in the following sections.

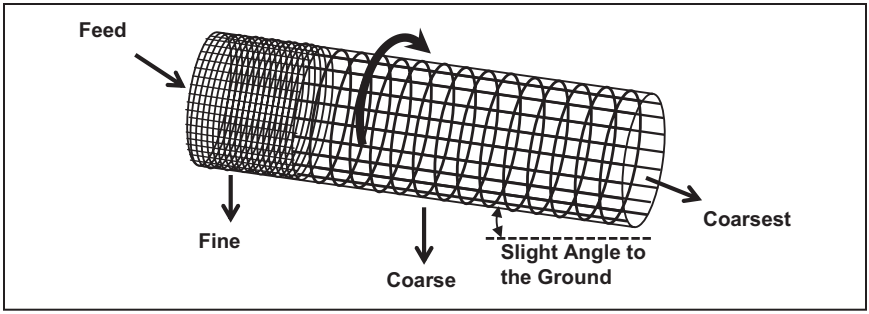


Figure 3.1 Trommel screen

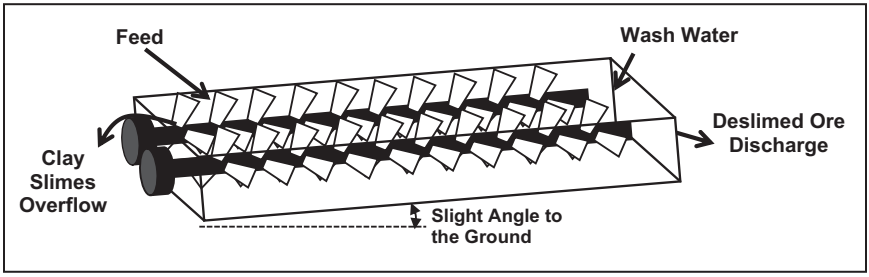


Figure 3.2 Log washer

Sizing and desliming are critical parts of an efficient phosphate beneficiation process. Siliceous sedimentary phosphate reserves are sized into coarse and fine size fractions. For the Crago double float process, the phosphate ore is initially sized into three size fractions (Guan 2009a):

1. Pebble fraction: +1 mm (+16 mesh)
2. Flotation feed: –1/+0.1 mm (16 × 150 mesh)
3. Clay fraction: –0.1 mm (–150 mesh)

Screens are used to separate the +16 mesh pebble fraction, which has traditionally been high enough quality to be considered phosphate concentrate and can be used in the phosphoric acid plant. Sometimes log washers (Figure 3.2) are used to remove slimes from the coarse pebble concentrate. Log washers use a countercurrent wash-water flow to remove clay slimes from ores. The remaining –16 mesh size fraction is sent to hydrocyclones to remove the –150 mesh clay slimes. The –150 mesh fines are discarded to the settling ponds. Removal of slimes from the flotation feed is important to

reduce reagent consumption and increase selectivity. The flotation feed (16 × 150 mesh) is usually sized further into 16 × 24 mesh, 24 × 35 mesh, and 35 × 150 mesh size fractions to increase flotation efficiency and significantly reduce reagent consumption (Oswald 1993; Wiegel 1999; Guan 2009a). The fine flotation feed (35 × 150 mesh) makes up the majority at approximately 80% (Zhang et al. 2006).

Hydrocyclones used in phosphate processing typically make a relatively sharp size separation while operating at fairly high capacities. The basic diagram of a hydrocyclone is shown in Figure 3.3. The hydrocyclone consists mainly of a cylindrical body connected to a conical bottom section. The feed slurry enters tangentially through the inlet, generating a swirling "cyclone" action. This flow imparts centrifugal forces on the slurry, which moves coarser, denser particles to the outside wall of the cyclone and eventually out the underflow. The finer, lighter particles stay in the liquid and are carried away with a large portion of the fluid through the vortex finder into the overflow. Hydrocyclone efficiency for a specific application depends largely on the design of the cyclone itself (cyclone diameter, angle of conical section, diameter of entrance and exits, etc.), operating parameters (feed flow rate, % solids in slurry, etc.), and feed ore characteristics (particle size distribution, particle

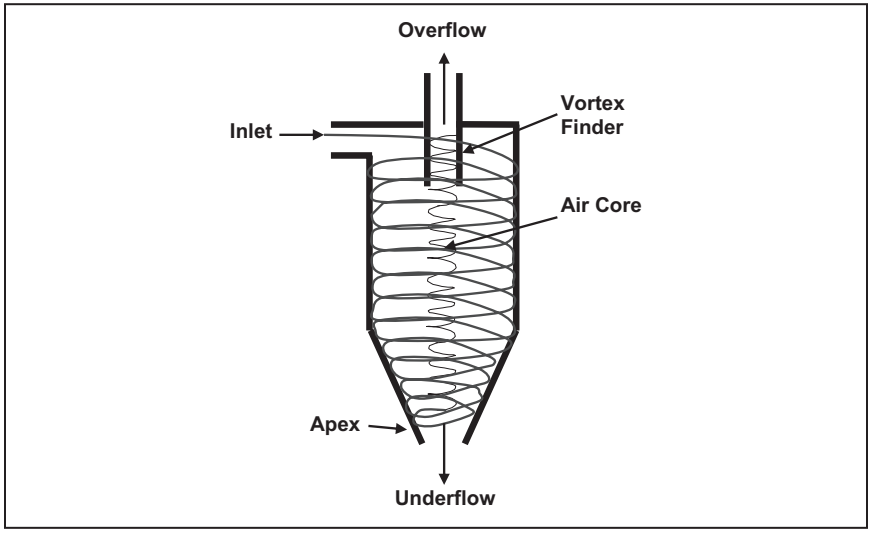


Figure 3.3 Hydrocyclone

density, particle shape, etc.). Hydrocyclones used for phosphate ore desliming are typically 24–30 inches (61–76.2 cm) in size (Lawver et al. 1978).

3.1.1 Industrial Phosphate Washing Plant

Figure 3.4 shows a simplified process flow diagram of the IMC Four Corners (Florida) phosphate washing plant as based on a report from a site visit by the U.S. Environmental Protection Agency (EPA 1994). The mined phosphate ore is first screened to remove the large +8 inch (20.3 cm) oversized debris. The ore passing −8 inch (20.3 cm) is sent to the first trommel screen, where it is sized at ½ inch (1.27 cm). The +½ inch fraction is sent to a second trommel screen, which sizes the ore at 2 inches (5.08 cm). The coarse +2 inch size fraction is sent to the tailings, while the −2 inch fraction is sent to a ball mill and then back to the first trommel screen.

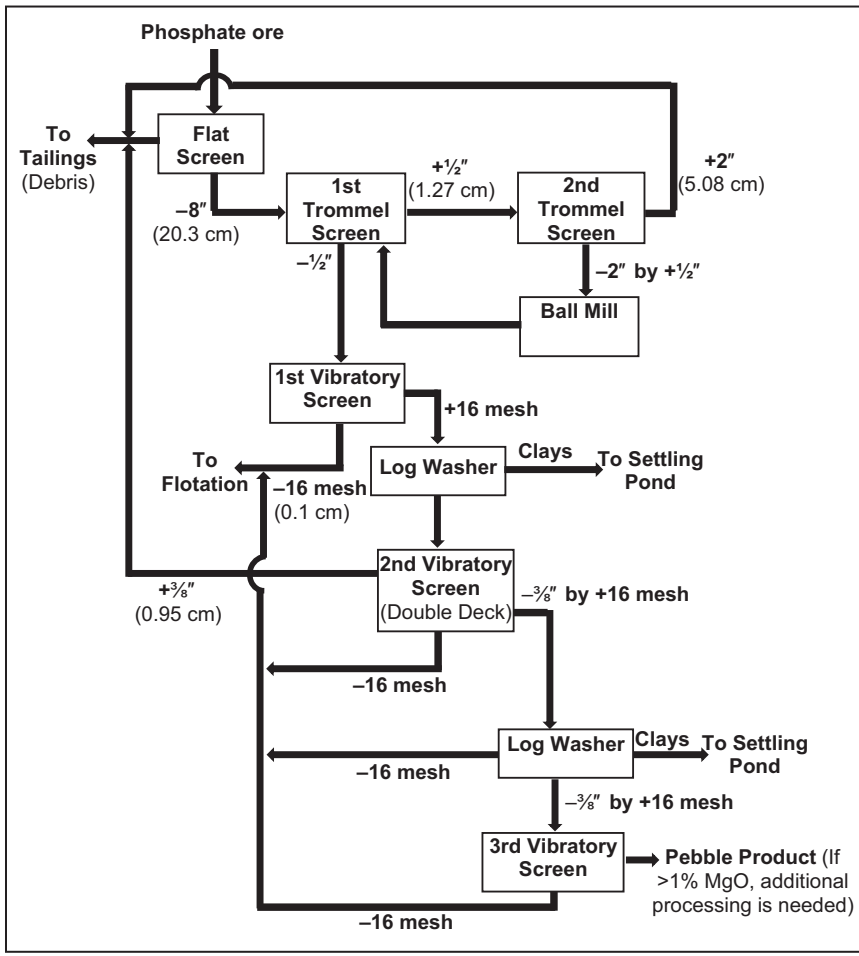
The –½ inch size fraction passing the first trommel screen is then sent through a series of vibratory screens and log washers. The log washers vigorously agitate the slurry to wash it of clay slimes. The clay slimes from the log washers are sent to clay settling ponds. The clays settling ponds are also a source for wash water that is used in the log-washing stages. The −16 mesh (−0.1 cm) size fractions from the first, second, and third vibratory screens are sent to screens and hydrocyclones to be sized for the flotation circuit. The −⅜ inch by +16 mesh size fraction from the third (final) vibratory screen is considered to be pebble product if it contains <1% MgO. If the MgO content is greater than 1% MgO, then the ore is stockpiled and additional processing is needed to remove dolomite (EPA 1994).

3.2 THEORY OF PHOSPHATE FLOTATION

Froth flotation is one of the most widely used mineral separation techniques. Flotation is particularly useful for processing fine feeds that are typically not separable with conventional gravity separation techniques. Selectivity in a froth flotation process depends on the ability to selectively induce hydrophobicity on one mineral while the other gangue minerals remain hydrophilic. The hydrophobic minerals attach to air bubbles in the flotation cell, rise to the top of the cell, and concentrate in the froth phase. The hydrophilic gangue stays in pulp phase and exits the bottom of the flotation cell in the tailings.

Although some minerals are naturally hydrophobic (i.e., coal, molybdenite, talc), most minerals require the addition of surfactants (collectors) to render their surface hydrophobic. Collectors generally fall into four major

categories: non-ionic, cationic, anionic, and amphoteric. Nonionic collectors are hydrocarbon-based collectors, such as fuel oil, that coat an already hydrophobic surface (i.e., coal) to make the surface more hydrophobic. Nonionic collectors are often referred to as "extenders" since they extend the hydrophobic surface. Fuel oil is often used as an extender in the anionic fatty acid flotation of phosphates. Sodium oleate is considered an anionic collector because of its negatively charged carboxylate group being the polar part of the



Source: Adapted from EPA 1994.

Figure 3.4 Simplified process flow diagram of washing plant at IMC Four Corners mine

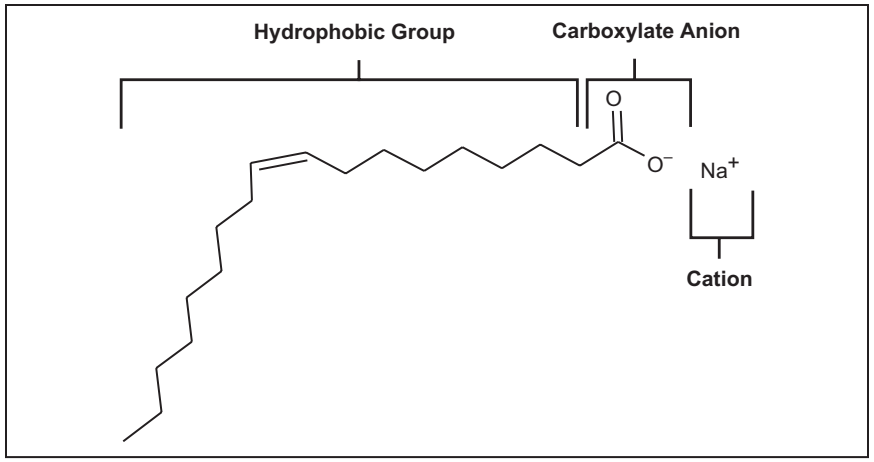
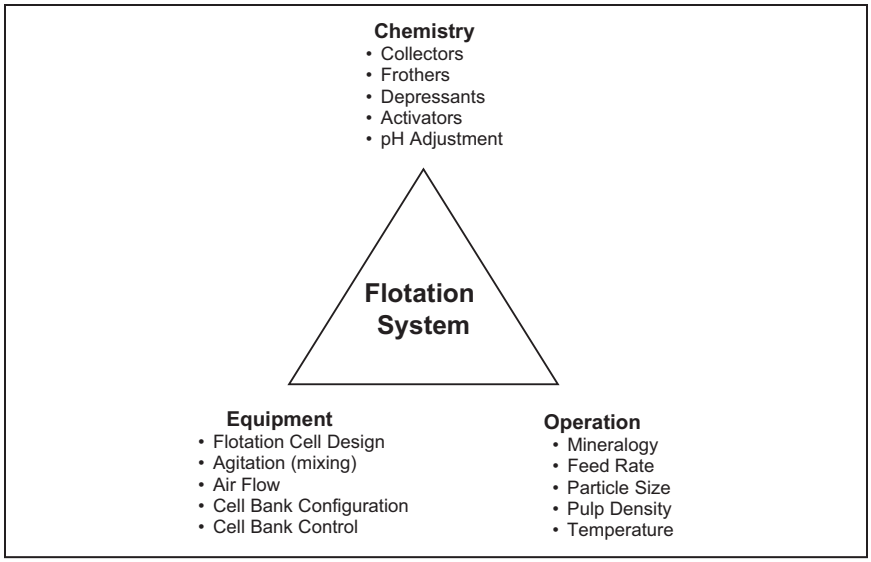


Figure 3.5 Sodium oleate is an anionic collector that can be used to render apatite hydrophobic in alkaline environments (pH ~9)

collector (Figure 3.5). Cationic collectors, on the other hand, such as amines, consist of positively charged cations as the polar group. Amphoteric collectors can be either anionic or cationic depending on the pH of the solution. The adsorption of surfactants onto mineral surfaces is primarily dependent on interfacial properties of the mineral particles, which are discussed in more detail in Section 3.2.1. Contact angle measurements can be used to determine the relative hydrophobicity of mineral surfaces. Contact angle theory and measurements are discussed in more detail in Section 3.2.2.

Overall, flotation systems can be very complex and consist of many interrelating variables. Klimpel (1995) explained the flotation system as three major categories as shown in Figure 3.6: (1) *Chemistry components* include collectors, depressants, frothers, pH adjusters, and other reagents needed in flotation systems; (2) *Equipment components* include type of flotation device, flotation cell size, flotation circuit configuration, and other parameters particular to specific flotation machines; and (3) *Operation components* include mineralogy of feed ore, particle size, pulp density, feed rate, and temperature. This chapter aims to describe the most important parts of the flotation system and to explain their significance in the flotation of siliceous phosphate ores.



Source: Adapted from Klimpel 1995.

Figure 3.6 Flotation system with three interrelating subsystems: chemistry, equipment, and operation components

3.2.1 Froth Flotation Devices

Two types of flotation machines are available: mechanical flotation cells and column flotation cells. New flotation devices are continually being developed, but mechanical cells and flotation columns are two of the most common devices in industrial froth flotation (Finch 1995). The majority of phosphate flotation processes have used banks composed of relatively small mechanical flotation cells (Wiegel 1999). However, column flotation has also seen some consideration for phosphate flotation, with the majority of interest in processing igneous phosphates in Brazil (Guimaraes and Peres 1999; El-Shall et al. 2000; Fortes et al. 2007; Oliveira et al. 2007, 2011; Santana et al. 2008). This section includes a brief description of each device, important operating parameters, and advantages and disadvantages of each device.

3.2.1.1 Mechanical Flotation Cells

The basic design of a mechanical flotation cell is shown in Figure 3.7. The slurry in the mechanical flotation cell is mixed by an impeller to ensure proper dispersion of slurry and air bubbles. The air can be either induced through

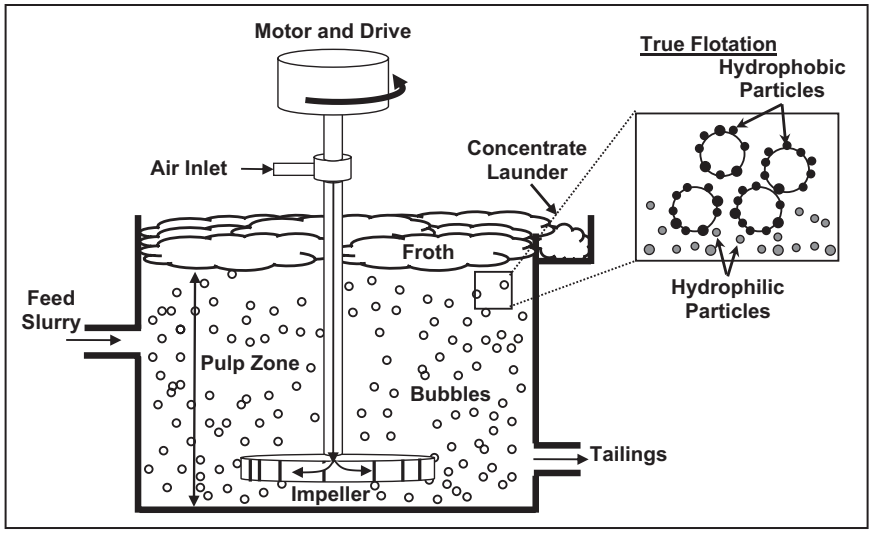


Figure 3.7 Mechanical flotation cell

the air inlet or forced through ("supercharged") by a blower. The hydrophobic minerals attach to the air bubbles in the pulp zone, are carried to the surface of the flotation cell, and are collected in the froth concentrate launder. Mechanical flotation cells often have paddles, or scrapers, which are used to remove the froth layer into the concentrate launder. Hydrophilic gangue particles are removed through the tailings exit at the bottom of the cell.

Important operating variables in mechanical flotation cells are reagent additions (collectors, frothers, depressants, etc.), aeration, impeller speed, feed properties (% solids, particle size), and position of the pulp–froth interface (or froth depth). One of the major differences between mechanical flotation cells and flotation columns is the use of impellers for mixing of the mechanical cells. Some authors have suggested that the mixing action of the impellers helps remove slimes from particle surfaces that have been known to hinder flotation selectivity. However, mixing of the pulp and air bubbles may not be as conducive to bubble–particle collision and attachment as the countercurrent (rising bubbles/falling particles) action in flotation columns (Wills and Napier-Munn 2006).

Overall, one of the greatest advantages of mechanical flotation cells is that they are well known. Operators are accustomed to them, and all previous

plant history includes the use of mechanical flotation cells. This leads to a certain level of comfort and reliability as to how the process will perform.

3.2.1.2 Column Flotation

Column flotation was first patented in the 1960s and started receiving much attention in the 1980s after it was successfully implemented in molybdenum concentrating plants (Finch and Dobby 1990). Flotation columns have two main advantages over mechanical cells: flotation columns do not have any moving parts, and entrainment is significantly reduced due to the use of wash water. A general schematic of a typical flotation column is shown in Figure 3.8. Flotation columns are usually cylindrical columns of approximately 9–15 m in height, with diameters ranging from 0.5–4 m.

Feed slurry enters around a third of the way down from the top of the column and starts descending downward through the column. Bubbles generated by either internal or external spargers enter at the bottom of the column and rise upward, countercurrent to the solids. As the feed slurry works its way downward through the "collection" zone, hydrophobic particles attach to the rising bubbles and are carried upward. The collection zone is comparable to the pulp zone in a mechanical flotation cell.

As air bubbles rise through the collection zone, they become loaded with hydrophobic particles and enter the "cleaning" zone. The cleaning zone, also called the froth zone, is where the loaded bubbles accumulate and flow over into the froth concentrate launder. Wash water is added by sprays at the top of the column to help stabilize the froth and wash it of "entrained" gangue (hydrophilic) particles (entrainment is discussed in detail in Section 3.2.3). Washed particles are sent back down into the collection zone; this is often referred to as "froth dropback" (Finch and Dobby 1990).

Utilization of wash water is a key component in column flotation producing high-grade froth concentrates. The water addition, called "bias" water, helps maintain the pulp–froth interface. Flotation columns are typically operated so that the liquid (pulp) is flowing toward the bottom of the column, which is referred to as "positive bias." Hydrophilic tailings exit the bottom of the column (Finch and Dobby 1990).

Important operating parameters for column flotation include

- Superficial air velocity,
- Bubble size,

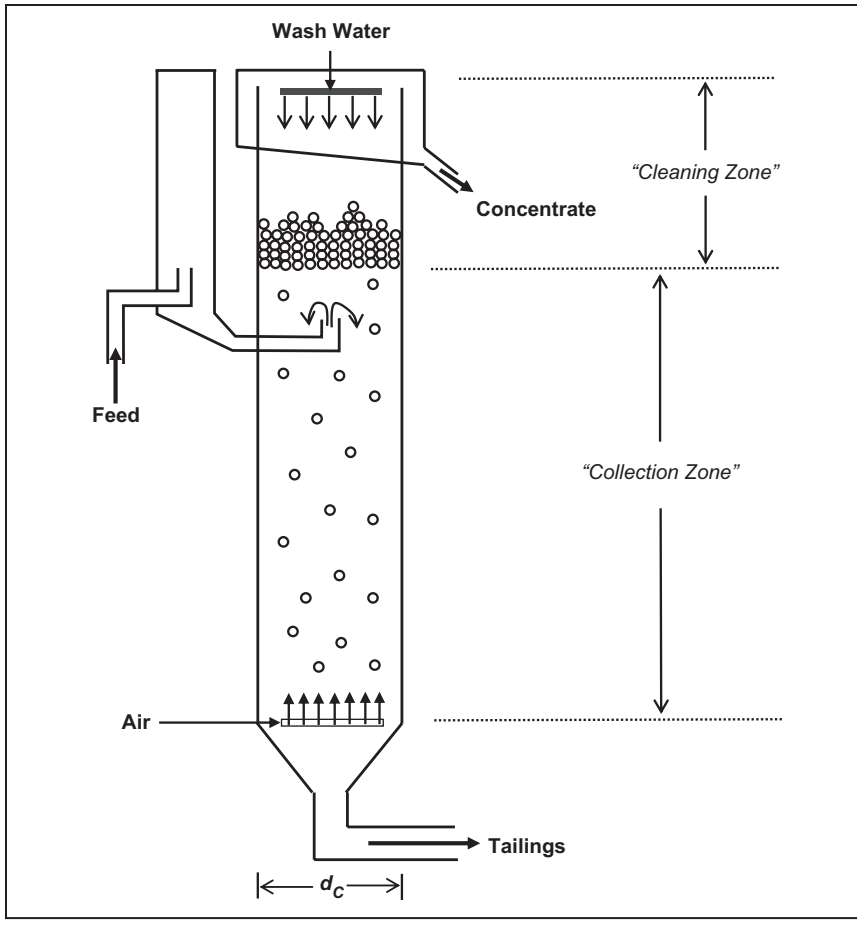


Figure 3.8 Schematic of a typical flotation column

- Superficial liquid velocity,
- Particle size, and
- Feed concentration.

Superficial air velocity, bubble size, and superficial liquid velocity are particularly important since they play major roles in determining "gas holdup." Gas holdup is the fraction of gas within a given volume of liquid in the column. Gas holdup is a key property in determining hydrodynamic conditions in the collection zone. Gas holdup must be at a low enough value that the air bubbles rise through the column at a fairly uniform rate, with a homogeneous

distribution of almost uniformly sized bubbles. This is referred to as "bubbly flow." If the gas holdup value is too high, larger bubbles will form and rise rapidly through the column, resulting in turbulent mixing. This is referred to as "churn-turbulent" conditions and is undesirable in column flotation (Finch and Dobby 1990). Since the bubble size, superficial air velocity, and superficial liquid velocity control the gas holdup value, and gas holdup must stay within the bubbly flow regime, there is a limit to how much bubble area will be rising through the column at a given air rate. This is termed the "superficial bubble surface rate" (Tavera et al. 2001). This idea plays a role in determining the max "carrying rate," or maximum amount of hydrophobic particles that can be carried by the bubbles into the froth. Overall, the need to operate the column in the bubbly flow regime sets limits for column capacity (Finch and Dobby 1990, 1991).

Axial mixing has been shown to significantly decrease the efficiency of flotation columns. Axial mixing occurs mostly in larger-diameter columns because there is nothing regulating fluid flow along the vertical axis of the column. Water is displaced upward toward the pulp–froth interface, which then descends downward causing the axial mixing effect. Several methods can be used to help decrease axial mixing. First, it is important that the column be installed perfectly vertical, since any tilting in the column will enhance axial mixing. Second, using relatively small bubbles with uniform size distribution will help limit axial mixing. Lastly, the addition of horizontal baffles (perforated plates) throughout the column has been shown to significantly decrease axial mixing and increase overall flotation performance (Kawatra and Eisele 1999, 2001). As shown in Figure 3.9, horizontal baffles break up the global axial mixing shown in the unbaffled column into smaller local mixing patterns without restricting fluid flow so much that plugging occurs. Packed columns eliminate axial mixing but negatively affect solids movement and are therefore prone to plugging. Kawatra and Eisele (1999) demonstrated the positive effects of baffles on the column flotation of phosphate ore. They found that a fully baffled column produced a significantly higher-grade phosphate concentrate (18.8%–20.3% P_2O_5) than a minimally baffled column (12.7%–13.2% P_2O_5), while still achieving similar phosphate recoveries (Kawatra and Eisele 1999). Other authors have used computational fluid dynamics (CFD) to simulate the benefits of baffles for the reduction of axial mixing in column flotation (Xia et al. 2006).

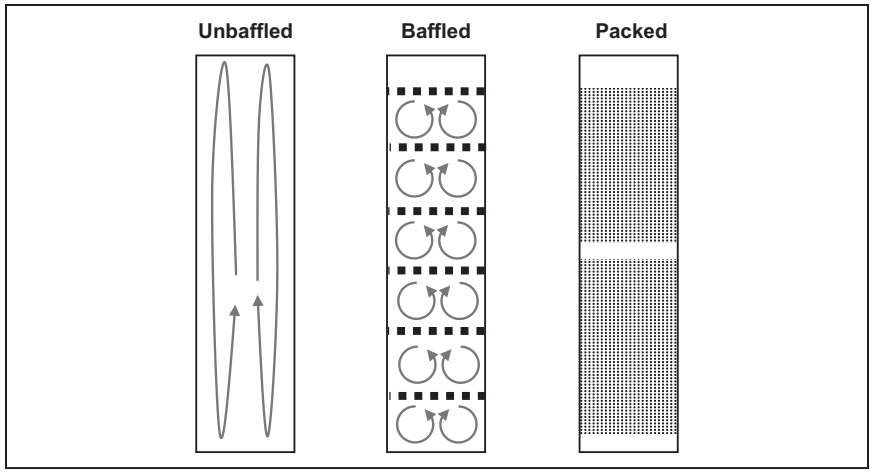
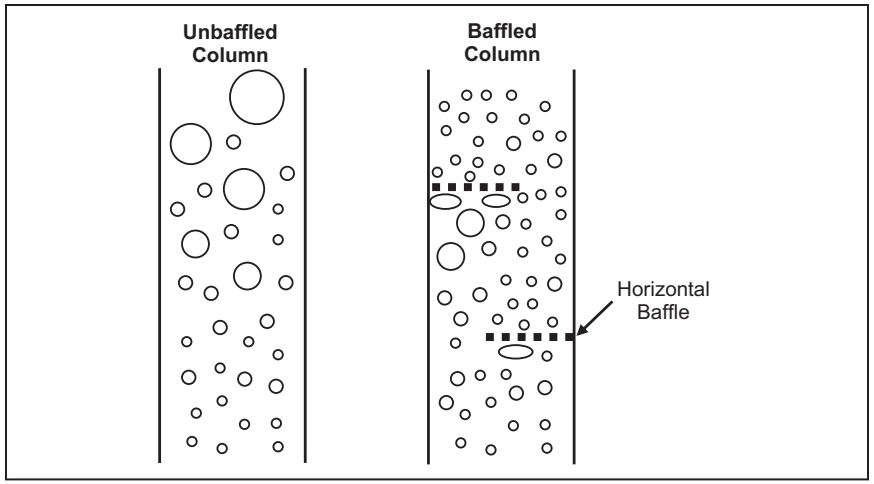


Figure 3.9 Comparison of axial mixing in unbaffled, baffled, and packed columns

Bubble growth is another problem that can occur in unbaffled columns. Smaller bubbles grow larger because of both bubble coalescence and the decrease in hydrostatic head as bubbles travel up the column. Larger bubbles rise faster and result in the transition from bubbly flow to churn-turbulent flow. This results in two main problems: larger bubbles have less surface area, and therefore reduce the bubble carrying capacity; and large bubbles disrupt the froth layer, often referred to as churning or burping, and decrease the efficiency of the froth washing process. Horizontal baffles help regulate bubble size within the flotation column by breaking up large bubbles into smaller bubbles, as shown in Figure 3.10.

Overall, the most significant advantage of flotation columns is that the countercurrent action (rising bubbles/falling particles) is more favorable for bubble–particle collision and attachment, resulting in improved metallurgical performance (grade and recovery). Flotation columns were first implemented in sulfide flotation (molybdenum and copper) as cleaners because of the significant increase in metallurgical performance over traditional cells. However, since flotation columns are relatively new compared to mechanical flotation cells, flotation engineers are less familiar with them and are more resistant to changing current operations. A comparison between mechanical cells and flotation columns is shown in Table 3.1.



Source: Adapted from Kawatra and Eisele 1999, 2001.

Figure 3.10 Comparison of bubble growth in unbaffled and baffled columns

Table 3.1 Comparison of mechanical flotation cells and column flotation

Mechanical Flotation Cells	Column Flotation
• Cell sizes ranging from ~0.1 to 350 m^3	• Available up to 4 m in diameter • Typical heights around 9–15 m
• Air induced or injected through impeller to generate bubbles	• Internal or external spargers generate air bubbles • Produces smaller bubbles
• Bubble–particle interaction through mixing by impeller • Less favorable for bubble–particle attachment	• Bubble–particle interaction through countercurrent action—descending slurry and rising bubbles • Generally considered more favorable for bubble–particle attachment • Better metallurgical performance (grade and recovery) • Axial mixing can significantly reduce overall performance (especially in larger-diameter columns) • No moving parts
• Well known to operators and easier to operate • Conventional plant operation history and knowledge based on mechanical cells	• Newer and less known by operators • Harder to operate

Source: Data from FLSmidth 2013 and Metso 2013.

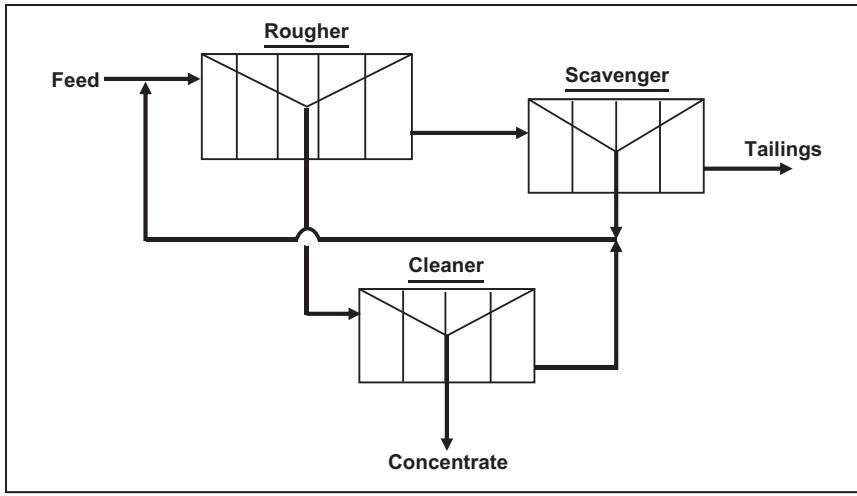


Figure 3.11 Rougher–scavenger–cleaner flotation circuit

3.2.1.3 Froth Flotation Circuits

Flotation processes in which the desired mineral is floated from the gangue mineral are referred to as "direct" flotation. Conversely, when the gangue mineral is floated from the desired mineral, it is referred to as "reverse" flotation. Flotation plants are usually set up as a circuit consisting of several flotation stages. Figure 3.11 shows a basic rougher–scavenger–cleaner flotation circuit. The purpose of the scavenger is to recover any valuable mineral that may not have been recovered during rougher flotation. The cleaner is used to remove any gangue mineral that may have reported to the froth concentrate during rougher flotation. Circuits can be set up in many ways and may consist of numerous cleaner stages to produce a high-grade concentrate.

3.2.2 Contact Angle Theory

Contact angle is a measurement used to quantify the wettability of a solid surface. When a drop of water is placed on a solid surface, it will either bead up or spread out depending largely on the surface energy of the solid. Solids with low surface energies tend to cause the drop of water to bead up, whereas solids with high surface energies result in a water drop spreading out and wetting the surface. Figure 3.12 illustrates the difference in wetting of high-energy and low-energy surfaces.

Figure 3.13 shows the surface energies and contact angle for a system consisting of a liquid drop on a solid surface in an air medium. Figure 3.14 shows the surface energies and contact angle for a system consisting of an air bubble on a solid surface in a liquid medium. Contact angle measurements are typically made using the liquid drop on a solid surface system due to ease of use.

Thomas Young related the surface energies of all three phases, and the resulting equilibrium balance is shown in Equation 3.1. Dupré's equation

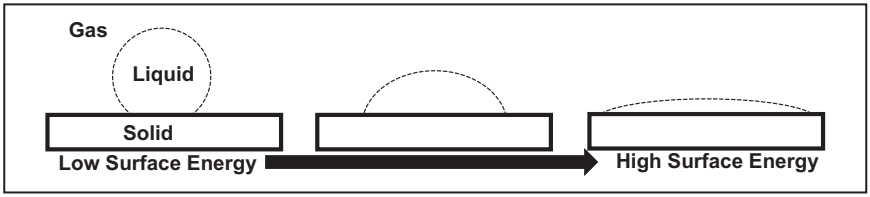


Figure 3.12 Low surface energies in solids (left) tend to make water bead up (larger contact angle), whereas high surface energies (right) result in wetting (low contact angle)

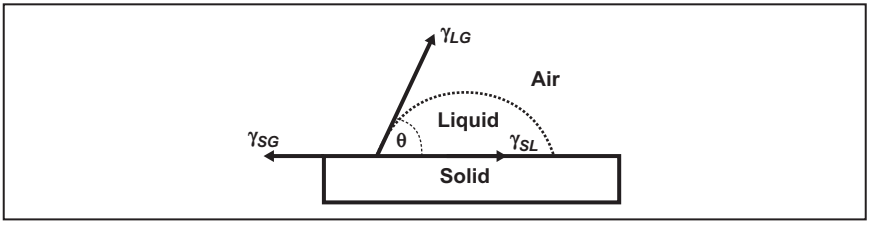


Figure 3.13 Surface energies and contact angle for a liquid drop on a solid surface

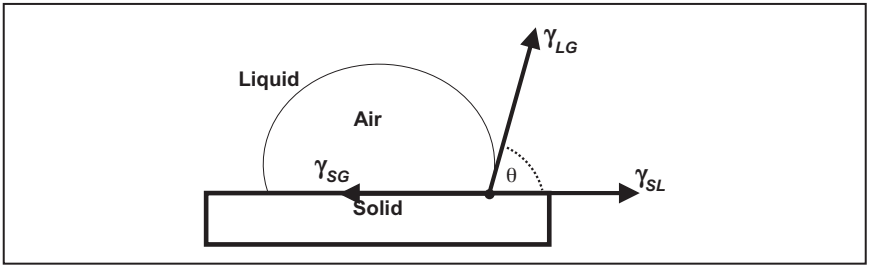


Figure 3.14 Surface energies and contact angle for an air bubble attached to a solid surface

(Equation 3.2) gives the ΔG associated with liquid–solid interface replacing the liquid–gas interface. Equation 3.1 is then substituted into Equation 3.2 and simplified into the Young–Dupré equation (Equation 3.3). This equation shows that an increase in contact angle corresponds to an increase in hydrophobicity of the solid surface (Adamson 1990; Wills and Napier-Munn 2006; Fuerstenau and Raghaven 2007). This means that the water is repelled from the surface and an air bubble is more likely to adhere. Greater contact angles are desired for froth flotation. A larger contact angle implies a more hydrophobic mineral surface, meaning that the mineral can be floated more easily.

Young's equation: $$0 = \gamma_{SG} - \gamma_{LG}\cos(\theta) - \gamma_{SL} \quad \textbf{EQ 3.1}$$

Dupré's equation: $$\Delta G = (\gamma_{SL} + \gamma_{LG}) - \gamma_{SG} \quad \textbf{EQ 3.2}$$

Young–Dupré equation: $$\Delta G = \gamma_{LG}(1 - \cos(\theta)) \quad \textbf{EQ 3.3}$$

where

γ_{SG} = surface energy of solid–gas interface
γ_{LG} = surface energy liquid–gas interface
γ_{SL} = surface energy of solid–liquid interface
ΔG = change in interfacial energy
θ = contact angle

Contact angles greater than 90° indicate a hydrophobic surface, meaning that air bubbles will stick to the particle surface and flotation will occur. Contact angles less than 90° indicate a hydrophilic surface, which means that water will wet the surface and air bubbles will not readily attach.

3.2.2.1 Application of Contact Angle Measurements

Contact angle measurements are useful in determining adsorption characteristics for collector/mineral systems. For example, glass is naturally hydrophilic because of its relatively high surface energy. The glass is readily wetted, resulting in low contact angle measurements, as shown in Figure 3.15. Surfactants, such as car windshield treatments, can be applied to the surface of the glass to reduce its surface energy. This makes the glass surface become hydrophobic, making the water bead up and giving very high contact angles. Contact angle measurements are used heavily in the characterization of materials.

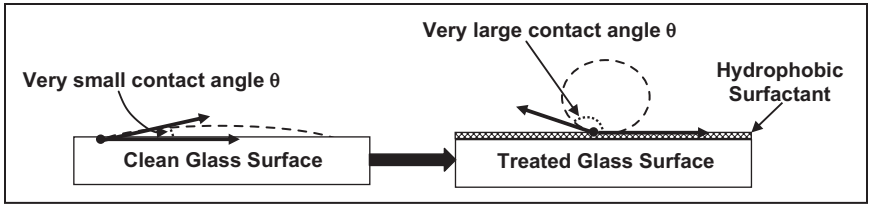


Figure 3.15 Hydrophobic surfactants can be used to treat glass surfaces and make water bead up

In minerals processing, contact angle measurements can be used to estimate the adsorption of surfactants onto minerals for froth flotation. For example, one could condition a mineral surface at a variety of conditions (i.e., pH, collector dosage, conditioning time, etc.) and measure the contact angles to determine optimal conditions for surfactant adsorption. Higher contact angles would correlate to better surfactant adsorptions, meaning more favorable conditions for froth flotation. Similar studies could be done on different types of minerals to estimate selectivity of specific collectors for a froth flotation separation. Even though contact angles are very important when researching new flotation schemes, very few contact angle studies can be found in the literature involving investigations of new reagents for flotation of dolomite from phosphate ores.

It is important to note possible disturbances when performing contact angle analysis on minerals. Disturbances include surface roughness, heterogeneity, water drop size, and sample preparation methods (Good and Koo 1979; Drelich et al. 1996). Finding mineral specimens large enough to be flattened for contact angle measurements and that do not contain any inclusion can be very difficult.

3.2.2.2 Contact Angle Measurements

Contact angles are typically measured using a goniometer. One variation of the goniometer is the Tantec contact angle meter (Cam-Plus Micro model) shown in Figure 3.16. This contact angle meter consists of the following:

- Variable position stage on which the solid flat sample sits
- Syringe located directly above the stage for placing a drop of water onto the solid flat sample

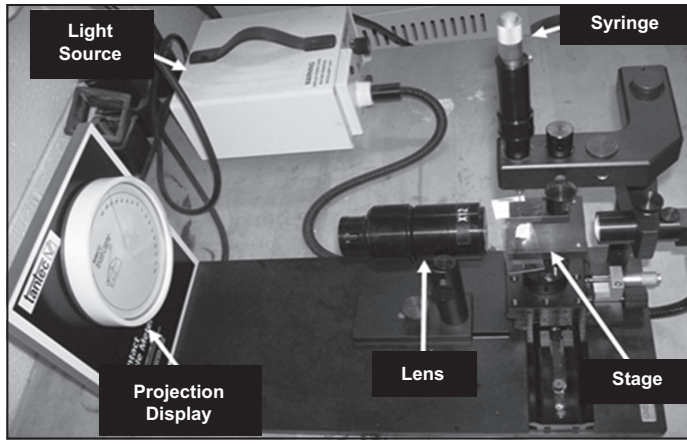


Figure 3.16 Tantec Cam-Plus Micro contact angle meter

- Light source and lens for projecting and focusing the image on the projection display
- Projection display with goniometer for measuring the contact angle

Some more advanced contact angle meters may have a camera in place of a projection display. In those contact angle meters, a camera connected to a computer records the projected image. The image is then displayed on a computer screen and saved for contact angle analysis. Figure 3.17 shows an example of a water drop on a hydrophobic surface. This particular device uses the "half-angle" technique to measure the contact angle.

Lu et al. (1997) studied the wetting of francolite and quartz, and how it affected the anionic fatty acid phosphate flotation system. They found the maximum advancing water contact angles on a francolite surface to be 104–120° when conditioning the surface with a sodium oleate collector (70–80 mg/L) at a pH of 9. The authors also examined the effects of conditioning pH on the wettability of francolite when conditioning the surface with 344 mg/L sodium oleate collector. They found that the greatest advancing contact angles (100–120°) occurred in an alkaline pH range of 9 to 11 (Lu et al. 1997). This pH range is in good agreement with the standard fatty acid phosphate flotation (pH 9–9.5) procedure used in the Crago double float process (Oswald 1993; Wiegel 1999; Guan 2009a).

Contact angle measurements can also be used to test the selectivity of potential collectors. Kawatra et al. (2012) tested the selectivity of potential

dolomite collectors by conditioning both dolomite and apatite pebbles and measuring contacts angles using the static sessile drop technique. Five dolomite pebbles and five apatite pebbles were ground into flat slices and conditioned with a proposed dolomite collector at the same conditions. Results shown in Table 3.2 indicate that the proposed collectors did not generate

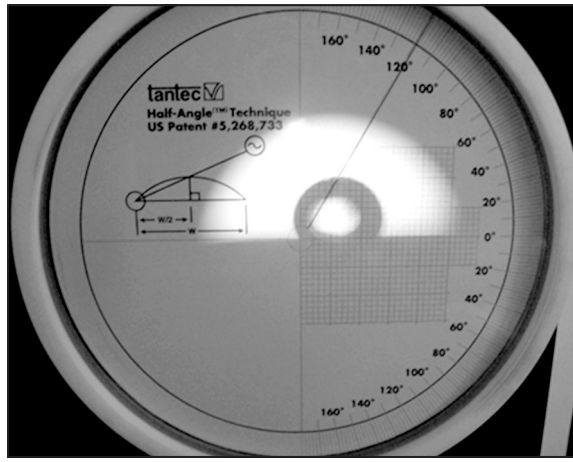


Figure 3.17 Example showing contact angle measurement using the half-angle method

Table 3.2 Testing selectivity of potential proprietary dolomite flotation reagents using contact angle measurements

		Contact Angle Measurement (degrees at 0 seconds, 30 seconds, 1 minute)		
Sample	**Pebble Type**	**MT2**	**MT3**	**MT6**
1	Dolomite	46, 34, 26	48, 44, 44	44, 26, 22
2	Dolomite	18, 0, 0	0	60, 32, 28
3	Dolomite	48, 30, 16	54, 28, 14	56, 34, 28
4	Dolomite	60, 36, 26	58, 44, 34	0
5	Dolomite	48, 38, 22	66, 50, 44	52, 36, 24
6	Apatite	20, 0, 0	32, 0, 0	0
7	Apatite	20, 0, 0	58, 36, 34	0
8	Apatite	36, 18, 16	54, 44, 38	38, 24, 20
9	Apatite	54, 28, 24	59, 44, 34	50, 38, 34
10	Apatite	34, 24, 18	50, 34, 28	32, 20, 16

high enough contact angles suitable for flotation. Furthermore, the collectors did not show selectivity between the dolomite and apatite pebbles (Kawatra et al. 2012).

3.2.3 Entrainment Theory

During froth flotation, particles can report to the froth concentrate by either "true flotation" or "entrainment." True flotation occurs when the hydrophobic particles attach to air bubbles and are carried up to the froth concentrate. True flotation selectively separates the hydrophobic particles from the hydrophilic particles, and it is the fundamental basis of froth flotation processes. Entrainment occurs when fine particles get caught in the water between bubbles and are carried into the froth concentrate. Figure 3.18 shows the differences between true flotation and entrainment. Entrainment is nonselective, so both hydrophobic and hydrophilic particles are equally capable of being entrained. However, since the majority of the hydrophobic mineral should be floating due to true flotation, entrainment usually results in increased gangue mineral recovery to the froth. Therefore, it is desired that entrainment be kept at a minimum to achieve greater selectivity and a higher froth concentrate grade.

The degree of particle entrainment is largely dependent on particle size. In the case of very fine clays (less than ~3 μm), recovery to the froth concentrate by entrainment is approximately equal to the percentage of water

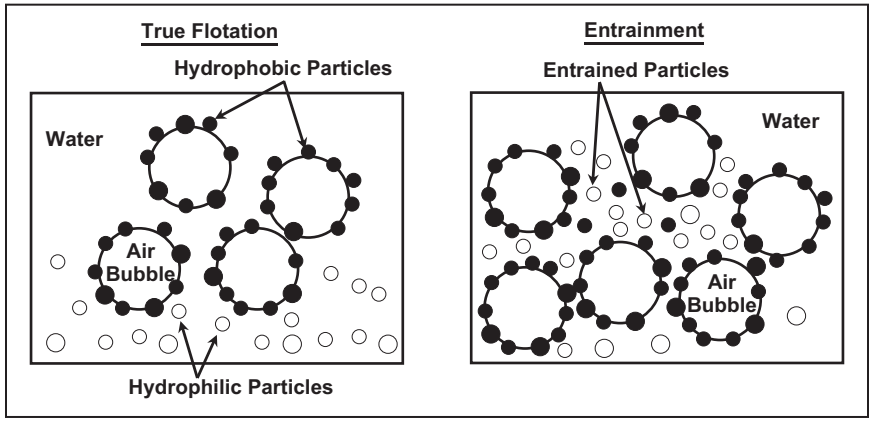
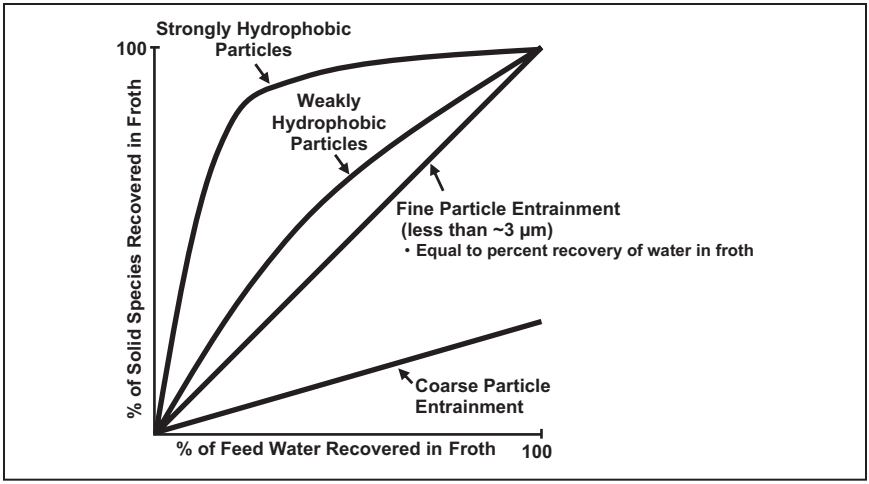


Figure 3.18 True flotation versus entrainment



Source: Adapted from Kawatra and Eisele 2001.

Figure 3.19 Effects of particle size and hydrophobicity on recovery versus water recovery

recovered to the froth. Coarser particles have higher settling velocities and can drain from the froth more quickly, resulting in less entrainment. Entrainment is not usually appreciable for particles coarser than 50 µm (Smith and Warren 1989; Savassi et al. 1998).

The effects of particle size and hydrophobicity on particle recovery versus water recovery are illustrated in Figure 3.19. Strongly hydrophobic particles float due to true flotation and therefore have a particle recovery that is mostly independent of water recovery. Weakly hydrophobic particles are recovered partly by true flotation and partly by entrainment. Fine hydrophilic particles are recovered by entrainment at a rate approximately equal to that of the amount of water recovered. Coarser hydrophilic particles drain more quickly from the froth, and therefore are entrained at a lower rate than finer hydrophilic particles (Kawatra and Eisele 2001). Based on this figure, it would be most efficient to operate a flotation system at the lowest water recovery that still achieves optimal recovery of the strongly hydrophobic mineral. As the water recovery rate is increased past the optimum point, the recovery of gangue particles due to entrainment significantly outweighs any additional recovery of the hydrophobic mineral.

Several factors can affect the level of entrainment that occurs in a flotation system. Some of the key factors are (Savassi et al. 1998; Kawatra and Eisele 2001)

- Froth depth and froth residence time;
- Particle size, shape, and density;
- Types and dosages of collectors, frothers, depressants, flocculants, etc.;
- Percent solids in pulp; and
- Pulp viscosity.

Froth depth plays a key role in determining the level of entrainment in a flotation cell. If the froth depth is deeper, meaning the pulp–froth interface is lower down from the froth overflow lip, the entrained particles will have more time to drain from the froth. However, if the froth layer is too deep, the loaded bubbles near the top of froth cell may become unstable and cause the froth to collapse. Other important parameters affecting entrainment and methods to minimize their effects are described in Table 3.3.

Determining entrainment values can be very difficult because of variations in the previously mentioned factors in specific flotation systems. In addition, if a particular solids species is either partially hydrophobic or consists of locked hydrophobic/hydrophilic particles, it becomes very difficult to accurately determine the amount of flotation due to entrainment. Several methods for determining entrainment levels exist (Trahar 1981; Warren 1985; Ross 1990; Kawatra and Eisele 2001). The methods vary significantly in accuracy, difficulty, and amount of data needed for entrainment calculations. In addition, several authors have attempted to generate models for entrainment (Savassi et al. 1998; Zheng et al. 2005, 2006; Martinez-Carrillo and Uribe-Salas 2008).

In phosphate flotation, some authors have suggested that entrainment could be the reason for fine silica reporting to the froth phosphate concentrate during the anionic flotation stage of the Crago double float process. It was suggested that because of the low floatability of sedimentary phosphates, larger amounts of fatty acid collector were needed during the anionic flotation stage, resulting in large and voluminous froths that caused silica to be entrained into the phosphate concentrate (Zhong et al. 1993). However, other authors have proposed that the flotation of silica during the fatty acid flotation of phosphate is due to hetero-coagulation of calcium carboxylate

Table 3.3 Factors affecting entrainment in froth flotation

Factor	Effect on Entrainment
Froth layer depth	• Deeper froth layers (i.e., higher froth residence time) give more time for entrained particles to drain from the froth. • There is a limit to how deep the froth layer can be before the froth becomes unstable and collapses.
Frother addition rate	• Too much frother can result in very small and very stable bubbles. • This can increase entrainment levels and cause significant problems in pumping. • Controlling froth conditions by modifying frother dosages can help reduce entrainment.
Frother type	• Stronger long-chained frothers can decrease the rate at which water drains from the froth, resulting in greater entrainment levels. • Using shorter-chained frothers can help increase the froth drainage rate and reduce entrainment.
Number of flotation stages	• The addition of cleaner stages reduces the overall effects of entrainment.
Desliming flotation feed	• Desliming the flotation feed will remove finer particles that are easily entrained. • This could also be detrimental if significant amounts of the desired material are also present in the very fine size fraction.
Wash water	• Spraying wash water on top of the froth layer, such as in column flotation cells, helps wash entrained particles from the froth. • This is a significant advantage of flotation columns as they are more efficient at froth washing than are mechanical cells.
Flocculants	• Flocculants can be used to flocculate the fine hydrophilic particles into larger flocs, which are less likely to be entrained. • It is important that the flocculation is selective, and that the hydrophobic particles are not also present in the flocs.

precipitates on the quartz surface (Ananthapadmanabhan and Somasundaran 1985; Guan 2009a).

3.2.3.1 Importance of Entrainment Versus Hydrophobicity

Understanding why a gangue mineral is reporting to the froth concentrate—either by true flotation (hydrophobicity) or entrainment—is very important when determining the best method to reduce the amount of gangue reporting

to the froth. For example, if a gangue mineral is reporting to the froth concentrate by means of true flotation, then a depressant could be used to make the gangue mineral hydrophilic. The gangue mineral would then be depressed and report to the hydrophilic tailings instead of the froth concentrate.

In the case of coal flotation, where coal is floated in order to separate it from pyrite and ash containing gangue minerals, there was once significant interest in the development of a pyrite depressant to reduce the amount of pyrite reporting to the froth concentrate (Kawatra et al. 1991; Kawatra and Eisele 1992, 2001). Kawatra and Eisele (1992) conducted many studies to determine why the pyrite was reporting to the froth concentrate. They determined that entrainment was the most dominant recovery mechanism for liberated pyrite particles. This means that the addition of pyrite depressants would be ineffective because the pyrite is already hydrophilic and is not reporting to the froth concentrate by true flotation (Kawatra and Eisele 2001). Given that the majority of pyrite was reporting to the froth due to entrainment, the best path for reducing the amount of pyrite that reports to the froth concentrate would be one that significantly reduces entrainment. Table 3.3 includes methods for reducing entrainment.

3.2.4 Surface Properties and Water Chemistry of Siliceous Phosphates

Variation in hydrophobicity between minerals is the fundamental mechanism for mineral separation by froth flotation. This is accomplished by the use of surfactants such as collectors and depressants. The adsorption of surfactants onto mineral surfaces is primarily dependent on interfacial properties of the mineral particles, which is mainly controlled by surface chemistry. When particles are placed into solution, they develop a surface charge. Surface charge is largely dependent on mineral properties, pH of solution, and concentration and type of dissolved ions in solution. Figure 3.20 describes the electrical double-layer model. In this model, a particle with a negative surface charge is placed in an aqueous solution. Since the surface charge is negative, hydrated counter ions are bound to the surface to form the Stern layer. Just outside the Stern layer is the shear plane, where the diffuse layer is able to slip along the surface-bound Stern layer. Zeta potential, or electrokinetic potential, is the potential measured at the shear plane. The parameters that determine zeta potential also play a large role in determining the selective adsorption of collectors (Fuerstenau and Raghaven 2007; Kawatra 2011). Phosphate flotation can be particularly complicated because of the semi-soluble nature of

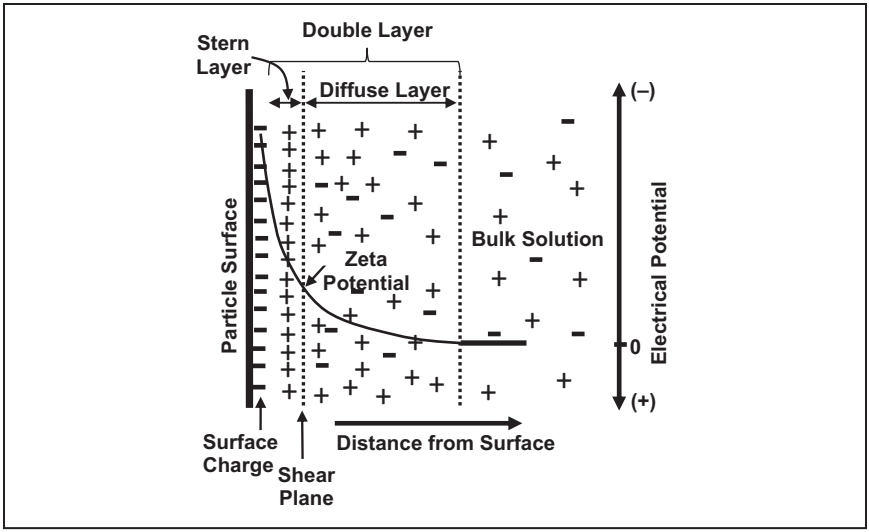
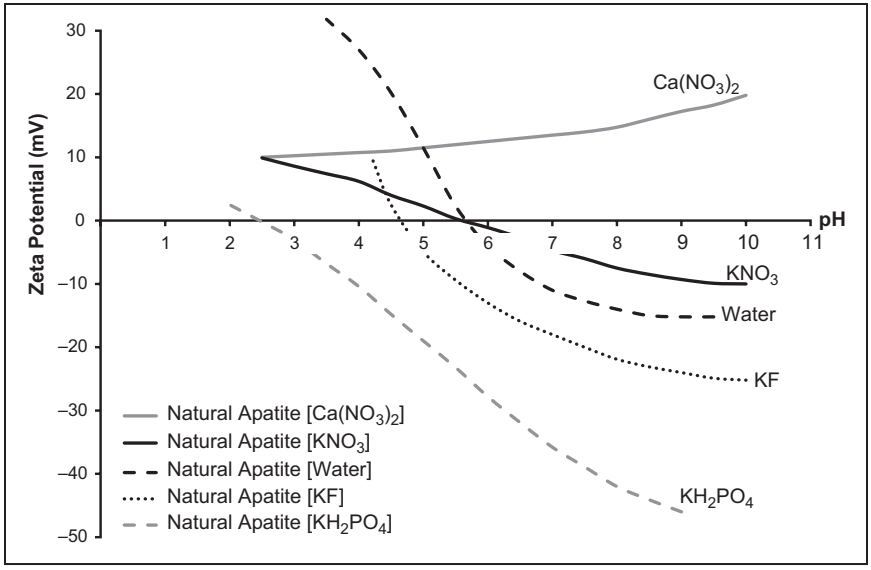


Figure 3.20 Simplified diagram of electrical double-layer model

phosphate minerals, along with associated gangues such as calcium carbonate and dolomite having similar properties (Mishra 1978; Somasundaran and Zhang 1999; Somasundaran and El-Mofty 2002).

As the high-grade phosphate reserves have decreased over the years, more focus has been put on improving the efficiency of the Crago process (discussed in detail in Section 3.3). In order to accomplish this, a better understanding of the surface chemistry and mechanisms involved in the silica/phosphate system was needed.

Somasundaran and Zhang (1999) examined the role of surface chemistry on the flotation of phosphate ores. The authors studied the effects of $Ca(NO_3)_2$, KNO_3, KF, and KH_2PO_4 salts on the zeta potential of natural apatite. Results are shown in Figure 3.21, with concentrations for each salt being 10^{-2} mol/L. The isoelectric point (IEP) for natural apatite in water is approximately 5.9. It was determined that K^+ and NO_3^- are not potential determining ions and therefore do not shift the IEP from that of apatite in water. Conversely, Ca^{+2}, F^-, and the various PO_4 complexes (PO_4^{-3}, HPO_4^{-2}, and $H_2PO_4^-$) significantly affect the zeta potential of apatite across the pH range, while also shifting the IEP. Phosphate ions make the zeta potential of apatite more negative at all pH values tested, while also shifting the IEP to approximately 2.5. Fluorine makes the zeta potential of apatite

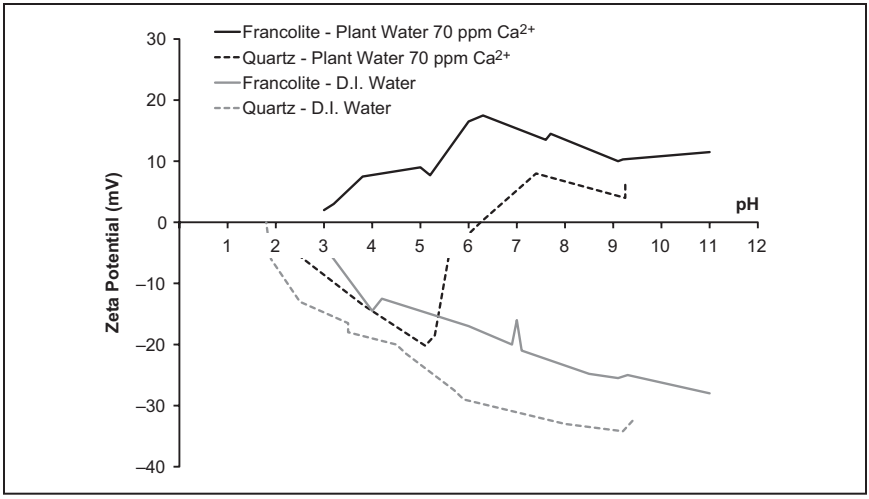


Source: Adapted from Somasundaran and Zhang 1999.

Figure 3.21 Effects of various salt solutions on the zeta potential of natural apatite

more negative at basic conditions and more positive at acidic conditions. One of the most important observations is that the addition of Ca^{+2} ions results in positive zeta potentials for apatite over the complete range of pH values tested (Somasundaran and Markovic 1998; Somasundaran and Zhang 1999).

Gruber et al. (1995) also studied the effects of water chemistry on the zeta potential of francolite $Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$ and quartz (SiO_2). Tests were run using deionized water and plant water (≈70 ppm Ca^{+2}). The results in Figure 3.22 show that both francolite and silica exhibit negative zeta potentials over the pH range when using distilled water. However, when plant water was used, the zeta potential of francolite becomes positive over the entire pH range because of the adsorption of Ca^{+2} ions (Guan 2009a). In the case of quartz, the plant water gives a positive zeta potential from a pH of 9.5–6. At pH 6, the zeta potential reverses back to a negative charge and follows the same trend as quartz in water from pH 5–2. The exact cause of charge reversal is not known, but it may be due to the presence of aluminum, magnesium, or calcium complexes present in the plant water (Gruber

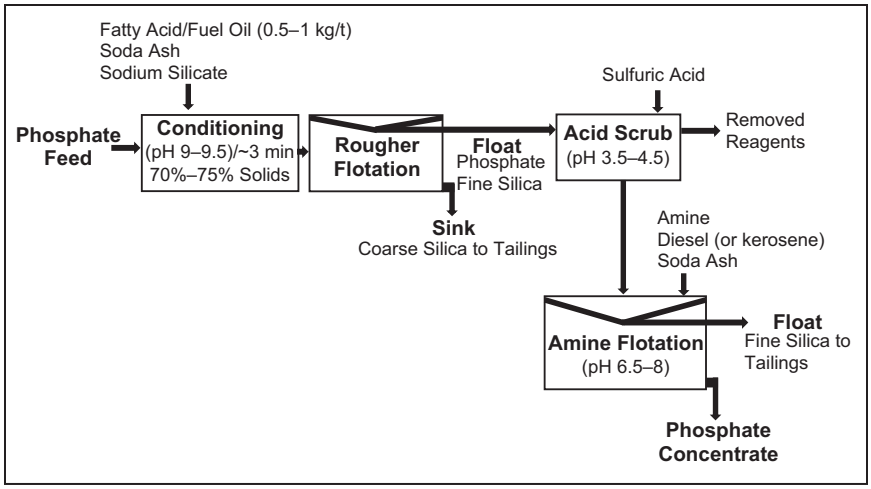


Source: Adapted from Gruber et al. 1995 and Guan 2009a.

Figure 3.22 Zeta potential of francolite and quartz in deionized (D.I.) water and plant water

et al. 1995). The adsorption of Ca^{+2} ions on quartz at a basic pH can be detrimental to the Crago double float process because of the hetero-coagulation of calcium carboxylate precipitates on the quartz surface. This results in some quartz floating along with the phosphate minerals during the anionic rougher flotation stage of the Crago double float process (Guan 2009a). This is explained in greater detail in the Section 3.3.

The sparingly soluble nature of phosphate minerals and associated gangue minerals can further complicate the phosphate flotation system. Apatite ($Ca_{10}(PO_4)_6(F)_2$), calcite ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$) can all be sources of potential determining ions (Ca^{+2}, F^-, and PO_4^{-3}) through dissolution (Ananthapadmanabhan and Somasundaran 1984; Amankonah and Somasundaran 1985; Amankonah et al. 1985; Somasundaran et al. 1985, 1991; Somasundaran and El-Mofty 2002). These potential determining ions can either affect the zeta potential directly or indirectly by forming complexes with other ions in solution (Somasundaran 1968; Saleeb and Bruyn 1972; Chander and Fuerstenau 1979; Zhong et al. 1993; Somasundaran and Markovic 1998; Perrone et al. 2002).



Source: Adapted from Guan 2009b.

Figure 3.23 Simplified process flow diagram for the Crago process

3.3 CRAGO DOUBLE FLOAT PROCESS

Since being patented in 1942, the Crago double float process has been the industry standard for the beneficiation of siliceous phosphate ores. The Crago double float process mainly consists of two stages (Guan 2009a):

1. *Rougher flotation* where the phosphate is floated from coarse silica using an anionic fatty acid collector, and
2. *Cleaner flotation* where fine silica is floated from phosphate concentrate using a cationic amine collector.

Figure 3.23 shows a simplified process flow diagram for the Crago process.

3.3.1 Stage 1—Anionic Fatty Acid/Fuel Oil Phosphate Flotation

In the first step, a sized and deslimed feed (as described in Section 3.1) is conditioned at pH 9–9.5 with a fatty acid/fuel oil (FA/FO) mixture (~0.5–1 kg/t) for approximately 2.5–3 minutes (Wiegel 1999). Exact dosage of the collector varies depending on which feed size fraction is being processed. Soda ash (Na_2CO_3) is commonly used for pH adjustment. The rougher conditioning is done at high percent solids (70%–75%). In the basic solution (pH 9–9.5), the fatty acid collector first undergoes saponification (Equation 3.4), where the fatty acid (RCOOH) is reacted with a base (OH^-) to produce carboxylate

ions ($RCOO^-$) and water (H_2O). The carboxylate ions then react with calcium on the francolite surface and render the francolite surface hydrophobic via chemisorption (Equation 3.5) (Maltesh et al. 1996; Guan 2009a). Chemisorption is the most prevalent adsorption mechanism for this system. However, some amounts of physisorption have been proposed because of the presence of dissolved calcium ions in plant water. At alkaline pH values, the zeta potential of apatite undergoes a charge reversal from negative to positive when Ca^{+2} ions are present (Figure 3.22) (Gruber et al. 1995). This results in conditions that are favorable for physical adsorption of negatively charged carboxylate ions (Maltesh et al. 1996).

$$RCOOH_{(aq)} + OH^- \rightarrow RCOO^-_{(aq)} + H_2O \qquad \text{EQ 3.4}$$

$$Ca^{+2}_{(aq)} + 2RCOO^-_{(aq)} \rightarrow Ca(RCOO)_{2(s)} \qquad \text{EQ 3.5}$$

Conditioning at high percent solids improves reagent dispersion, which results in more mechanical spreading of FA/FO droplets onto the surface of the phosphate particles (Oswald 1993; Lu et al. 1997). However, it is important that the conditioner does not generate excessive amounts of slimes as they will significantly lower selectivity and recovery during phosphate flotation.

Some authors have noted beneficial effects from adding a sodium silicate dispersant near the end of the conditioning stage. These benefits have been attributed mainly to the removal of clay impurities and calcium containing precipitates from quartz surfaces (Dho and Iwasaki 1990; Guan 2009a). After conditioning is completed, the ore is sent to flotation cells where the hydrophobic phosphate ore is floated. The coarse quartz reports to the sinks and is removed to the tailings. Significant amounts of fine silica reports to the phosphate concentrate and must be removed later by amine flotation. Some authors have proposed that flotation of the fine silica occurs mainly by means of entrainment, where the fine silica is entrained in the water that reports to the phosphate concentrate. Entrainment of silica is said to be due to the large froths generated from relatively high fatty acid collector dosages required to float sedimentary phosphates (Zhong et al. 1993). However, the flotation of silica during the fatty acid flotation is generally considered to be due to hetero-coagulation of calcium carboxylate precipitates on the quartz surface (Ananthapadmanabhan and Somasundaran 1985; Maltesh et al. 1996; Guan 2009a). The phosphate flotation feed is often sized into 16 × 24 mesh, 24 ×

35 mesh, and 35 × 150 mesh size fractions to achieve better flotation efficiency, with less silica reporting to the phosphate concentrate (Oswald 1993; Wiegel 1999; Guan 2009a).

The fatty acid phosphate flotation stage is traditionally carried out in banks composed of relatively small mechanical flotation cells (Wiegel 1999). Column flotation has also seen some consideration for phosphate flotation, but has only been implemented at a plant scale for processing igneous phosphates in Brazil (Guimaraes and Peres 1999; El-Shall et al. 2000; Fortes et al. 2007; Oliveira et al. 2007, 2011; Santana et al. 2008).

Small-sized flotation cells are desirable in phosphate flotation, which goes against the general mineral processing trend toward larger flotation cells. Two main issues with phosphate flotation have made small cells necessary:

1. A large amount of the feed reports to the froth concentrate. In the anionic phosphate flotation stage, the majority mineral in the feed (phosphate) is floated. As much as 40%wt of the total feed reports to the froth phosphate concentrate, while other industries generally float less than 10%wt of the feed.
2. Particle flotation is coarse. Phosphate flotation feed is relatively coarse in size compared to other industries.

With up to 40%wt reporting to the froth concentrate during phosphate flotation, traditional froth removal techniques such as paddles struggle to keep up when using large flotation cells. One option to increase the froth removal rate would be by "flooding" the cell. This is undesirable as it significantly decreases the grade of the phosphate concentrate. A more favorable option is to use more small-sized flotation cells instead of a large cell. The major advantage of smaller flotation cells is that they have a higher froth overflow lip length to cell volume ratio. This results in a higher froth removal rate without sacrificing grade. Another reason for using smaller flotation cells is due to the relatively coarse-sized flotation feed. With coarse particle flotation, it is beneficial if air bubbles do not have to float coarse particles a long distance to the froth concentrate overflow. For this reason, smaller flotation cells are better for coarse particle flotation (Oswald 1993). In the phosphate industry, up to 20 m^3 sized mechanical flotation cells are typically used for rougher flotation of the fine 35 × 150 mesh feed (Lawver et al. 1978; Wiegel 1999). Smaller cells can be used as cleaners.

3.3.2 Stage 2—Cationic Amine Silica Flotation

Before amine flotation, the rougher phosphate concentrate must be "acid scrubbed" to remove adsorbed FA/FO collector from the phosphate surface. In the acid scrubbing process, sulfuric acid is used to adjust the pH to around 3–4.5 and the slurry is reacted in stirred tank reactors for 2–3 minutes. The chemisorbed FA/FO collector is removed from the francolite surface so that it does not interfere with the amine flotation stage. The slurry is then diluted with several stages of water, which is followed by hydrocyclones and elutriators to remove the detached FA/FO collector. This washing stage is important because any residual collector and/or sulfate ions can decrease the effectiveness of the amine flotation stage (Wiegel 1999; Guan 2009b).

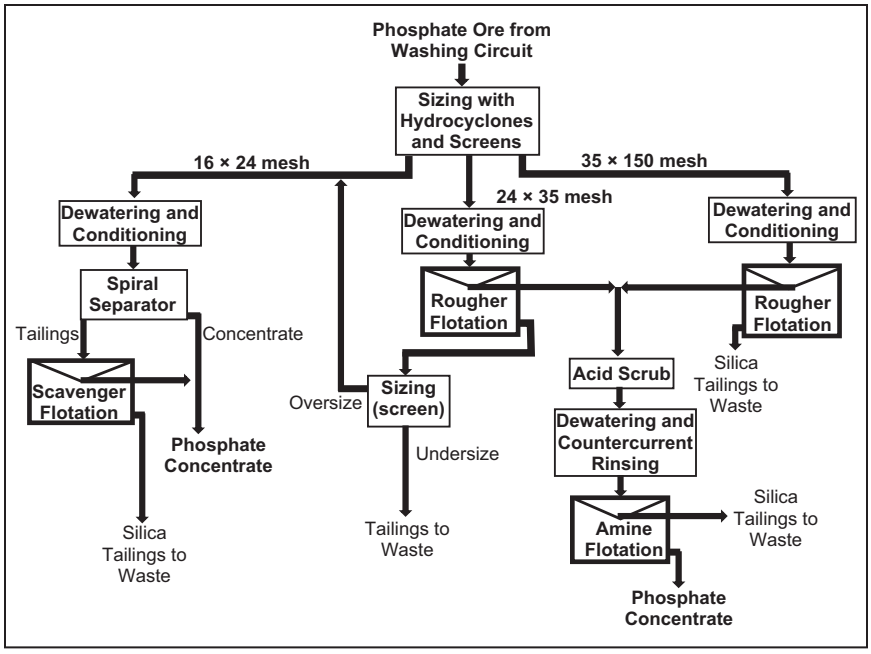
Amine flotation is the final stage of the Crago process, in which the cationic amine collector removes fine silica from the phosphate concentrate. An amine collector, typically a condensate amine, is added to the acid-scrubbed phosphate slurry as a 5%–10% aqueous solution (Zhang et al. 2002a). The flotation is carried out at a pH of 6.5–8, which can be adjusted with soda ash if necessary. Since the amine quickly attaches to the silica surface, the collector is often added directly to the flotation cell. Diesel oil or kerosene can be added to increase collector efficiency and froth properties (Wiegel 1999; Guan 2009b). It is important that the slimes concentration be kept low since the amine collector will rapidly absorb to any fine clays, resulting in a significant increase in reagent consumption.

Although the Crago process has been considered the industry standard since it was introduced, the need to process lower-grade ores has led to an increase in research dedicated to finding more efficient alternatives. The resulting alternative processes aim to increase collector efficiency and reduce processing costs as a whole (Clifford et al. 1998).

3.3.3 Industrial Flotation Plant for Siliceous Sedimentary Phosphate Ores

Figure 3.24 shows a simplified process flow diagram of the IMC Four Corners (Florida) flotation plant, based on a report from a site visit by the EPA (1994). The −16 mesh phosphate flotation feed from the washing plant (Figure 3.4) is first sized into the spiral feed (−16 by +24 mesh), coarse flotation feed (−24 by +35 mesh), and fine flotation feed (−35 by +150 mesh).

The coarse and fine flotation feeds each go through the Crago double float process to achieve a phosphate concentrate. As discussed in Section 3.3,



Source: Adapted from EPA 1994.

Figure 3.24 Simplified process flow diagram of flotation plant at IMC Four Corners mine

the Crago double float process is a two-stage procedure that separates silica from phosphate. An acid scrubbing process is used after the anionic rough flotation to remove any absorbed collector before going to the amine flotation stage.

The spiral feed is first conditioned with a FA/FO collector and then sent to spiral film flotation (Wiegel 1999). As shown in Figure 3.25, spirals are a density separation device that separates light particles from dense particles using centrifugal forces. As the feed flows down the trough-like chute, the light particles are pushed to the outside of the spiral while the dense particles remain near the center. Splitters are used to separate and collect the coarse and light fractions. The concentrate from the spiral is of high enough quality to be considered phosphate concentrate. The tailings from the spiral are sent to scavenger flotation to recover phosphate that was not separated during spiral film flotation (EPA 1994).

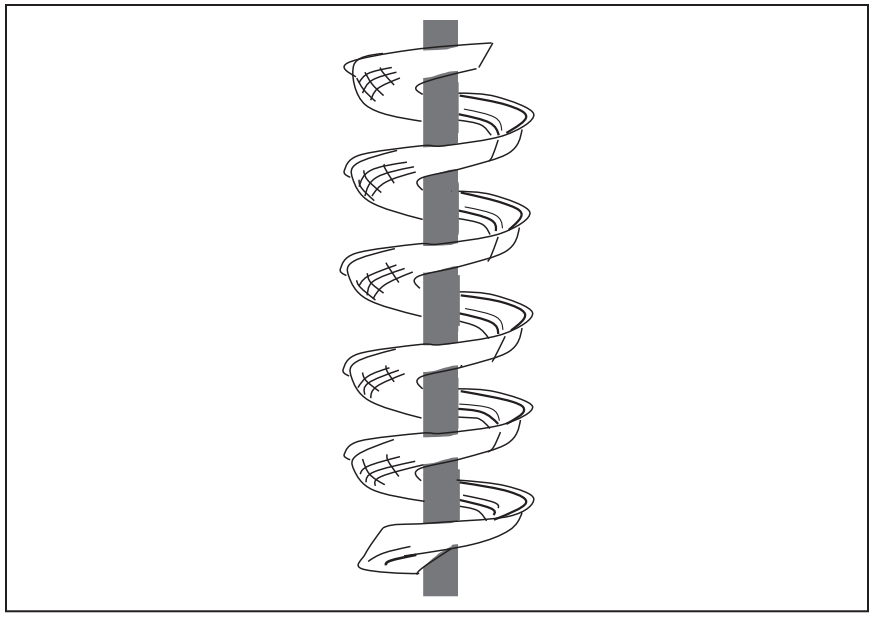


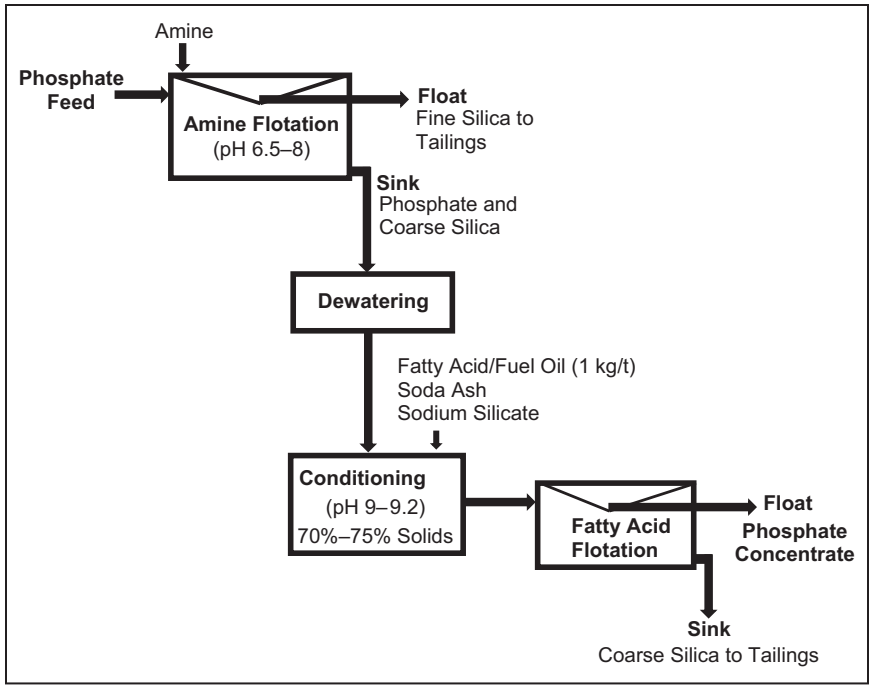
Figure 3.25 Spiral concentrator

3.4 PROPOSED ALTERNATIVES TO THE CRAGO DOUBLE FLOAT PROCESS

As high-grade phosphate reserves become depleted, phosphate companies are being forced to mine and process lower-grade phosphate deposits. This has made companies reevaluate the efficiency of the traditional Crago process (Clifford et al. 1998). Zhang et al. (1997) identified that in terms of collector efficiency, the Crago double float is inefficient because the fine silica is floated twice: it is floated along with the phosphate in the FA/FO flotation and again during the amine flotation step (Zhang et al. 1997). This has led to the development of three proposed alternatives to the Crago process: the reverse Crago process, the all-anionic process, and the all-cationic process.

3.4.1 Reverse Crago Process

The "reverse Crago" process was developed by the Florida Institute of Phosphate Research (FIPR) as a proposed alternative to the Crago double float process. The proposed flow sheet for the reverse Crago process is shown in Figure 3.26. In this process, the fine silica is first floated with an amine collector at a neutral pH. Amine flotation takes place in stages to minimize



Source: Adapted from Clifford et al. 1998.

Figure 3.26 Simplified process flow diagram for reverse Crago process

phosphate losses to the silica tailings. The phosphate concentrate is then dewatered and conditioned with a FA/FO collector at a pH of 9–9.2. Soda ash is used as a pH adjuster. After conditioning, the phosphate is floated from the coarse silica to give the final phosphate product.

In the case of a feed containing more coarse particles, the process can be further optimized by sizing the amine flotation concentrate. Since the amine flotation stage floats the fine silica from the phosphate feed, sizing the phosphate concentrate at the appropriate particle size should result in a fine phosphate-rich concentrate that does not need to go through FA/FO flotation. This would further reduce reagent consumption by lowering the demand on the FA/FO flotation stage. The reverse Crago process has many potential benefits that could make it considerably more cost-effective than the traditional Crago double float process (Zhang et al. 1997; Clifford et al. 1998):

- Removal of acid scrubbing stage,
- Reduced reagent consumption,

- Reduced acid consumption,
- Reduced soda ash consumption,
- Reduced water consumption, and
- Increased plant capacity.

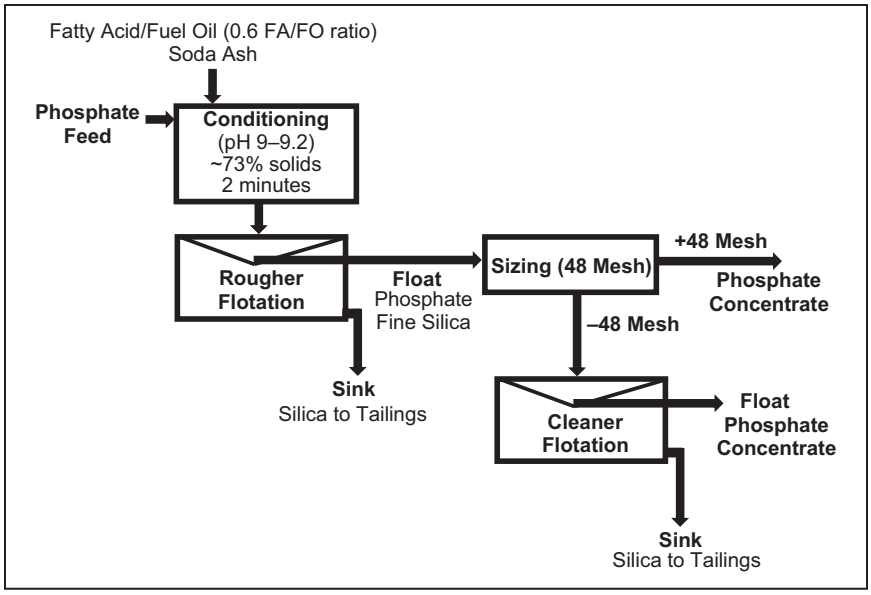
The majority of these benefits comes from the fact that fine silica is only floated once in this process. This reduces the demand on the fatty acid flotation stage, resulting in reduced reagent consumption per amount of ore fed. Elimination of the acid scrubbing stage is also an important benefit of this process because it reduces sulfuric acid consumption.

3.4.2 All-Anionic (Fatty Acid/Fuel Oil Collector) Process

The second proposed alternative to the Crago double float process is the "all-anionic" process. This method attempts to completely eliminate the more expensive amine flotation stage and only uses anionic flotation. The all-anionic process separates apatite from silica using a FA/FO collector to float phosphate from silica in a rougher–cleaner flotation circuit. Potential benefits of an all-anionic process would come from (Zhang et al. 2002b):

- Removal of the acid scrubbing stage,
- Lower reagent consumption,
- Elimination of the expensive amine flotation stage, and
- Reducing water and energy usage.

Zhang et al. (2002b) proposed the FIPR/SAPR (single-collector, all-anionic phosphate recovery) "all anionic process" for the beneficiation of siliceous phosphate ores. A simplified process flow diagram for this process is shown in Figure 3.27. First, the phosphate feed is conditioned with a 0.6 FA/FO ratio at approximately 73% solids for 2 minutes. Conditioning is carried out at a pH of 9–9.2 (adjusted with soda ash). After rougher flotation, the floated phosphate is sized at 48 mesh. The +48 mesh size fraction is typically pure enough to be phosphate concentrate, while the –48 mesh size fraction is sent to the cleaner flotation. No new reagents are added in the cleaner flotation stage. The floated phosphate from the cleaner product is combined with the coarse phosphate product to make up the final phosphate product (Zhang et al. 2002b).



Source: Adapted from Zhang et al. 2002b.

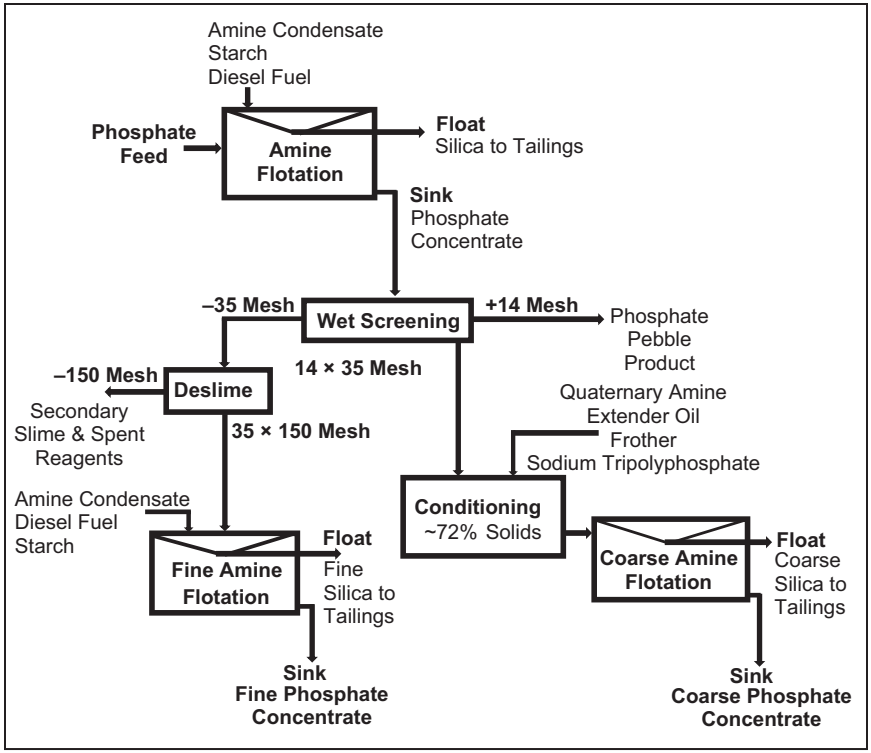
Figure 3.27 Simplified process flow diagram for FIPR/SAPR all-anionic process

3.4.3 All-Cationic (Amine) Process

The all-cationic process attempts to beneficiate siliceous phosphate ores using only amine flotation stages. This process aims to use amine collectors, along with effective phosphate depressants, to selectively float silica from phosphate in multiple flotation stages. Potential benefits from an all-cationic process include (Snow et al. 1996)

- Removal of the acid scrubbing stage,
- Removal of the FA/FO flotation stage, and
- Lower power usage.

Snow et al. (1996) proposed an all-cationic flotation process as an alternative to the Crago double float procedure for the beneficiation of siliceous phosphate ores. A simplified process flow diagram for this process is shown in Figure 3.28. In the first stage, condensate amine and diesel fuel are used as a silica collector. Starch is also added to depress phosphates. After the amine rougher flotation, the phosphate concentrate is sized into three size fractions:



Source: Adapted from Snow et al. 1996.

Figure 3.28 Simplified process flow diagram for the all-cationic process

+14 mesh, 14 × 35 mesh, and –35 mesh. The +14 mesh size fraction is of high enough quality to be phosphate pebble product. The –35 mesh size fraction is first deslimed to remove secondary slimes (–150 mesh). After desliming, the 35 × 150 mesh size fraction goes through a fine amine flotation stage that uses the same reagent scheme as the rougher flotation. The 14 × 35 mesh size fraction is conditioned at approximately 72% solids for approximately 15 seconds with quaternary amine collector, extender oil, sodium tripolyphosphate (phosphate depressant), and frother. Flotation yields a coarse phosphate product and coarse silica tailings.

The efficiency of an all-cationic process depends greatly on finding an effective phosphate depressant. Snow et al. (1996) evaluated five phosphate depressants:

1. Hydrofluosilicic acid,
2. Sodium tripolyphosphate,
3. Starch,
4. Diphosphonic acid, and
5. Phosphoric acid.

It was determined that starch was the best phosphate depressant for the fine particle flotation (35 × 150 mesh), whereas sodium tripolyphosphate worked better for coarse particle flotation (14 × 35 mesh).

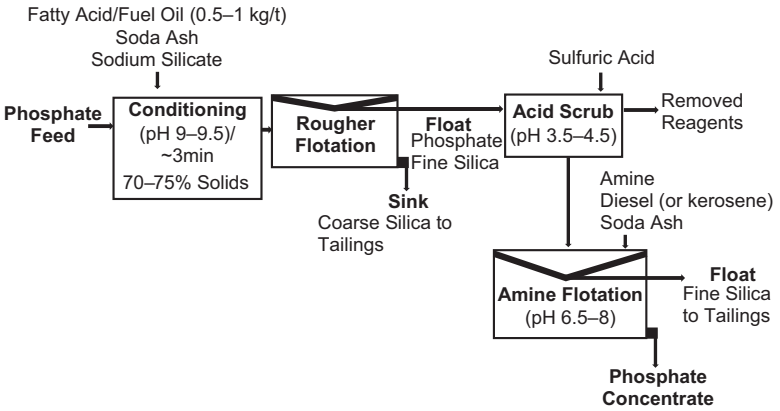
The one downfall of the all-cationic process may be the generally higher costs of amines compared to the anionic FA/FO collectors. The authors determined that scrubbing before each amine flotation stage resulted in significantly better phosphate recoveries. Scrubbing breaks down clay chips and reduces slimes that if present will greatly increase reagent consumption.

3.5 CONCLUSIONS FROM SILICEOUS SEDIMENTARY PHOSPHATE ORE PROCESSING

The Crago double flotation process has proven to be an industry standard over several decades for the processing of siliceous sedimentary phosphate ores (Guan 2009a). The efficiency of this flotation process depends heavily

Table 3.4 Summary of Crago process for beneficiation of siliceous sedimentary phosphates

Crago Double Float



(table continues)

Table 3.4 Summary of Crago process for beneficiation of siliceous sedimentary phosphates (continued)

Process

1. Phosphate rougher flotation (anionic flotation)

- Fatty acid/fuel oil (FA/FO) collector (0.5–1 kg/t)
- pH 9–9.5, adjusted with soda ash
- Conditioned at 70%–75% solids for 2–3 minutes in stirred tank reactors
- Flotation carried out in relatively small cells (~20 m^3)
- Sodium silicate removes Ca^{+2} from the quartz surface, limiting physisorption of anionic fatty acid collector
- ***Float***—Phosphate and fine silica; ***Sink***—Coarse silica

2. Acid Scrubbing

- Acid scrubbing is needed to remove (FA/FO) surfactant from the phosphate before amine flotation
- If not removed, phosphate will be lost to the silica tailing
- Sulfuric acid is added to reduce pH to 3.5–4.5
- Reversing the chemisorption reaction and driving the surfactant from the phosphate surface

3. Silica flotation (cationic flotation)

- Cationic amine collector (as 5%–10% aqueous solution)
- pH 6.5–8, adjusted with soda ash
- Diesel increases collector efficiency and froth properties
- ***Float***—fine silica; ***Sink***—Phosphate concentrate

Reactions

* Saponification reaction of fatty acid collector(pH 9–9.5):

$$RCOOH_{(aq)} + OH^-_{(aq)} \rightarrow RCOO^-_{(aq)} + H_2O$$

* Chemisorption to Ca^{+2} sites on phosphate surface:

$$Ca^{+2}_{(aq)} + 2RCOO^-_{(aq)} \rightarrow Ca(RCOO)_{2(s)}$$

* Reversing chemisorption of fatty acid collector (pH 3.5–4.5):

$$Ca(RCOO)_{2(s)} \rightarrow Ca^{+2}_{(aq)} + 2RCOO^-_{(aq)}$$

* Cationic amine collector preferentially physically adsorbs to the quartz, which has a more negative zeta potential than apatite (francolite) at these conditions.

(table continues)

Table 3.4 Summary of Crago process for beneficiation of siliceous sedimentary phosphates (continued)

Important Process Considerations
Desliming
• Clays adversely affect flotation efficiency and reagent consumption.
• Flotation feed goes through trommels, log washers, and hydrocyclones to remove clays.
Sizing
• Flotation feed is typically sized to three size fractions: 16 × 24 mesh, 24 × 32 mesh, and 35 × 150 mesh.
• The 35 × 150 mesh size fraction makes up the majority (~80%).
• Sizing allows for more efficient use of collector and better selectivity during anionic flotation.
High % solids conditioning
• Increases phosphate grade and recovery during anionic flotation.
• Higher reagent concentrations and more mechanical spreading of FA/FO collector on phosphate surface.

on a properly operated sizing and desliming process. A summary of the Crago double float process can be found in Table 3.4.

The reverse Crago process proposes the removal of fine silica first, followed by FA/FO flotation of phosphate. The all-anionic process proposes a fatty acid/fuel collector in a rougher–cleaner flotation circuit to achieve a phosphate concentrate. Finally, the all-cationic process proposes the use of amine collectors, paired with appropriate phosphate depressants, to achieve a high-quality phosphate concentrate. All alternatives have a common advantage over the Crago process in that they completely remove the acid scrubbing stage. However, these processes are still in development and need to go through more evaluation to determine whether they are capable of achieving a high-enough-quality phosphate concentrate. Implementation of any of the alternatives will depend greatly on the difference in cost between fatty acid and amine collectors. In addition to process costs, the expenditure of reconstructing the current plant must be taken into consideration.

4

Beneficiation of High-MgO Sedimentary Phosphate Ores

Dolomite ($CaMg(CO_3)_2$) is one of the most troublesome of the gangue minerals because it has mineral properties that are very similar to those of the phosphates, and is therefore difficult to separate with conventional techniques such as froth flotation. If not removed, dolomite hinders the wet-process production of phosphoric acid in two ways: it increases sulfuric acid consumption; and it increases fluid viscosity, which lowers filtration rates when separating solid gypsum crystals from the valuable phosphoric acid. Over the years, large research efforts have been dedicated to finding an economical method for removing dolomite from sedimentary phosphate ores. This chapter reviews the methods proposed throughout the literature for beneficiation of high-MgO sedimentary phosphate ores. This includes acid leaching (weak and strong), thermal decomposition, physical separation methods, flotation, and selective flocculation. Strengths and weaknesses of each process with respect to dolomite removal are analyzed.

4.1 MINERALOGY OF HIGH-MgO SEDIMENTARY PHOSPHATE ORES

Dolomite is an intolerable impurity because of its MgO content. The general goal of any method for dolomite removal is to obtain a phosphate concentrate that contains less than 1% MgO. In sedimentary phosphates, magnesium is present in three forms (Dufour et al. 1980; Lawver et al. 1982; Blanchard et al. 1986; Moudgil and Ince 1991):

1. Discrete liberated dolomite particles,
2. Fine dolomite inclusions in apatite, and
3. Ionic substitution into the lattice structure of apatite.

The importance of inherent MgO in the francolite structure has been noted by several authors. Lawver et al. (1982) determined that the MgO levels due to ionic substitution of Mg into the francolite structure ranged from 0.1% to as high as 1% MgO, with an average MgO content of 0.4% for a study of 31 francolite samples. A similar range of 0.13%–0.60% MgO was reported by McClellan (1980) for a study of various francolites from the United States, Morocco, and Tunisia. Finally, a study by Blanchard et al. (1986) used a quantitative X-ray diffraction (XRD) method to determine an average substituted MgO level of 0.57% from 18 phosphorite samples. When designing a separation process, it is important to take into consideration the MgO level due to the ionic substitution as it is the theoretical minimum MgO level obtainable by physical separation. However, the practical minimum MgO level may be even higher because of very fine dolomite inclusions into the francolite pebbles. Blanchard et al. (1986) determined that fine dolomite inclusions can be as small as several microns to submicron in size, making it impractical to crush to complete liberation.

4.2 ACID LEACHING OF CARBONACEOUS PHOSPHATE ORES

Dissolution of carbonaceous impurities using both inorganic (strong) and organic (weak) acids has been proposed to beneficiate low-grade phosphate ores. At a basic level, the acid leaching process involves reacting an acid solution with a carbonaceous mineral (i.e., dolomite, $CaMg(CO_3)_2$) to produce gypsum ($CaSO_4 \cdot 2H_2O$), magnesium sulfate ($MgSO_4$), and CO_2 gas. It is desired that the acid solution only attacks the carbonate minerals, while the phosphate minerals remain solid and unaltered. The reacted ore then goes through a filtration/washing step to separate the upgraded solid phosphate ore from the dissolved carbonates and acid solution. Figure 4.1 shows a simplified process flow diagram for this method. The details of strong acid and weak acid leaching are discussed in the following sections.

4.2.1 Strong Acid Leaching

Strong, inorganic acids (i.e., sulfuric acid) are known to dissolve carbonate minerals at high rates. As shown in Equation 4.1, sulfuric acid reacts with

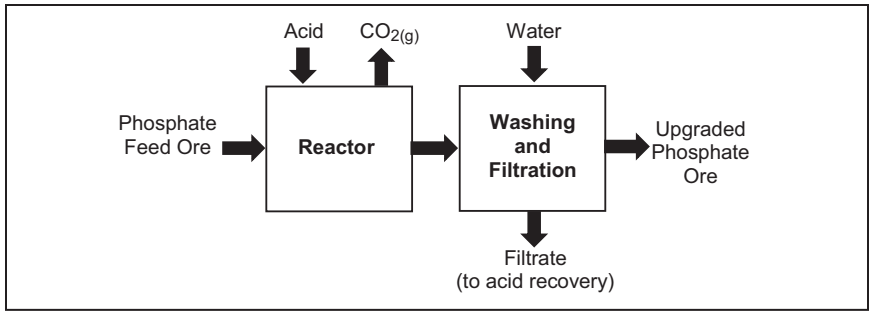


Figure 4.1 Simplified process flow diagram for acid leaching process

dolomite to produce gypsum, magnesium sulfate, and carbon dioxide gas. Magnesium sulfate is highly soluble and can be filtered from the remaining phosphate.

$$CaMg\left(CO_3\right)_{2(s)} + 2H_2SO_{4(l)} \rightarrow CaSO_4 \cdot 2H_2O_{(s)} + MgSO_{4(s)} + 2CO_{2(g)} \quad \text{EQ 4.1}$$

The major problem associated with strong acid leaching is the tendency of strong acids to attack the valuable phosphate minerals. Rule et al. (1970) showed that as much as 6% BPL (bone phosphate of lime) was lost when using a dilute sulfuric acid leaching solution. Other drawbacks associated with strong acid leaching include possible issues with equipment corrosion, environmental hazards, and slow filtration caused by the generation of fine gypsum particles (Rule et al. 1970). For these reasons, most of the current research in acid dissolution of carbonates has been focused on using organic acids.

4.2.2 Organic Acid Leaching

Organic acid leaching has proven to be a more promising method than strong acid leaching for removal of carbonaceous impurities from phosphate ores. Organic acids that have been discussed in the literature include formic acid, acetic acid, lactic acid, and succinic acid. At optimum leaching conditions, organic acids selectively leach carbonate minerals while resulting in minimal phosphate losses (Abu-Eishah et al. 1991; Fredd and Fogler 1998; Economou et al. 2002; Ashraf et al. 2005; Sengul et al. 2006; Zafar et al. 2006; Zafar and Ashraf 2007; Gharabaghi et al. 2010).

4.2.2.1 Organic Acid Leaching Reactions

In the organic acid leaching process, a weak organic acid reacts with calcium carbonate to produce carbon dioxide gas, water, and an organic salt. For the case of a monocarboxylic organic acid such as acetic acid (CH_3COOH), the acetic acid reacts with calcium carbonate in a 2:1 molar ratio, as shown in Equation 4.2. The resulting organic salts, calcium and magnesium acetate, are highly soluble in the leaching solution (Zafar 1993). The solubility product of the organic salt is very important because it allows for a simple washing and filtering process to be used to separate the solid unreacted phosphate concentrate from the organic acid salt solution.

$$CaCO_{3(s)} + 2CH_3COOH_{(aq)} \rightarrow Ca\left(CH_3COO\right)_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \quad \text{EQ 4.2}$$

$$MgCO_{3(s)} + 2CH_3COOH_{(aq)} \rightarrow Mg\left(CH_3COO\right)_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \quad \text{EQ 4.3}$$

Equation 4.4 shows a simplified version of Equation 4.2 for the case of monocarboxylic acids. In the case of dicarboxylic acids, Equation 4.5 is used.

$$MCO_{3(s)} + 2HX_{(aq)} \rightarrow M\left(X\right)_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \quad \text{EQ 4.4}$$

$$MCO_{3(s)} + H_2Y_{(aq)} \rightarrow MY_{(aq)} + CO_{2(g)} + H_2O_{(l)} \quad \text{EQ 4.5}$$

where

$M = Mg^{+2}$ or Ca^{+2}
X = formate ($CHOO^-$), acetate (CH_3COO^-), or lactate ($CH_3CH(OH)COO^-$)
Y = succinate ($H_2C_4O_4^{-2}$)

4.2.2.2 Important Parameters Involved in Organic Acid Leaching

The rate of carbonate dissolution primarily depends on the following leaching parameters (Sadeddin and Abu-Eishah 1990; Ashraf et al. 2005; Sengul et al. 2006; Zafar et al. 2006; Zafar and Ashraf 2007; Gharabaghi et al. 2010):

1. Acid type
2. Acid concentration
3. Liquid-to-solid ratio
4. Particle size
5. Reaction time
6. Reaction temperature

The following sections will discuss each acid type and the optimal parameters found by a multitude of authors.

4.2.2.2.1 Acetic Acid

Acetic acid is one of the most studied organic acids for the leaching of carbonaceous impurities from phosphate ores (Abu-Eishah et al. 1991; Zafar 1993; Economou et al. 2002; Sengul et al. 2006). Acetic acid (CH_3COOH) is a monocarboxylic acid, with a pKa of 4.76 at 25°C (Lide 1995). Wide availability and relatively low cost make acetic acid particularly attractive for this application. Brief summaries of pertinent studies on carbonate dissolution with dilute acetic acid solutions are as follows.

- Sadeddin and Abu-Eishah (1990) investigated the effects of acetic acid concentration, liquid-to-solid ratio, and reaction time on the dissolution of carbonates from medium-hard and hard (mineral strength) low-grade phosphate ores. The authors found that optimal leaching conditions occur at an acetic acid concentration of 6%–7%, with a liquid-to-solid ratio of 5:1. Softer phosphate ores showed higher dissolution rates compared to harder phosphate ores.
- Abu-Eishah et al. (1991) studied the effects of acetic acid concentration, liquid-to-solid ratio, and reaction time on the beneficiation of a carbonate-rich Jordan phosphate ore composed of collophane and dahllite. Using a continuous stirred tank reactor, the authors determined that the best results were accomplished with a 6%–7% acetic acid concentration at a 5:1 liquid-to-solid ratio and total reaction time of approximately 30–35 minutes. A concentrate containing 70%–75% BPL and 3.6–4.2% CO_2 was achieved from feeds composed of an average of 59.44% BPL and 10.71% CO_2. Acid concentration greater than 10% started to dissolve the phosphate minerals. The authors also

indicated a noticeable increase in leaching efficiency when processing softer phosphate ores, which can be attributed to increased porosity.

- In 1993, Zafar also examined the effects of acetic acid concentration, reaction time, and liquid-to-solid ratio on the dissolution of carbonates from a low-grade Pakistan phosphate ore. The author found that the optimal acetic acid concentration is dependent on the liquid-to-solid ratio used. For a 5:1 liquid-to-solid ratio, it was determined that a 6% solution was best. At a 45-minute leaching time, optimal leaching conditions achieved a concentrate of approximately 69% BPL and 5.8% CO_2 from a 12 × 270 mesh feed containing 56.0% BPL and 14.2% CO_2. Zafar also noted that the temperature at which the reaction was carried out appeared to have negligible effects, although the range of temperatures were not given and may have been minimal.
- Sengul et al. (2006) studied the effects of acetic acid concentration, reaction time, temperature, particle size fraction, stoichiometry, and stirring speed on the selective dissolution of calcite from low-grade Turkey phosphate ores. Optimal leaching conditions were determined as approximately 3% acetic acid concentration at a liquid-to-solid ratio corresponding to a stoichiometric amount of acetic acid (2 mol acetic acid:1 mol calcite). For a feed sized to 45 × 60 mesh, a concentrate of approximately 63.3% BPL was achieved from a feed containing 27.7% BPL with a 40-minute leach time. The authors also determined that a minimum stirring speed (≈200 rpm) helps to remove the evolved CO_2 gas from the surface of the carbonate mineral and increases the dissolution rate.

4.2.2.2.2 Formic Acid

Formic acid (HCOOH) is a monocarboxylic acid with a pKa of 3.75 at 20°C (Lide 1995). A potential benefit of formic acid is that it has a smaller molecular size than other carboxylic acids, which may help the acid penetrate into the pores for increased dissolution rates (Zafar et al. 2006). Descriptions of the relevant literature follow.

- Zafar et al. (1996a) studied the effects of formic acid concentration, liquid-to-solid ratio, process temperature, and reaction time for dissolution of carbonates from low-grade phosphate ores. Optimal results occurred at a formic acid concentration of 4.5% and a liquid-to-solid

ratio of 4:1. When leaching a 4 × 65 mesh phosphate feed containing an average of 57.5% BPL and 13.8% CO_2, a phosphate concentrate of approximately 76.0% BPL and 5.8% CO_2 was achieved after a 25-minute leaching time. Increased leaching time did not result in any significant increases to the concentrate grade. Increasing the reaction temperature also had no noticeable effects on carbonate dissolution rate. The authors also determined that losses in phosphate became evident when formic acid concentrations exceeded 8%.

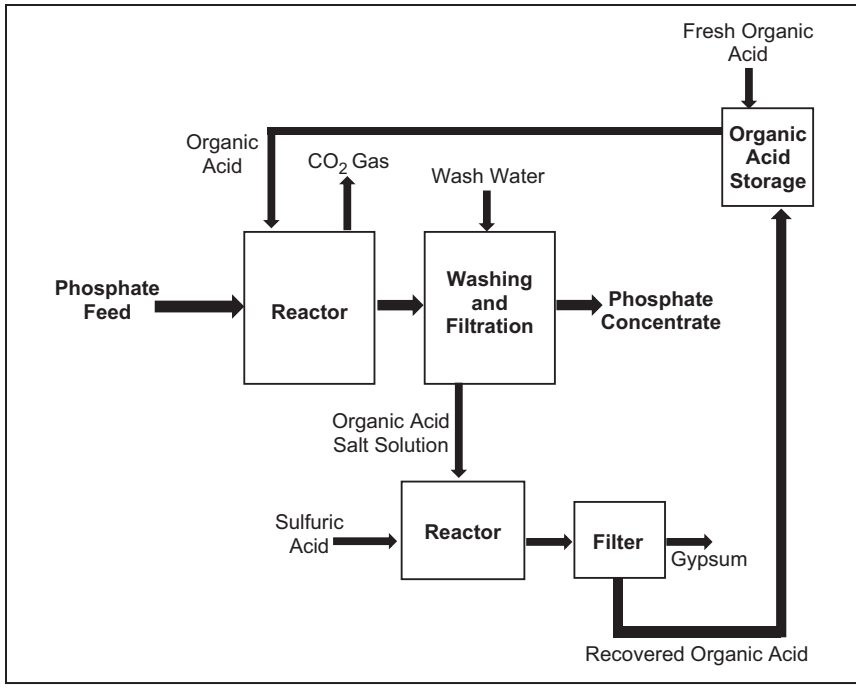
- In another study by Zafar et al. (2006), operating conditions for the selective leaching of carbonates from low-grade phosphate ores using formic acid were optimized. Optimal leaching conditions appeared to be a 5%–6% formic acid concentration at a 5:1 liquid-to-solid ratio. It was also determined that the optimum leaching temperature is 50°C. The authors indicated that the lower efficiencies occurring at temperatures exceeding 50°C may be attributed to the decrease in formic acid solubility. Overall, using a 4 × 65 mesh phosphate feed containing approximately 56.8% BPL and 14% CO_2, a phosphate concentrate of roughly 74.5% BPL, and 4.5% CO_2 was achieved after 25 minutes of leaching at the optimized parameters.

4.2.2.2.3 Lactic Acid

Lactic acid ($CH_3CH(OH)COOH$) is a monocarboxylic acid with a pKa of 3.86 at 25°C (Zafar and Ashraf 2007). Zafar and Ashraf (2007) studied the effects of lactic acid concentration, liquid-to-solid ratio, particle size, and temperature on the dissolution kinetics of carbonate from low-grade Pakistan phosphate ores. Experiments were carried out in a temperature-controlled 500-mL stirred reactor using a 100 × 150 mesh phosphate feed that contained approximately 48.9% BPL and 20.1% CO_2. Optimum leaching conditions were determined to be an 8% lactic acid concentration at a 7:1 liquid-to-solid ratio, which resulted in a concentrate of approximately 76.5% BPL and 6.1% CO_2. The authors also noted an increase in the carbonate dissolution reaction rate up until approximately 45°C.

4.2.2.2.4 Succinic Acid

Succinic acid ($HOOCCH_2CH_2COOH$) is a dicarboxylic acid with a pKa_1 of 4.16 and a pKa_2 of 5.16 at 25°C (Lide 1995). Ashraf et al. (2005) investigated the effects of succinic acid concentration, liquid-to-solid ratio, and



Source: Adapted from Zafar et al. 2006.

Figure 4.2 Simplified process flow diagram of an organic acid leaching process

reaction temperature on the dissolution of carbonaceous gangue from low-grade Pakistan ores. Using a feed sized to 80 × 115 mesh, optimum leaching conditions were determined to be an 8% succinic acid concentration and liquid-to-solid ratio of 7:1. The authors also noted an increase in reaction rate as temperature was increased up until around 70°C.

4.2.2.3 Process Considerations

Given that a variety of dilute organic acids have been proven to be capable of selectively leaching carbonates from phosphate ores, acid choice is going to be significantly influenced by price, availability, and recoverability of the organic acid. Solubility of the organic acid and its corresponding salts also plays an important role in the process. As shown in Figure 4.2, high solubility of organic salts in the leaching solution allows for a simple filtration and washing process to be used to separate the solid phosphate concentrate from the leaching solution (Zafar 1993; Zafar et al. 1996b).

Particle size can greatly affect the efficiency of the organic acid leaching process for obvious reasons. As particle size is decreased, the efficiency of the leaching process increases. This is due in large part to increased surface area along with greater liberation of the fine carbonaceous micro inclusions found in the phosphate pebbles. However, grinding to finer sizes could significantly inhibit the filtration of the phosphate concentrate from the organic acid salt solution (Gharabaghi et al. 2010). Addition of energy-intensive grinding will also increase the cost of the process as a whole.

4.2.2.4 Organic Acid Recovery

One of the major drawbacks of the organic acid leaching process is the high costs associated with organic acids. In order for organic acid leaching to be economically feasible, a method for recovering and recycling of the organic acid must be included. Several methods for organic acid recovery have been proposed in the literature, which are described in the following sections.

4.2.2.4.1 Recovery of Organic Acid by Reaction with Sulfuric Acid

The most feasible method for regenerating the organic acid could be by reaction with sulfuric acid. In the case of acetic acid (Equation 4.6), calcium acetate is reacted with sulfuric acid to produce acetic acid and gypsum. The insoluble gypsum is then filtered out from the recovered acetic acid. The sulfuric acid should be added at stoichiometric amounts to eliminate the possibility of excess sulfuric acid making it into the recovered organic acid. Any excess sulfuric acid remaining in the organic acid could result in significant phosphate losses during the leaching phase (Abu-Eishah et al. 1991; Zafar 1993; Zafar et al. 1996b, 2006; Gharabaghi et al. 2010).

$$\mathrm{Ca}\left(\mathrm{CH_3COO}\right)_{2(aq)} + \mathrm{H_2SO_{4(l)}} + 2\mathrm{H_2O} \rightarrow 2\mathrm{CH_3COOH}_{(aq)} + \mathrm{CaSO_4 \cdot 2H_2O}_{(s)} \qquad \textbf{EQ 4.6}$$

4.2.2.4.2 Recovery of Organic Acid by Reaction with CO_2 in a Pressurized Reactor

Another possible method for organic acid recovery is reacting CO_2 gas with the organic acid salt solution. In a pressurized CO_2 reactor, Equation 4.7 could be used to regenerate acetic acid under the correct conditions (Zafar 1993; Abouzeid 2008).

$$\mathrm{Ca(CH_3COO)_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \rightarrow 2CH_3COOH_{(aq)} + CaCO_{3(s)}} \qquad \textbf{EQ 4.7}$$

4.2.2.4.3 Recovery of Organic Acid by Ion Exchange Process

Organic acid could also be recovered by using an ion exchange bed process. In this process, the salt of the organic acid (e.g., calcium acetate) is passed through an ion exchange bed where the H^+ ions on the active sites of the bed are replaced by Ca^{+2} ions. One downfall of this process is that ion exchange beds eventually become charged with Ca^{+2} ions. The ion exchange bed must then be regenerated, or recharged, with H^+ ions. Regeneration for such a process could be accomplished by passing HCl through the charged bed (Zafar 1993).

4.2.3 Summary of Acid Leaching for the Removal of MgO (Dolomite, $CaMg(CO_3)_2$) from Phosphate Ores

Most of the current research in acid leaching for upgrading phosphate ores has been focused on the removal of calcium carbonates. In the case of MgO removal, acid leaching has the following advantages: (1) organic acids have been shown to selectively leach carbonates (calcium carbonate and dolomite) from phosphate ores without significant phosphate losses; and (2) fine dolomite inclusions inside apatite particles need only be exposed to the acid solution for leaching to proceed, and not be fully liberated from the apatite as is needed for physical separation methods such as flotation. However, grinding to very fine sizes has its disadvantages, as it poses potential problems during filtration of the concentrated phosphate solids and adds additional energy costs to the process. Other significant costs associated with acid leaching are organic acid costs and organic acid recovery costs.

Another potential problem with leaching dolomite from phosphate ores using organic acids involves the removal of MgO from the leaching solution. As seen in Equation 4.3, soluble magnesium acetate ($Mg(CH_3COO)_2$) is formed when dolomite reacts with acetic acid. The solubility of magnesium acetate is beneficial during filtration of the leaching solution from the upgraded phosphate ore, but it poses some problems during the organic acid regeneration step. The preferred method of organic acid regeneration

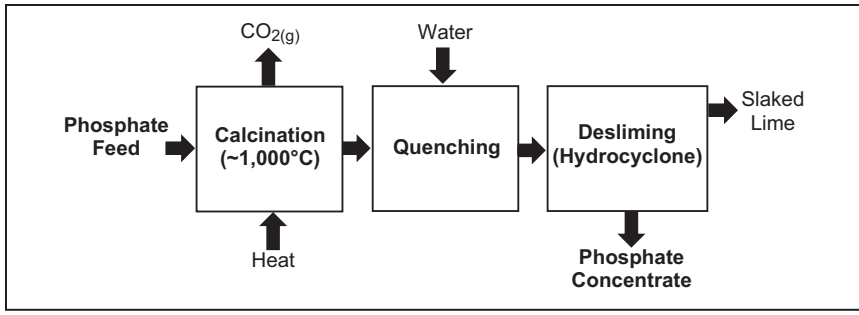


Figure 4.3 Simplified process flow diagram of thermal decomposition process for beneficiation of carbonaceous sedimentary phosphates

by reacting with sulfuric acid is not expected to work because of the high solubility of magnesium sulfate (Zafar et al. 1996b). This means that some other method, possibly ion exchange, must be used to remove magnesium from the system.

4.3 THERMAL DECOMPOSITION (CALCINATION)

Calcination is a method used to upgrade carbonaceous phosphate ores by heating at high temperatures to thermally decompose carbonates. Calcium carbonate decomposes at temperatures around 800–1,000°C to release carbon dioxide gas, while solid calcium oxide remains behind (Abouzeid et al. 1980; Abouzeid 2008). The calcined phosphate ore is then quenched with water and put through a hydrocyclone to remove the slaked lime slimes from the phosphate minerals. Figure 4.3 shows a simplified process flow diagram for calcination of phosphate ores. Calcination is capable of removing essentially all carbonates from phosphate ores. However, high energy requirements and reduced phosphate product reactivity are considered to be significant drawbacks to the calcination process.

4.3.1 Calcination Reactions and Decomposition Temperatures

During the calcination process, the carbonaceous phosphate ore goes through many reactions as the temperature is increased. The main steps of the thermal decomposition process are drying, removal of organics, decomposition of carbonate minerals, and defluorination (Abouzeid et al. 1980; Abouzeid 2008). Noted temperatures for each stage are approximate and vary depending on specific heating conditions.

4.3.1.1 Drying (105–150°C)

The majority of the world's phosphate production comes from sedimentary phosphate ores. These ores are typically strip mined and can contain significant moisture, which is evaporated as part of a simple drying process.

4.3.1.2 Removal of Combined Water and Organic Matter (150–500°C)

Organic matter is present in phosphate ores in variable amounts depending on the origin of the deposit. Sedimentary phosphate reserves located in North Africa, Colombia, the western United States, and North Carolina have significant amounts of organic matter (Hignett et al. 1977; Nathan 1990). Abouzeid et al. (1980) note that removal of organic matter and adsorbed water occurs up until approximately 500°C.

Blazy and Bouhaouss (2005) investigated the removal of organic matter from Morocco phosphate ores by flash calcination. Thermogravimetric analysis of organic "black" phosphate ores showed that organic matter is removed in the temperature range of 210–475°C (Blazy and Bouhaouss 2005). Depending on the level of organic matter present in the ore, the burning of the organic matter could contribute significantly to the energy requirements of the calcination processes (Abouzeid 2008).

4.3.1.3 Decomposition of Calcite, Dolomite, and Carbonate-Rich Fluorapatite (500–1,000°C)

4.3.1.3.1 Calcite ($CaCO_3$)

Thermal decomposition temperatures of calcite can vary significantly depending on the atmosphere in which the decomposition takes place, particle size, total amount of sample, and heating rate. When calcium carbonate is heated, it decomposes into calcium oxide and carbon dioxide gas (Equation 4.8).

$$CaCO_{3(s)} \rightarrow CO_{2(g)} + CaO_{(s)} \quad (\sim 500\text{–}1{,}000^{\circ}C) \qquad \textbf{EQ 4.8}$$

In an air atmosphere, a 500-mg (–200 mesh) sample heated at 120°C/h resulted in the decomposition of calcite from 600–800°C. The same sample heated under a CO_2 atmosphere decomposed from 900–920°C (Duval 1963). Complete understanding of calcination operating parameters is important to ensure optimal thermal decomposition of calcite. Heating the ore for longer times, at higher than needed temperatures, would result in a large waste of energy and could potentially cause other problems in further processing.

4.3.1.3.2 Dolomite ($MgCa(CO_3)_2$)

Thermal decomposition of dolomite has been shown to decompose in two steps (Duval 1963; McIntosh et al. 1990; Sharp et al. 1991). The magnesium carbonate part of dolomite decomposes in the first step, as shown in Equation 4.9, which is followed by the decomposition of the remaining calcium carbonate, as shown in Equation 4.10 (Duval 1963).

$$MgCa\left(CO_3\right)_{2(s)} \rightarrow CO_{2(g)} + MgO_{(s)} + CaCO_{3(s)} \quad (\sim 500\text{–}750°C) \quad \textbf{EQ 4.9}$$

$$MgO_{(s)} + CaCO_{3(s)} \rightarrow CO_{2(g)} + MgO_{(s)} + CaO_{(s)} \quad (\sim 750\text{–}1{,}000°C) \quad \textbf{EQ 4.10}$$

Abouzeid et al. (1980) noted that dolomite starts to decompose from approximately 600°C and continues until around 900°C. The differential thermal analysis (DTA) curves indicated two peaks at 780°C and 830°C, indicating the two stages of thermal decomposition of dolomite.

Exact thermal decomposition temperatures can vary to some extent based on the following parameters (McIntosh et al. 1990; Sharp et al. 1991; Wilburn et al. 1991; Wilburn and Sharp 1993):

- Sample mass (bed depth),
- Heating rate,
- Partial pressure of CO_2, and
- Particle size.

4.3.1.3.3 Carbonate-Rich Fluorapatite

Carbonates are not only present as free calcite and dolomite, but also as carbonate that is substituted into carbonate-rich fluorapatites (i.e., francolite, collophane, dahllite). Silverman et al. (1951) studied the differences in thermal decomposition of calcite and carbonate-rich fluorapatite. They found that carbonate-rich fluorapatite decomposes over the same temperature range as calcite, but gave a smoother DTA curve as opposed to the defined endothermic peak that is associated with calcite decomposition.

Abouzeid et al. (1980) studied the rate of thermal decomposition of a carbonate-rich francolite that contains calcite and a carbonate-rich francolite that is free of calcite. They indicated that the carbonate-rich francolite without calcite has a slightly higher rate of decomposition. It was proposed that the CO_2 from the carbonate-apatite is given off more easily as a result of internal stresses.

4.3.1.4 Removal of Fluorine from Sedimentary Phosphate Ores (>1,000°C)

At temperatures ranging from approximately 1,370–1,510°C, fluorine is driven off. This creates a high-purity phosphate concentrate that contains a high enough phosphorus-to-fluorine ratio to be suitable as an animal feed supplement (Abouzeid 2008). However, when producing phosphate concentrates suitable for wet process feed, temperatures higher than 1,000°C have negative effects on the reactivity of the calcined product (Abouzeid et al. 1980; El-Jallad et al. 1980).

4.3.2 Quenching and Desliming of Calcined Phosphate Ore

When calcium carbonate thermally decomposes, it produces CO_2 gas and solid calcium oxide (CaO). The CaO is separated from the phosphate minerals by first quenching with water, which is followed by size separation with hydrocyclones. When hot calcined ore is quenched with water, CaO goes into the slime phase as slaked lime ($Ca(OH)_2$). In the case of MgO, quenching results in $Mg(OH)_2$, which has a very low solubility in water. In a study that tested different quenching solutions, Al-Fariss (1993) found that quenching with 5% NH_4NO_3, 5% NH_4Cl, and water gave the best results.

After quenching the hot calcined ore, the fine slaked lime slimes are separated from the phosphate concentrate using classifiers such as hydrocyclones (Zafar et al. 1996b). In order to ensure an efficient separation of the $Ca(OH)_2$ and $Mg(OH)_2$ from the phosphate ore, the feed ore should not be crushed too finely. Tight control of attrition scrubbing and desliming is important in order to reduce phosphate losses to the fine slaked lime rejects (Al-Fariss 1993).

4.3.3 Effects of Calcination on the Reactivity of Phosphate Products

Calcined phosphate concentrate has a lower reactivity during the wet process production of phosphoric acid. This is undesirable because it reduces the rate at which phosphoric acid can be produced. Reduced reactivity can be attributed to the chemical and physical changes that the phosphate ore goes through during the calcination process (Abouzeid et al. 1980; El-Jallad et al. 1980; Zafar et al. 1996b; Abouzeid 2008).

Phosphate ore goes through a series of physical changes while being heated, which significantly affects the crystal size. El-Jallad et al. (1980) found that changes in crystal size begin when temperatures exceed 500°C, with two

main factors attributing: recrystallization of fluorapatite and crystal growth. As calcination temperatures reach approximately 600°C, the carbonate-rich apatite starts to recrystallize into the more stable fluorapatite. As the temperatures are raised even further, almost all of the carbonate apatite has transformed into fluorapatite and crystal growth begins. Finally, fluorapatite crystal growth becomes significant as the temperature approaches 950°C. Overall, calcination affects phosphate reactivity by transforming carbonate-rich fluorapatite into the more stable fluorapatite and by decreasing the specific surface area (Abouzeid et al. 1980; El-Jallad et al. 1980).

4.3.4 Process Considerations for Calcination of Carbonaceous Sedimentary Phosphate Ores

One major process consideration for calcination involves determining which type of calcination unit works best. Some of the more popular units include the rotary kiln, fluidized bed reactor, and flash calciner (Cardeal Pereira et al. 1988; Kaljuvee and Veiderma 1995; Ozer 2003; Blazy and Bouhaouss 2005; Abouzeid 2008).

Ozer (2003) studied important variables involved in the calcination of low-grade Turkey phosphate ores in a fluidized bed reactor. The parameters of interest included process temperature, air flow rate, and particle size. Process temperatures ranging from 500–900°C were tested at a calcination time of 15 minutes, which was then followed by a quenching and washing step. It was found that 800°C was the optimal calcination temperature under these conditions. An initial carbonaceous phosphate feed ore that was sized to 25 × 35 mesh and contained 46.7% BPL was upgraded to 74.9% BPL. It was found that higher temperatures resulted in the production of more phosphate fines, which were consequently lost during the washing stage. In another set of experiments, as particle size was decreased, calcination efficiency increased, which is most likely due to increased liberation of carbonate at finer sizes. However, the quenching and washing step becomes less effective at finer sizes because of the loss of phosphate fines to the slaked lime slime rejects. Air flow velocity was an important parameter in the design of fluidized bed calciners. Higher flow rates produce significant amounts of fines because of particle–particle and particle–wall collisions.

Rotary kilns are another well-known calcination unit that can be used in the thermal beneficiation of carbonaceous phosphate ores. Rotary kilns are widely used in cement processing and also in the production of iron ore pellets.

Regardless of the type of calcination unit, the most important parameters remain similar: calcination temperature, calcination time, particle size, and bed depth (total feed rate). These parameters are the most influential on the amount of CO_2 removed and the quality of the calcined phosphate concentrate. It is desired that the calcination unit be capable of rigid temperature control with a high throughput. Dust control is also necessary, as it is in any dry process containing very fine particles.

4.3.5 Calcination as a Method for the Removal of MgO from Phosphate Ore

The calcination process is capable of eliminating all carbonates from carbonaceous phosphate ores. The overall process uses calcination, quenching, attrition scrubbing, and desliming stages to generate a high-grade phosphate concentrate. In the case of calcium carbonate, thermal decomposition leaves behind CaO, which is transformed into slaked lime (calcium hydroxide) upon quenching. The slaked lime is then separated from the coarser phosphate concentrate using hydrocyclones.

In the case of dolomite, both CaO and MgO are left behind after thermal decomposition. The MgO transforms into insoluble magnesium hydroxide, which can be separated from the phosphate ore with hydrocyclones. As an alternate method, Al-Fariss (1993) tested potential washing solutions including water, NH_4OH, NH_4NO_3, NH_4Cl, HCl, and acetic acid. He found that better MgO removal could be achieved by washing the calcined carbonaceous phosphate ore with a 5% NH_4NO_3, 5% NH_4Cl, and water solution. Overall, calcination is capable of removing all magnesium content that is associated with the dolomite impurities.

The major drawbacks to calcination include the following:

- It is energy intensive,
- It produces a phosphate concentrate of low reactivity, and
- The high capital cost of calcination plants.

On the other hand, calcination may be a viable process in areas where energy is cheap and water is scarce. Calcination is also capable of removing all carbonates and produces a phosphate concentrate suitable for the production of high-grade defluorinated phosphoric acid.

4.4 BENEFICIATION OF PHOSPHATE ORE BY PHYSICAL SEPARATION METHODS

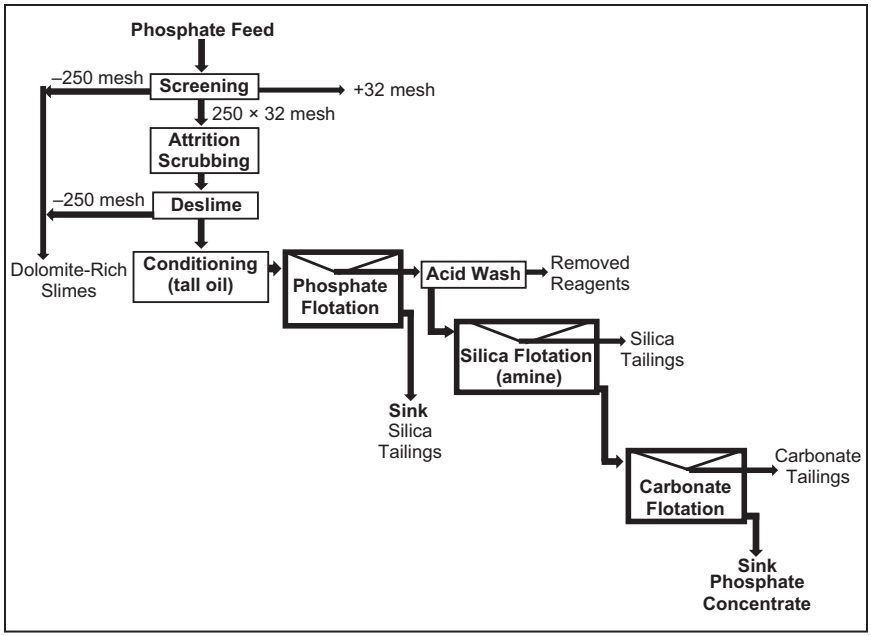
Physical separation techniques currently play an important role in the processing of phosphate ores. Classification techniques such as screening, desliming, and attrition scrubbing have been used to remove fine clay impurities from phosphate ores. Thorough removal of clays, along with a good, sharp size separation, is of great importance for effective operation of the traditional Crago double float process used to upgrade siliceous phosphate ores (Oswald 1993; Guan 2009a). In the case of high-MgO sedimentary phosphate ores, several gravity separation methods including heavy-media cyclones, jigs, and spirals, have been attempted for removal of dolomite (Lawver et al. 1982; Zhang 1993; Abouzeid 2008). The importance of physical separation methods in the processing of phosphate ores is discussed in this section.

4.4.1 Desliming, Attrition Scrubbing, and Sizing

Fine clays such as montmorillonite ($Si_8Al_{3.5}Mg_{0.5}O_{20}(OH)_4$), palygorskite ($(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$), and kaolinite ($Al_4(Si_4O_{10})(OH)_8$) are present in many types of sedimentary phosphate ores. If not removed, these clays will consume large amounts of collector because of their high surface areas. In addition to increased reagent consumption, clays can coat the desired phosphate particles and significantly reduce flotation selectivity (Oswald 1993; Guan 2009a). Phosphate ores are typically deslimed to −150 mesh using 24–30-inch hydrocyclones. Rejected slimes are then sent to settling ponds (Lawver et al. 1978).

In the case of dolomitic phosphate ores, scrubbing and desliming may be beneficial as a technique for removing fine dolomite slimes. Dolomite pebbles are more porous and fragile than phosphate pebbles, which means they have a greater tendency to abrade and produce significant amounts of fines (Lawver et al. 1982; Zhang 1993). Therefore, high-MgO phosphate ores typically contain significant amounts of dolomite slimes that can be efficiently removed by the desliming process. However, desliming is only capable of removing a portion of the total MgO, and the resulting phosphate preconcentrate must go through further processing to remove the coarser dolomite-rich pebbles (Gao et al. 2002).

In addition to the dolomite slimes, magnesium is also present as fine dolomite inclusions in phosphate pebbles, magnesium substituted into



Source: Adapted from Dufour et al. 1980.

Figure 4.4 Simplified process flow diagram for attrition scrubbing-flotation process

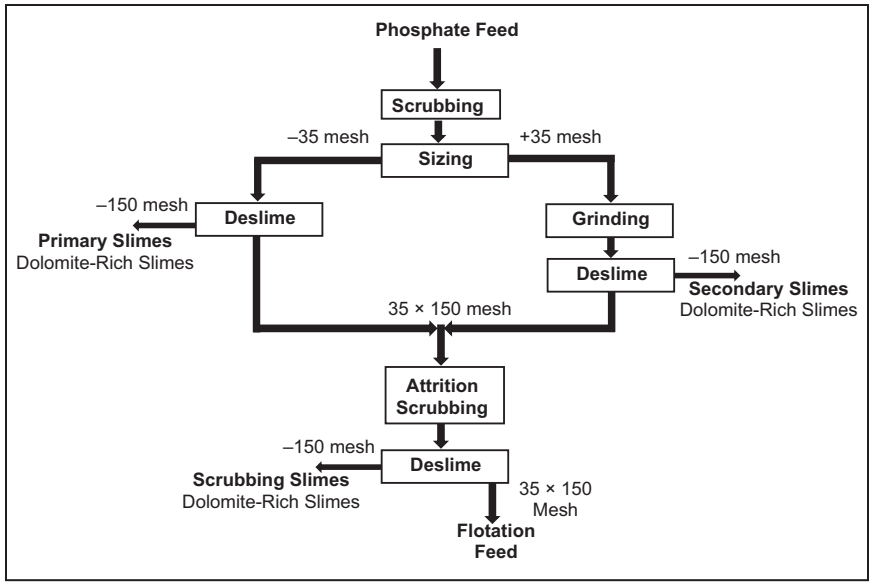
the phosphate lattice, and as distinct dolomite-rich particles. Much of the dolomite-rich pebbles are softer and more fragile than the phosphate pebbles. Several investigators have attempted to take advantage of the hardness differences by using an attrition scrubbing-desliming process for removal of MgO from phosphate ores. Summaries of the main studies are described here.

- Dufour et al. (1980) investigated the feasibility of dolomite removal by attrition scrubbing and desliming. High-MgO phosphate samples from Florida's Hardee County, of various size fractions and mineral composition, were tested using an attrition scrubbing process. Samples were first subjected to attrition scrubbing, then sized into dolomite-rich rejects (–250 mesh slimes) and phosphate concentrate (+250 mesh). When testing a 16 × 32 mesh sample containing 35.47% BPL and 2.67% MgO, a phosphate concentrate containing 1.57% MgO and 37.2% BPL was achieved at a BPL recovery of 91.0%, while rejecting approximately 49.0% of the total MgO.

Further testing was done on a coarser 3 × 16 mesh phosphate sample that contained 3.29% MgO and 46.04% BPL. First, the 3 × 16 mesh high-MgO phosphate sample was crushed in a rod mill to an 80% passing size of 480 μm (~32 mesh). The grinding resulted in a significant amount of dolomite-rich fines (–150 mesh), which were removed as rejects. The coarser size fraction was then put through the attrition scrubbing process and sized at 150 mesh. The resulting phosphate concentrate contained 49.59% BPL and 2.34% MgO. The process had an overall BPL recovery of 73.2%. The authors proposed that attrition scrubbing should be part of a beneficiation process, in which the attrition scrubbed-deslimed product would go through further processing to create a salable phosphate product. A simplified process flow diagram for the proposed process is shown in Figure 4.4. After sizing and attrition scrubbing, a conventional two-stage flotation process is used to remove both the coarse and fine silica. Finally, carbonate is removed from the phosphate concentrate by flotation with an anionic carbonate collector at a slightly acid pH (≈5.5) (Dufour et al. 1980).

- Llewellyn et al. (1982) investigated crushing, sizing, and attrition scrubbing for the removal of dolomite from Florida phosphate ores. In this study, two separate phosphate ores from Manatee and Hardee counties were put through the following process (Figure 4.5) to generate a flotation feed. The flotation preparation process generates three separate dolomite-rich slime tailings:
  - *Primary slimes:* slimes from the original feed
  - *Secondary slimes:* slimes after crushing the coarse (+35 mesh) size fraction of the original feed
  - *Scrubbing slimes:* slimes from the flotation feed after attrition scrubbing

  For this study, the Manatee County phosphate ore sample initially contained 4.92% MgO and 15.40% BPL, while the Hardee County phosphate ore sample initially contained 5.18% MgO and 17.33% BPL. Under the procedure shown in Figure 4.5, using the Manatee County sample, a phosphate concentrate containing 0.57% MgO and 17.76% BPL was achieved with a BPL recovery of 72.8%. Approximately 92.7% of the total MgO was rejected with the slimes (primary + secondary + scrubbing). For the Hardee County sample, a phosphate



Source: Adapted from Llewellyn et al. 1982.

Figure 4.5 Simplified process flow diagram for scrubbing, sizing, grinding, and desliming for preparation of flotation feed

concentrate containing 1.12% MgO and 19.51% BPL was achieved with a BPL recovery of 76.2%. Approximately 85.4% of the total MgO was rejected with the slimes.

4.4.2 Sizing and Selective Crushing

Several authors have shown that in the case of many high-MgO sedimentary phosphate ores, dolomite is concentrated in the coarser natural size fraction. A significant amount of dolomite is also concentrated into the very fine (−100 μm) natural size fraction, which is sometimes referred to as dolosilt (Houot 1982; Lawver et al. 1982; El-Shall et al. 1996; Wiegel 1999). Lawver et al. (1982) noted that approximately 74% of the total dolomite in a high-MgO Florida phosphate ore sample could be removed by screening off the +3 mesh coarse pebble fraction and desliming at −150 mesh.

Selective crushing is a method that attempts to take advantage of the noted hardness difference between the dolomite and phosphate pebbles. Crushing methods such as high-pressure roll mills (HPRMs) have been used to selectively crush the softer dolomite, which is then followed by desliming

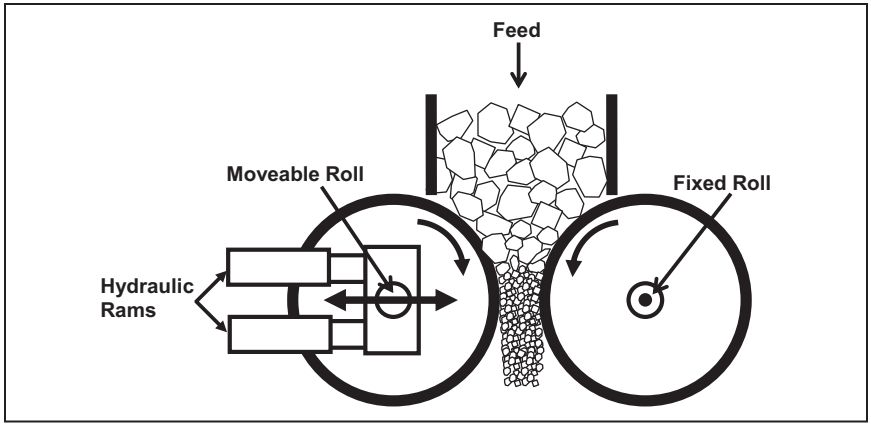


Figure 4.6 Diagram of high-pressure roll mill

to remove the dolomite-rich fine particle fraction. A diagram of an HPRM is shown in Figure 4.6. HPRMs consist of two rolls, one stationary and the other moveable. Hydraulic rams keep the movable roll at a set pressure and gap width. The main advantage of the HPRM is that the particles are forced against each other and crush each other. HPRMs must be choke fed in order to work most efficiently. The Florida Institute of Phosphate Research has reported results from a selective crushing study that used an HPRM to process a feed containing 2.22% MgO and 58.12% BPL. A phosphate concentrate containing 1.10% MgO and 61.38% BPL was achieved, at a BPL recovery of 89.17% (Clifford et al. 1998). However, selective crushing was not capable of producing a phosphate concentrate containing less than 1% MgO and therefore would need to be used in conjunction with another separation method to produce a salable product (Gao et al. 2002).

4.4.3 Heavy-Media Separation

Heavy- (or dense-) media separation (HMS), often referred to as the sink-float process, is one of the simplest gravity separation methods. Figure 4.7 shows a simplified diagram of the HMS process. The HMS process uses a heavy medium (fluid) with a density between the dense and light particles in the feed ore. When the feed ore is placed in the heavy medium, the light particles (less dense than the medium) will float and the dense particles (denser than the medium) will sink. The two most important things to consider when using heavy-media separation are:

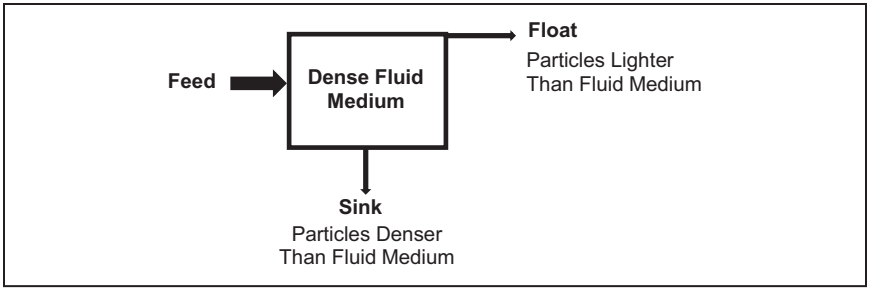


Figure 4.7 Simplified process flow diagram of heavy-media separation

1. What type of heavy-medium fluid should be used?
2. What type of separator vessel will work best for a given feed ore?

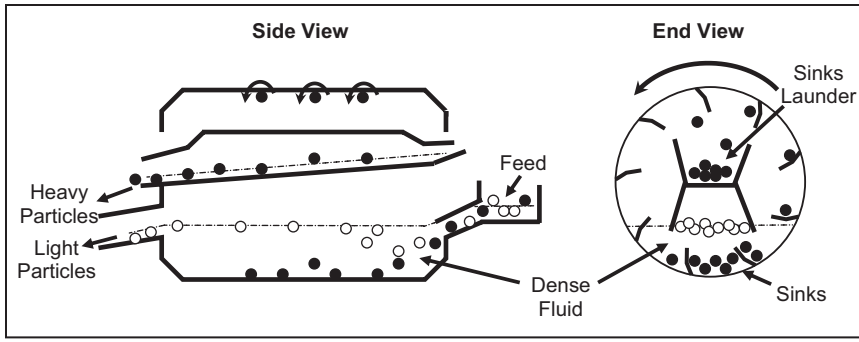
4.4.3.1 Dense-Medium Fluids

Choosing the appropriate dense-medium fluid depends on the density of the minerals being separated. Ideally, the density of the heavy-medium fluid should be between the density of the dense mineral and the density of the light mineral. There are several categories of dense-medium fluids, which include

1. Dissolved salts in water ($CaCl_2$ and $ZnCl_2$),
2. Fine particle suspensions (fine magnetite suspension),
3. Heavy organic liquids, and
4. Paramagnetic salt solution or ferrofluid with a magnetic field gradient.

Of the four categories, only fine particle suspensions and dissolved salts solutions are generally considered feasible for industrial-scale processes. Heavy organic fluids are usually very toxic and/or carcinogenic, and therefore not used industrially. Ferrofluids are capable of generating high-density fluids, but are generally not feasible for plant operations. Fine particle suspensions are the most widely used dense medium for HMS. The following fluid properties must be considered when choosing an appropriate heavy-medium suspension:

1. Fine particle hardness and resistance to abrasion
2. Chemical stability with feed ore
3. Wearing of equipment
4. Stability of fine particle suspension



Source: Adapted from Wills and Napier-Munn 2006.

Figure 4.8 Heavy-medium rotating drum separator

5. Fluid viscosity
6. Specific gravity achievable (at reasonable viscosities)
7. Cost-efficient regeneration method
8. Cost of fluid

Fine magnetite is widely used because it is capable of generating stable suspensions with specific gravities up to around 5. Magnetite is also beneficial because it can be easily recycled using magnetic separators, assuming the feed ore is nonmagnetic. Magnetite is also relatively inexpensive and widely accessible.

4.4.3.2 Heavy-Medium Separation Using Dense-Medium Cyclones

After choosing which heavy-medium fluid should be used, an appropriate separating device must be chosen. Many types of HMS separators exist, with the most common devices being drum separators and dense-medium cyclones. The traditional drum separator, shown in Figure 4.8, uses gravitational forces to separate the light and dense particles. The feed enters the drum and the dense particles sink through the dense-medium fluid to the bottom of the rotating drum. Lifters collect the dense particles and carry them to the top where they fall into the dense-particle launder. Particles lighter than the dense medium float and exit the drum in the light-particle launder. HMS using a rotating drum separator is limited to feed sizes ranging from approximately 0.6–60 cm in diameter (Gupta and Yan 2006).

The heavy-medium cyclones differ from the traditional drum separator in that they use centrifugal forces instead of gravitational forces to separate

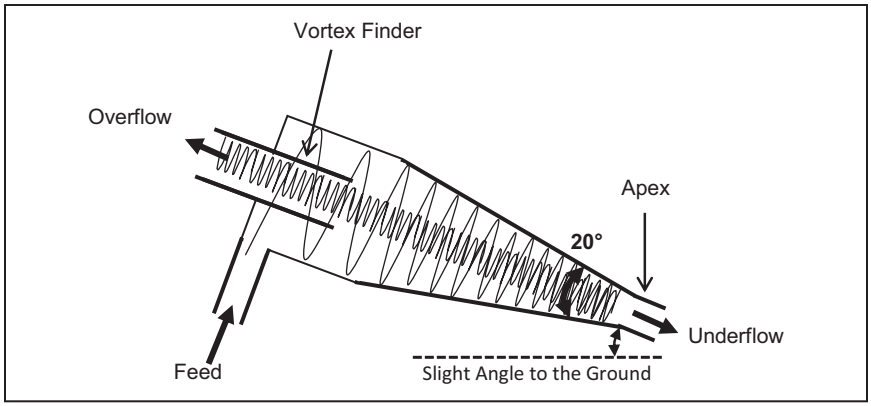


Figure 4.9 Simplified diagram of a heavy-medium cyclone

the light and dense minerals. Heavy-medium cyclones are constructed very similar to traditional classification hydrocyclones. Figure 4.9 shows a simplified diagram of a heavy-medium cyclone. Heavy-medium cyclones consist of a tangential feed into a cylindrical section, which is connected to a lower conical-shaped section. As the feed enters the cyclone, the denser particles are pushed to the outside edge and exit through the underflow. The light particles stay near the core of the cyclone and exit through the overflow. Heavy-medium cyclones typically have a cone angle of 20° and are orientated at a slight angle with the ground to allow for drainage during shutdown.

4.4.3.3 Theory and Operation of Heavy-Medium Cyclones

As previously mentioned, heavy-medium cyclones use centrifugal forces to separate light particles from dense particles. Near the entrance to the cyclone, the feed experiences forces up to 20 times greater than in the rotary drum separator. These centrifugal forces can increase up to 200 g's as the cyclone diameter decreases in the conical section. As the feed whirls around inside the cyclone, particles denser than the heavy-medium fluid will move radially toward the outside of the cyclone into the downward axial flow and out the underflow. The particles lighter than the dense-medium fluid stay near the center of the cyclone and follow the upward axial flow through the overflow (Gupta and Yan 2006). Separation of light and dense particles in a heavy-medium cyclone is shown in Figure 4.10.

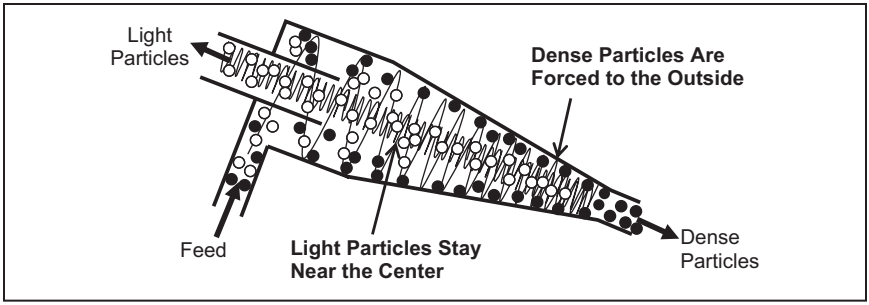
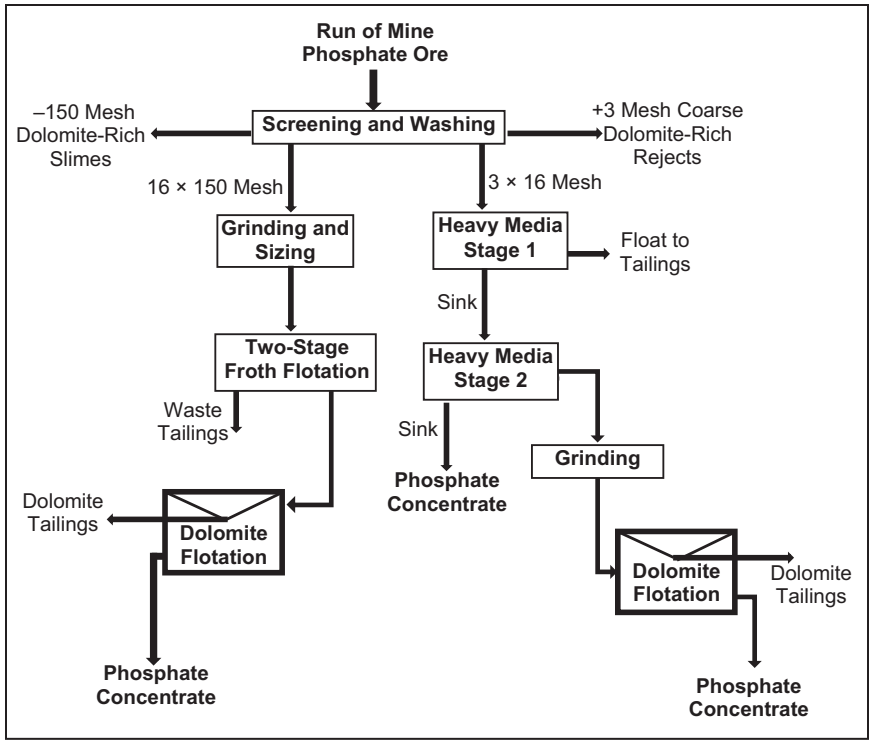


Figure 4.10 Particle separation in a heavy-medium cyclone

The significantly higher forces produced by the heavy-medium cyclone give it the advantage of being able to process feeds down to 0.6 mm in size. Heavy-medium cyclones also have a relatively high capacity compared to their size. Commercially available heavy-medium cyclones typically range from around 50–140 cm in diameter, with the larger cyclones having higher capacities. Heavy-medium cyclones are mostly used in the cleaning of coal, where medium-to-coal ratios ranging from 5:1 to 3:1 are used. Heavy-medium cyclones usually operate at inlet pressures around 140 kPa, with higher pressure need for larger cyclones (Gupta and Yan 2006). Pressure to the cyclone can be achieved by simply pumping slurry containing the feed ore and dense medium directly to the cyclone. This method is generally not desired for friable feeds that tend to abrade and break down easily. Instead, a head tank located some distance (~5–13 m, depending on cyclone size) above the cyclone inlet should be used to reduce abrasion of the feed.

4.4.3.4 Beneficiation of High-MgO Sedimentary Phosphate Ores with Heavy-Medium Cyclones

HMS has been shown to be useful in removing a portion of the dolomite in high-MgO phosphate ores. Dolomite pebbles and phosphate pebbles have very similar densities, with some density overlap due to varying compositions and porosity. Several authors have stated that HMS takes advantage of the notable higher porosity of the dolomite pebbles. It is believed that the heavy media will trap air or water in the pores of the dolomite pebbles but not penetrate the pores themselves. This results in a reduction of the apparent density of the dolomite pebbles and, more importantly, an increased apparent



Source: Adapted from Lawver et al. 1982.

Figure 4.11 Simplified process flow diagram of a heavy-media flotation process for beneficiation of phosphate ore

density difference between the dolomite and apatite pebbles (Baumann and Snow 1980; Lawver et al. 1982; Zhang 1993). However, if the heavy media does enter the dolomite pores, the efficiency of the gravity separation process would be significantly hindered (Gao et al. 2002).

Lawver et al. (1982) conducted an in-depth study on the feasibility of heavy-medium cyclones for the removal of dolomite from high-MgO Florida phosphate ores. The specific gravity of the heavy media was varied from 2.0 to 2.8. It was determined that both the nature of the ore and the specific gravity of the heavy media played a big role in determining the efficiency of the separation. Lower media densities (2.4–2.6) gave phosphate concentrates containing less than 1% MgO at BPL recoveries ranging from 47%–64%, from a feed containing approximately 1.73% MgO. However, at higher MgO feeds (3.53%–3.95%), the only reported phosphate concentrate containing less

than 1% MgO (0.71%) had a significantly lower BPL recovery of 21.7%. As expected, the concentrate grade and recovery depends not only on the operating parameters (heavy-media density), but also the feed characteristics (Lawver et al. 1982).

Lawver et al. (1982) proposed a process flow diagram (Figure 4.11) that included sizing, flotation, and HMS for the beneficiation of high-MgO phosphate ores. First, the phosphate ore is sized to –150 mesh, 16 × 150 mesh, 3 × 16 mesh, and +3 mesh size fractions. The –150 mesh dolomite-rich slimes and +3 mesh dolomite-rich coarse pebbles are rejected. The 16 × 150 mesh size fraction goes through sizing and grinding to achieve the upper particle size limit for flotation (24–48 mesh). The flotation feed then goes through a conventional Crago double float process to remove silica, followed by dolomite flotation to produce a phosphate concentrate. For the 3 × 16 mesh high-dolomite pebble, a two-stage HMS process is used to produce a phosphate concentrate (Stage-2 sinks) and dolomite-rich tailings (Stage-1 floats). The middlings (Stage-2 floats) are then ground, sized, and put through the dolomite flotation process (Lawver et al. 1982).

Several factors affect the efficiency of the HMS process. Tight control of the heavy-media density is crucial because of the narrow density difference between the dolomite and phosphate pebbles. In addition, there can also be a significant amount of phosphate and dolomite pebbles agglomerated together, which further reduces the efficiency of the heavy-media process. For these reasons HMS is usually proposed as a preconcentrating process that needs further processing to produce a salable product.

In the early 1990s, the IMC Four Corners phosphate plant located in Florida implemented an HMS plant to process phosphate pebble containing greater than 1% MgO. The high-MgO –⅜ inch by +16 mesh pebble product from the washing plant (see Figure 3.4) was first sized into three size fractions (EPA 1994):

1. *+5 mesh (0.4 cm).* This coarse pebble fraction typically contained large amounts of MgO and was stored for other uses such as fertilizer filler or road building.
2. *–5 mesh by +16 mesh (0.1 cm).* This size fraction was fed to the HMS plant to remove dolomite and reduce MgO content. The heavy media used in this process was a magnetite suspension.
3. *–16 mesh.* This size fraction was sent back to the flotation circuit.

4.4.4 Jigging

4.4.4.1 Theory, Design, and Operation of Jigs

Jigging is a gravity concentration method that separates minerals of different densities by a continuous expansion and compaction of a particle bed. Figure 4.12 shows a simplified schematic of a plunger-style Harz jig. For this type of jig, a plunger generates the pulsation and suction strokes, which expand and contract the particle bed. Pulsation rate (or pulsation frequency) can be controlled with a variable-speed motor, while stroke length is modified by moving the plunger radially along the disk. Pulsation rates typically range from 50–300 pulsations per minute. Feed ore enters on one side of the jig and is stratified as it moves across the screen. Water is often added through the bottom of the jig to aid in the fluidization of the particle bed. The importance of pulsation rate, stroke length, and other jigging parameters are discussed in greater detail in the following sections.

Many types of industrial jigs are commercially available. Jig types differ mainly by the type of mechanism that is used to generate the pulsation and suction strokes. In addition to the pulsation mechanism, the type of jigging process used can differ from jig to jig. The Harz jig is one of the oldest jig

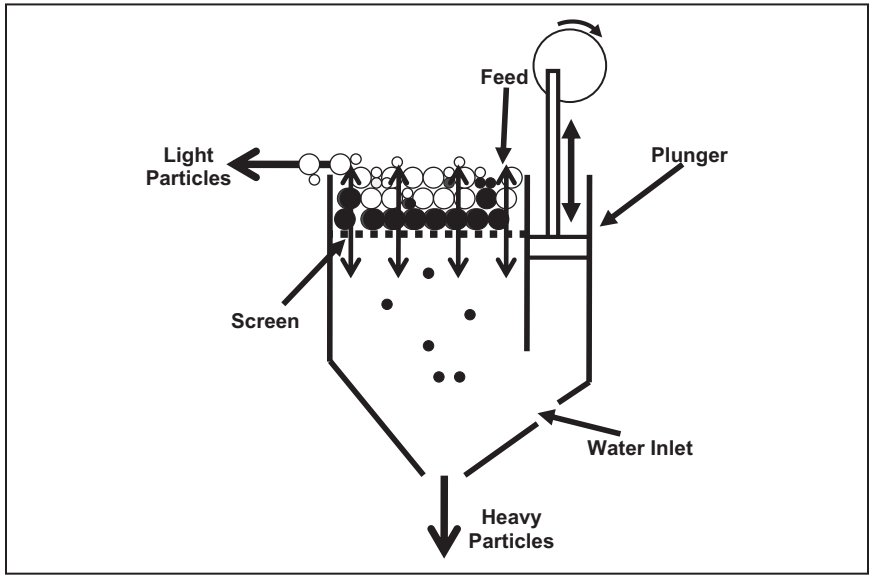


Figure 4.12 Simplified diagram of a Harz-style jig

types and uses a plunger as the pulsation mechanism. Other jig types, such as the Baum and Batac jigs, use air chambers to pulsate the fluid. Also available are duplex-style jigs such as the Pan-Am jig, which uses flexible diaphragms located underneath the jig to generate the fluid pulsation. Baum and Batac jigs are mostly used in coal cleaning, whereas duplex-style jigs are used for concentration of placer gold. Some major advantages of the jigging process include the following:

1. Jigs can operate with coarse particle feeds.
2. Jigging is relatively inexpensive compared to HMS and flotation.
3. Jigs have a relatively high throughput.
4. Jigs can be selective when operated correctly (assuming sufficient liberation and density difference).

4.4.4.2 Theory of Jigging Process and Mechanisms of Separation

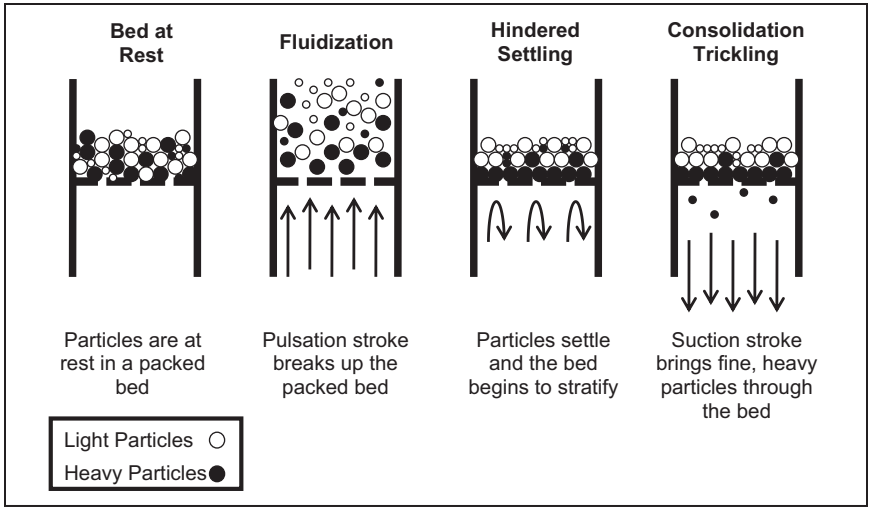
The jigging cycle can be broken down into two main parts: pulsation stroke and suction stroke. Figure 4.13 describes the different mechanism of separation occurring during the jigging process. The jigging cycle begins with a particle bed resting on top of the screen. As the pulsation stroke starts, the particle bed begins to fluidize, and the main mechanism of separation is *differential acceleration*. As the fluid approaches a maximum, *hindered settling* takes over as the key mechanism of separation. Finally, the particle bed compacts during the suction stroke and *consolidation trickling* of fine particles occurs.

The first mechanism of separation is *initial differential acceleration,* which occurs at the very beginning of the pulsation stroke. Initial differential acceleration separates purely on density differences. When considering the forces acting on a particle settling in a fluid (Figure 4.14), Equation 4.11 shows a force balance on a particle.

$$M_s a_p = F_G - F_B - F_D \qquad \textbf{EQ 4.11}$$

where

M_s = mass of the solid particle
a_p = acceleration of the particle
F_G = force due to gravity
F_B = force due to buoyancy
F_D = force due to drag



Source: Adapted from Gupta and Yan 2006.

Figure 4.13 Mechanisms of particle stratification occurring during the jigging process

Equation 4.11 is simplified by dividing through by M_s, resulting in Equation 4.12. Since this is "initial" differential acceleration, it occurs at the very beginning of the pulsation stroke ($t \approx 0$). Therefore, the particle velocity is negligible, and drag force (F_D) is assumed to be zero. After some simplification, Equation 4.13 shows that differential acceleration is only dependent on the densities of the fluid and the particle. Since the same fluid is acting on any particular particle in the jig bed, separation due to differential acceleration is based on the density differences of the particles (Gupta and Yan 2006).

$$a_p = g - \left(\frac{\rho_f}{\rho_s}\right) g - \frac{F_D}{M_s} \qquad \text{EQ 4.12}$$

$$a_p = g\left(1 - \frac{\rho_f}{\rho_s}\right) \qquad \text{EQ 4.13}$$

where

g = gravitational acceleration constant
ρ_f = density of fluid
ρ_s = density of solid particle

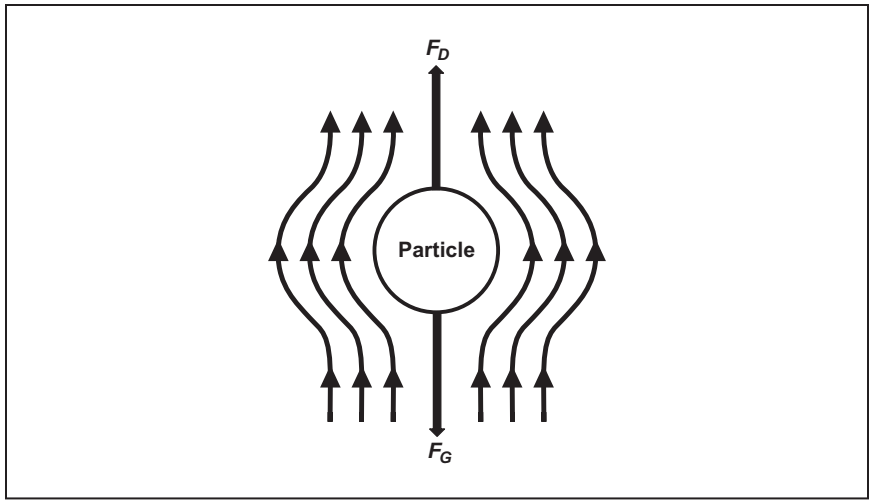


Figure 4.14 Particle settling in a fluid under "free settling" conditions

The second mechanism of separation, *hindered settling,* occurs during the pulsation stroke and leading into the suction stroke, and separates based on both particle size and particle density. After initial differential acceleration, the fluid flow velocity during the pulsation stroke increases, and the drag force (F_D) becomes significant. If the percent solids in a system are high, such as the particle bed in a jig, hindered settling is prevalent over free settling. In hindered settling, a particle experiences resistance due to increased turbulence, particle–particle interactions, and particle–wall interactions, as shown in Figure 4.15 (left). Overall, hindered settling enhances separation based on particle densities, while decreasing the effects of particle size.

The final mechanism of separation is *consolidation trickling*, wherein the suction stroke pulls fine, heavy particles through the void spaces of the larger heavy particle bed on top of the screen. Figure 4.15 (right) shows a diagram of consolidation trickling. Consolidation trickling separates particles mainly based on size. The size ratio, defined as the diameter of the fine (penetrating) particle divided by the diameter of the coarse particle (d_F/d_C), determines the particle size limit for consolidation trickling. For perfect spheres, a size ratio of 0.41 is the theoretical limit for penetration of fines (Mukherjee and Mishra 2006).

Even though the separation mechanisms involved in the jigging process are known, the interaction between key jigging parameters is not well

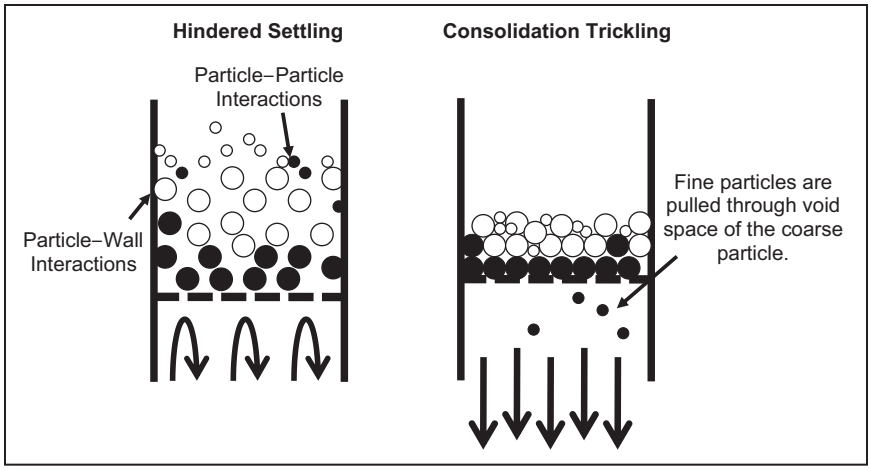


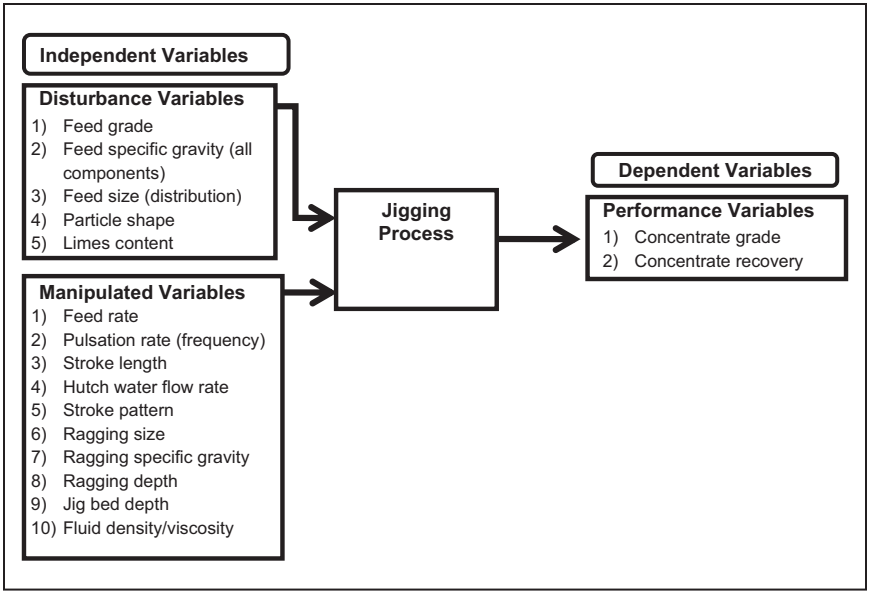
Figure 4.15 Hindered settling (left) and consolidation trickling (right)

understood (Mishra and Adhikari 1999). Some of the most significant jigging parameters include total jigging time, pulsation rate, pulsation stroke length, and water flow rate. Stroke length and pulsation rate are the most important jigging parameters aside from total jigging time (Mukherjee and Mishra 2006). Optimization of jigging parameters is discussed in detail in the next section.

4.4.4.3 Jigging Parameters and Optimization

Jigging is a relatively complex process because of the many interrelating variables and parameters. A list of independent and dependent variables involved in the jigging process can be found in Figure 4.16. The independent variables can be broken down into disturbance variables and manipulated variables. Disturbance variables are mainly properties of the feed ore, making them mostly unchangeable. In the case of processing high-MgO sedimentary phosphate ores, an example of an important disturbance variable would be the minimum achievable MgO grade. Manipulated variables are essentially jigging parameters that can be optimized for a particular separation. Depending on the disturbance variables (i.e., feed size, density, slimes content, etc.), particular jig settings can be used to take advantage of the different mechanisms of separation discussed in the previous section.

Dependent variables are metrics that can be used to quantify the efficiency of the jigging process. Some of the more useful measurements for



Source: Adapted from Karantzavelos and Frangiscos 1984.

Figure 4.16 List of variables involved in the jigging process

gravity separation processes include grade and recovery of the dense and light particle concentrates. Overall, the large amount of interrelated jigging variables make it very difficult to develop mathematical models that can be used to determine how well jigging will work for a specific body of ore. Instead, laboratory-scale tests are usually needed to determine if jigging would be feasible for a particular ore body.

4.4.4.3.1 Pulsation Rate and Stroke Length

Apart from total jigging time, pulsation rate and stroke length are the most important jigging parameters because they directly control the magnitude and duration of each stroke. For a plunger-style jig, the magnitude and direction of the fluid flow can be modeled as a sinusoidal function (Figure 4.17), where fluid flow in the positive direction corresponds to the pulsation stroke and fluid flow in the negative direction corresponds to the suction stroke. In the case shown in Figure 4.17, where there is no water added to the jig, the duration of the pulsation and suction strokes is equal. Equation 4.14 can be used to determine the duration of the pulsation and suction stroke.

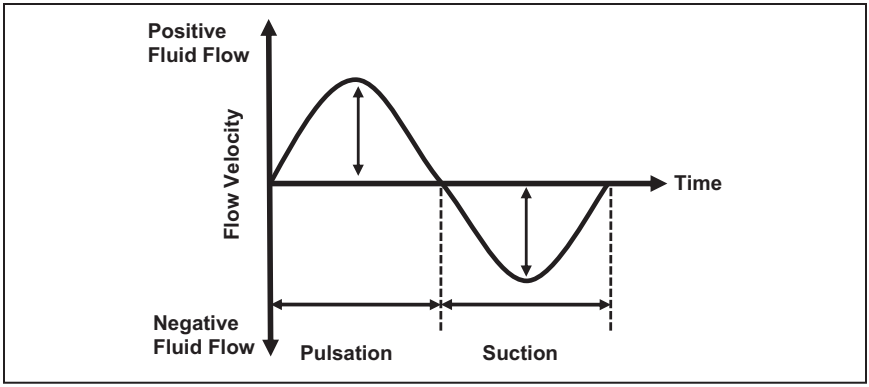


Figure 4.17 Simple harmonic motion can be used to describe the fluid flow during the jigging cycle for a plunger-style jig

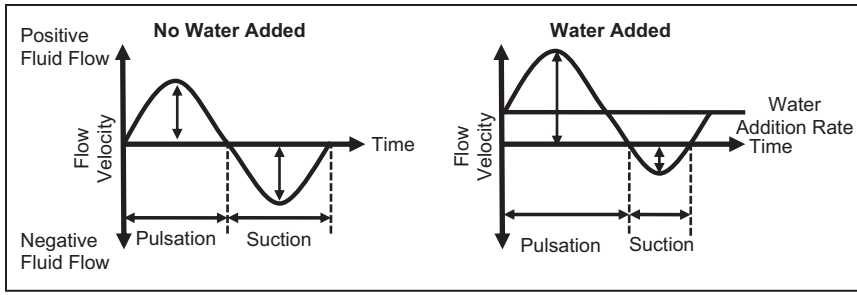
$$T = \frac{1}{2\left(\frac{N}{60}\right)} \qquad \text{EQ 4.14}$$

where

T = duration of a single pulsation or suction stroke
N = total number of pulsations per minute

Since pulsation rate plays a major part in determining the velocity of the fluid, along with determining the duration of the pulsation and suction strokes, it is the most important jigging parameter. However, stroke length is also an important factor in determining the maximum velocity of the pulsation stroke. *Stroke length* is defined as the distance travelled by the piston for a given stroke. In the case of the Harz jig shown in Figure 4.12, the stroke length is the distance between the highest and lowest points that the plunger travels.

Pulsation rate and stroke length are usually optimized together for certain situations depending on feed properties. For example, consider a feed containing a relatively large sized pebble feed, with a considerably large density difference between the dense and light particles. A situation like this would benefit from a lower pulsation rate with a long stroke length. These settings would effectively increase the duration of the pulsation stroke and take advantage of hindered settling to a greater degree. Now consider a finer sized feed



Source: Adapted from Wills and Napier-Munn 2006.

Figure 4.18 Effects of water addition on fluid flow velocity throughout the jigging cycle

ore, where the density difference between the dense and light particles is a lot narrower. For this situation, a higher pulsation rate and smaller stroke length would be desired. These parameters would increase the separation effects from differential acceleration. Overall, it is apparent that pulsation rate and stroke length should be optimized together to achieve the most efficient separation.

4.4.4.3.2 Increasing Upward Flow by Water Addition

It is common practice in jigging to add some constant upward flow of water to aid in fluidizing the particle bed. This can be particularly advantageous when dealing with coarser, narrowly sized feeds that can compact tightly during the suction stroke, significantly reducing separation by consolidation trickling. As shown in Figure 4.18, the addition of a constant water flow shifts the sinusoidal fluid flow curve upward by the velocity at which the water is rising through the jig. This results in increasing the magnitude and duration of the pulsation stroke, while consequently reducing the magnitude and duration of the suction stroke. However, addition of too much water can result in the misplacement of fine, dense particles into the light particle overflow.

4.4.4.4 "Over the Screen" Versus "Through the Screen" Jigging

Two major categories of jigging processes are "over the screen" jigging and "through the screen" jigging. A comparison of the two methods is shown in Figure 4.19.

In the over-the-screen jigging process, all particles in the feed are larger than the screen and separation occurs on top of the screen. The light particle layer is separated from the dense particle layer by a "gate and dam" discharge

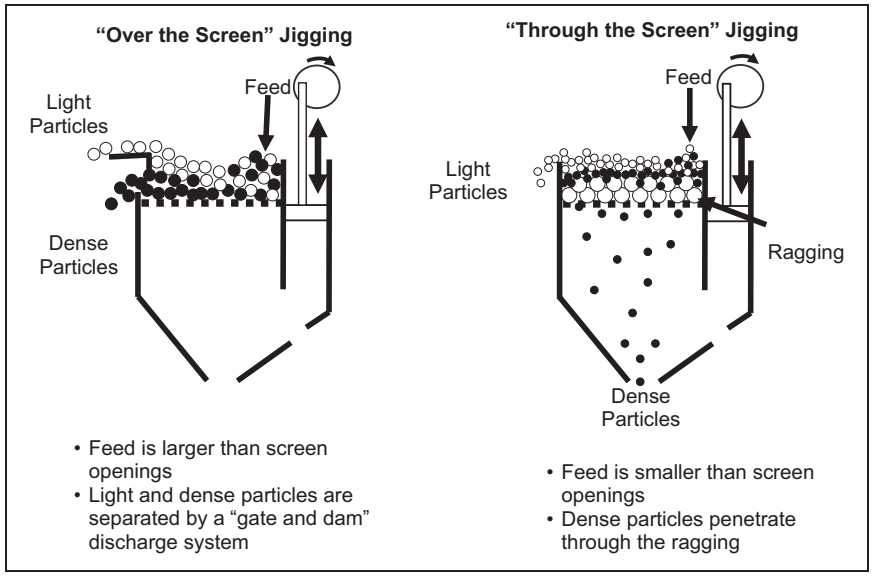


Figure 4.19 "Over the screen" versus "through the screen" jigging

system. This is one major advantage of over-the-screen jigging, since the quality of the dense particle concentrate and discharge rate can be controlled by varying the position of the gate. Many of the modern, commercially available jigs are highly instrumented to control the quality of the product.

For through-the-screen jigging, all particles in the feed are smaller than the openings in the screen. To keep the feed from just passing straight through the screen, a coarse layer of "ragging" is placed on top of the screen. The fine, dense particles separate from the light particles and penetrate through the ragging via consolidation trickling. The light particles move across the ragging and are discharged to the light particle concentrate. Through-the-screen jigging is common when using duplex-style jigs for concentrating placer gold. Steel shot is often used as the ragging for gold processing. For consolidation trickling to occur, the ragging should theoretically be at least 2.43 times larger than the coarsest particle in the feed.

4.4.4.5 Concentration Criterion

Because jigging is a gravity separation method, the efficiency of the process is highly dependent on the density difference between the minerals being separated, density of fluid medium, and particle size. The concentration criterion

(Equation 4.15) may be used to predict the efficiency of a gravity concentration processes (Gupta and Yan 2006). This equation is very similar to the hindered settling ratio.

$$\text{concentration criterion} = \frac{D_h - D_f}{D_l - D_f} \qquad \textbf{EQ 4.15}$$

where

D_h = density of the heavy material
D_f = density of the fluid
D_l = density of the light material

In general, a concentration criterion <1.25 indicates the separation is not economically feasible with current gravity concentration methods. Conversely, a concentration criterion >2.5 is considered to be relatively easy. However, as particle size decreases, the minimum concentration criterion value for an efficient gravity separation increases.

When analyzing Equation 4.15, it is apparent that there are two possible methods for increasing the concentration criterion:

1. Increasing the apparent density difference between the dense and light minerals; and
2. Increasing the density of the working fluid.

Increasing the apparent density difference between the light and dense minerals could potentially be accomplished by adding a flotation aspect to a gravity separation process (Figure 4.20). One potential method for achieving this could be a flotation/jigging process. In the example, air bubbles would selectively attach to dolomite pebbles and make them appear lighter. This would increase the apparent density difference between the light and dense particles, and thus increase the efficiency of the separation. However, this process would require the use of a highly selective collector for dolomite flotation, which has been proven problematic for the dolomite/apatite system due to very similar surface chemistries.

Increasing the density of the jigging fluid is another potential method to increase the concentration criterion. Possible dense liquids that could be used include dissolved salt solutions and dense particle suspensions (magnetite suspension). Increasing the density of the fluid medium would result in

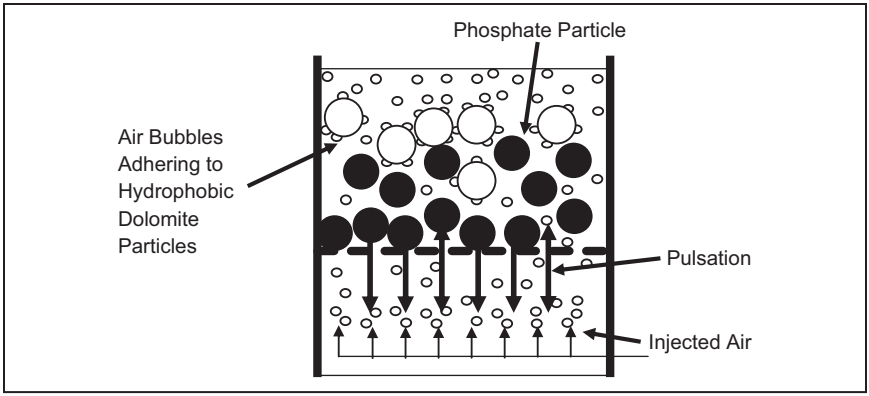


Figure 4.20 Potential flotation/jigging process

an increase in the concentration criterion. However, increasing the viscosity of the jigging fluid could hinder particle movement and reduce separation efficiency in the jigging process (Schachter et al. 1964; Gupta and Yan 2006). It would be desirable that the density of jigging fluid be increased without significantly increasing the fluid viscosity.

4.4.4.6 Jigging for Beneficiation of High-MgO Sedimentary Phosphate Ores

Kawatra et al. (2012) investigated jigging for the removal of dolomite from high-MgO Florida land-pebble phosphate ore. This approach was suitable because of the high degree of liberation between phosphate and dolomite pebbles in these ores. Given that a significant amount of the MgO is present as discrete dolomite pebbles, crushing and grinding is not needed to liberate the dolomite.

The advantages of jigs for phosphate processing are listed here:

- They are relatively simple, low-cost machines that provide a high processing capacity.
- There is no need for chemical reagents such as those used for froth flotation, or expensive media-recovery circuits such as those needed for heavy-media processing.
- They do not require grinding of the feed if the material to be processed is liberated. Jigs can produce effective separations up to particle sizes of

several inches, as opposed to froth flotation which requires particles to be ground before it becomes effective.
- Jigs separate particles based on relative density rather than absolute density. As long as one mineral in a mixture is denser than the other, a jig can separate them regardless of the actual numerical value of those densities.

For these experiments, a 4-inch- (10-cm-) diameter laboratory-scale jig was designed and built to examine the feasibility of jigging as a process for separating dolomite from phosphate pebble. This jig had a variable pulsation frequency, with a rate of 200 pulses per minute found to be optimum for separating phosphate pebbles. The jig was operated as a through-the-screen jigging process, with the higher-density phosphate particles passing through a bed of spherical balls (ragging) to be collected in the bottom of the jig. The lower-density dolomite-rich particles worked their way to the top of the jig, where they were rejected in the overflow launder.

Samples of high-MgO phosphate were studied from two Florida mines, with MgO levels ranging from 1.37%–2.35% MgO for two different samples from mine A, and 2.75%–3.22% MgO for mine B. In the case of sample 1 from mine A, the natural ore was sized for a jig feed that was −5/+20 mesh (−4.00/+0.85 mm), which is coarser than the sizes that can be effectively processed by froth flotation. For sample 2 from mine A, the high-MgO phosphate ore contained a significant amount of very large (+6.73 mm) pebbles, and was therefore crushed and sized to the −6/+20 mesh size fraction used in jigging experiments. For the plant B sample, it was requested that the shipped sample be sized to −6/+20 mesh. While an industrial jig would be able to process particles coarser than 6 mesh (3.4 mm), the large particle size relative to the mass of sample used per test with the lab-scale jig made preparation of accurate replicate samples impractical. In a production-scale jig, it would be feasible to process particles as large as several centimeters, eliminating the need for any high-cost crushing and grinding facilities.

For sample 1 from plant A, a −5/+20 mesh sized phosphate feed averaging 1.55% MgO was tested at high (~157 g/min) and low (~53 g/min) feed rates. Results in Table 4.1 show that the best results gave a phosphate concentrate containing 0.89% MgO at a BPL recovery of 32.0%. A grade recovery curve for these tests can be found in Figure 4.21. Testing of hand-picked phosphate pebbles indicated that the phosphate particles from mine A

contained approximately 0.5% MgO, and so the levels reached by jigging are approaching the minimum theoretical achievable level for this material without any crushing or grinding.

For phosphate sample 2 from mine A, it was possible to achieve MgO levels less than 1% while still reaching 55% BPL recovery (Table 4.2). A grade recovery curve for these tests can be found in Figure 4.22.

Table 4.1 BPL recovery and %MgO in concentrate achieved by jigging high-MgO phosphate sample 1 from mine A

Test No.	Concentrate %MgO	%BPL Recovery
1	1.18	62.1
2	1.18	65.6
3	1.16	68.7
4	0.84	23.6
5	0.82	25.5
6	0.89	32.0

Note: The feed was sized to −5/+20 mesh (−4.00/+0.85 mm) and averaged 1.55% MgO.

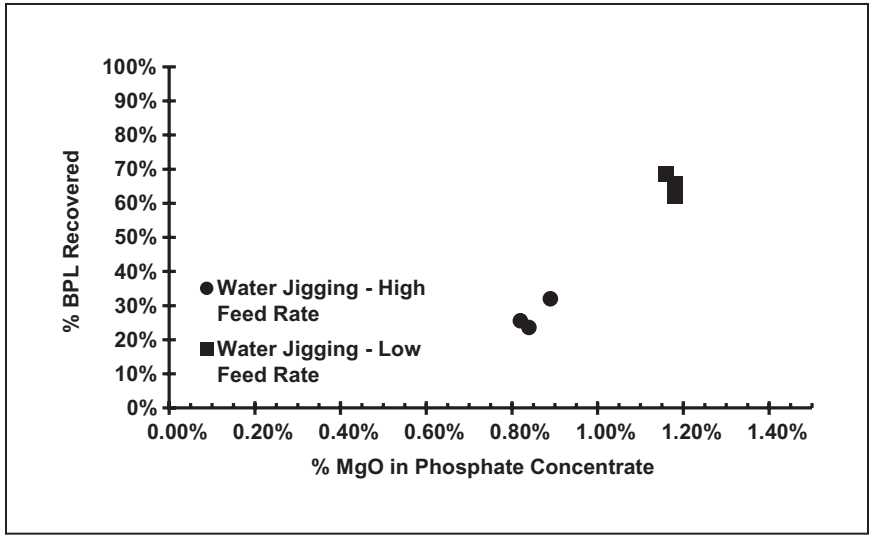


Figure 4.21 Grade versus recovery curve for experiments using higher-MgO phosphate feed sample 1 from mine A that was sized to –5/+20 mesh (–3.35/+0.85 mm)

The phosphate ore from mine B had higher dolomite levels than those of mine A, and a correspondingly higher quantity of MgO in the phosphate pebbles. As a result, it was more difficult to reach MgO levels below 1%. Results for trials using a –6/+20 mesh phosphate sample from mine B are shown in Table 4.3. Trials were run at high (~303 g/min) and low (~170 g/min) feed rates.

Table 4.2 Feed MgO, BPL recovery, and %MgO in concentrate achieved by jigging high-MgO phosphate sample 2 from mine A

Test No.	Feed %MgO	Concentrate %MgO	%BPL Recovery
1	2.35	1.29	55.0
2	1.71	1.10	76.1
3	1.94	1.19	74.5
4	2.06	0.84	55.4
5	2.08	1.05	63.1
6	2.13	0.76	53.9

Note: The feed was crushed and sized to –6/+20 mesh (–3.35/+0.85 mm) and averaged 2.05% MgO.

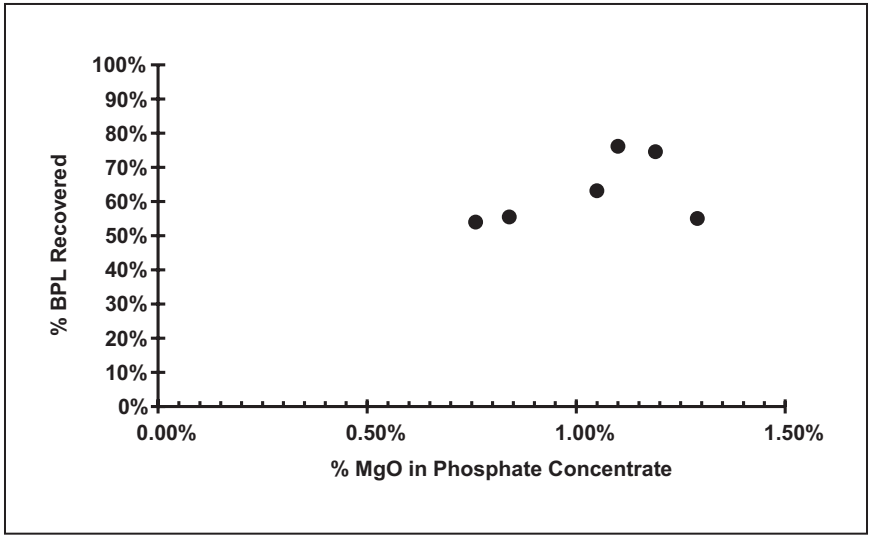


Figure 4.22 Grade versus recovery curve for experiments using a crushed higher-MgO phosphate sample 2 from mine A that was sized to –6/+20 mesh (–3.35/+0.85 mm)

Table 4.3 Feed %MgO in concentrate and BPL recovery achieved by jigging phosphate from mine B

Test No.	Concentrate %MgO	%BPL Recovery
1	1.54	85.1
2	1.51	87.6
3	1.38	74.7
4	1.67	85.7

Note: The feed was sized to −6/+20 mesh (−3.35/+0.85 mm) and averaged 3.07% MgO.

Table 4.4 Estimated total costs (2011 dollars) for a jig plant, heavy-media plant, and froth flotation plant on a basis of 100 MT/h

Process	Estimated Total Costs	Notes
Jigging	$50,000	Includes motors, ragging, and pumps
Heavy media	$1,031,000	Includes motors, pumps, heavy media, and heavy-media recovery systems (washing screens, magnetic separators, sumps, controllers)
Froth flotation	$322,000	Includes pumps, launders, motors

Jigging is effective for removing the discrete dolomite-rich pebbles at a minimal cost. Depending on the nature of the phosphate feed ore, it could be possible to reduce MgO to less than 1%. For other deposits, jigging may provide a low-cost method for quickly removing significant amounts of dolomite from the phosphate before grinding occurs. It may therefore be a useful pretreatment step before more expensive processes (i.e., flotation, calcination, acid leaching, etc.) are applied for dolomite removal.

One of main advantages of the jigging process is the low capital cost. Table 4.4 shows capital costs comparisons of jigs, HMS, and froth flotation cells. Capital costs were calculated using standard cost estimation tables, with a 100 MT/h plant for the basis. Estimates show that jigs have a significantly lower capital cost when compared to heavy media and froth flotation. In addition, froth flotation would also need significant capital costs for crushing and grinding to achieve a particle size fine enough for froth flotation to be effective.

4.4.5 Summary of Physical Separation Methods for Removal of MgO from Phosphate Ores

Physical separation methods have several advantages when it comes to the removal of MgO from phosphate ores. Desliming, which is currently part of conventional phosphate processes, works well for the removal of fine dolomite (−150 mesh) from high-MgO sedimentary phosphate ores. In many phosphate reserves, the coarse pebble fraction (+3 mesh) contains very high amounts of dolomite, which can be removed without significant phosphate loss by choosing an appropriate top size screen.

HMS is a possible solution for removal of dolomite from intermediate-sized (3 × 16 mesh) phosphate pebbles. However, separation efficiency can suffer severely from the narrow density differences of the two minerals and from the presence of interlocked dolomite and phosphate pebbles. For this reason, HMS has been considered only as a preconcentration method, and additional processing is needed to achieve a salable product. Jigging, a less expensive method that is capable of achieving similar results as HMS, suffers from the same efficiency issues listed previously.

Overall, physical separation methods such as heavy media and jigging have the advantage that they can be used to process coarse pebbles. This could potentially result in increased savings by reducing crushing and grinding costs. However, this depends greatly on the degree of liberation of the pebble-sized phosphate ore. One of the main disadvantages of physical separation processes is that they cannot be used to remove the micron-sized dolomite inclusions in the phosphate pebbles or Mg substituted into the lattice structure of the francolite.

4.5 FLOTATION

Froth flotation is a major part of phosphate beneficiation around the world. The efficiency of the flotation process for phosphate beneficiation depends greatly on the surface properties of the minerals being separated. In the case of large phosphate deposits of the Bone Valley in central Florida, where silica is the main impurity, the Crago double float has been successfully utilized as the main method of beneficiation since it was patented in 1942 (Sis and Chander 2003; Guan 2009a). The Crago double float process is thoroughly explained in Section 3.3. In the case of high-MgO sedimentary phosphate ores that contain significant amounts of carbonates (calcite and dolomite),

flotation becomes significantly more difficult because of very similar surface properties between phosphates and carbonates (Somasundaran and Zhang 1999). In the Crago double float process, the anionic fatty acid collector chemisorbs to dolomite surfaces in the same manner as francolite (phosphate), and therefore reports to the phosphate concentrate. This means that some other reagent schemes (i.e., collector, pH, depressant, etc.) must be used to selectively separate dolomite from francolite by froth flotation.

Several other problems associated with high-MgO sedimentary phosphate ores significantly hinder the effectiveness of froth flotation for the separation of carbonates from phosphates. The most influential are listed as follows:

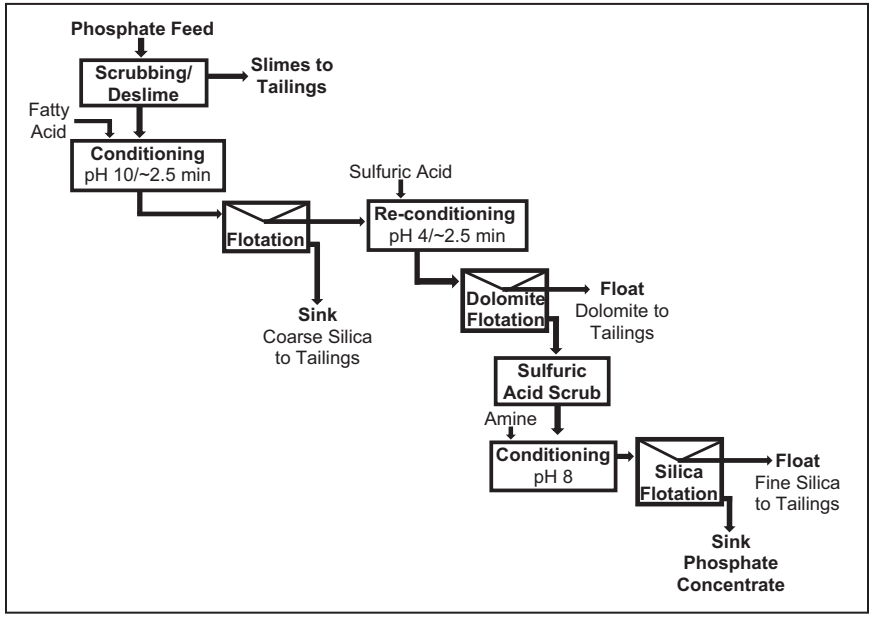
- *High degree of substitution in the crystal lattice of the phosphate mineral*. As was discussed in Chapter 2, sedimentary phosphate ores can contain different forms of apatite that vary based on the degree of ionic substitution into the lattice structure. One of the most abundant sedimentary phosphate ores, francolite, is a carbonate-rich apatite that contains significant amounts of CO_3^{-2} and F^- substituted for PO_4^{-3}, along with the cationic substitutions of Na^+ and Mg^{+2} for Ca^{+2} (McClellan and Van Kauwenbergh 1991; Baudet and Save 1999; Prasad et al. 2000).
- *High slimes production*. Because of the soft nature of sedimentary phosphate ore, specifically the softer dolomite-rich pebbles, large amounts of slimes are produced during the conditioning stage. This can significantly increase reagent consumption while reducing the selectivity of the flotation process (Wiegel 1999).
- *Porous nature of sedimentary phosphates*. Sedimentary phosphate particles are typically formed of very small crystallites, which results in micron-sized pores. These "micropores" can significantly increase total surface area of the particles and increase reagent consumption (Baudet and Save 1999).
- *Very fine liberation size*. Phosphate particles can contain fine (micron to submicron sized) dolomite inclusions. Grinding to such a size as to liberate the fine dolomite inclusions would significantly reduce selectivity of flotation processes (Moudgil and Ince 1991; Baudet and Save 1999).

Research in the beneficiation of phosphate ores is vast and covers a wide range of processes. This section includes summaries of significant research

throughout literature pertaining to the removal of dolomite from phosphate ores by means of froth flotation.

4.5.1 University of Florida Two-Stage Conditioning Process

Moudgil and Chanchani (1985b) proposed a two-stage conditioning process for the removal of dolomite from carbonaceous sedimentary phosphate ores. This process used a fatty acid collector (sodium oleate) and two stages of conditioning to selectively float dolomite from apatite. Figure 4.23 shows a simplified process flow diagram for bench-scale testing of this process (Moudgil et al. 1990). A deslimed phosphate feed is first conditioned (Stage 1) at a pH of 10 with a fatty acid collector. After conditioning, the dolomite, phosphate, and fine silica are floated from the coarse silica. The ore is then reconditioned (Stage 2) at a pH of 4, which is followed by selective flotation of dolomite from the phosphate and fine silica. At basic pH values (~10), the anionic fatty acid collector chemisorbs to dolomite and apatite in a similar manner



Source: Data from Moudgil and Chanchani 1985, Moudgil and Vasudevan 1988, and Moudgil et al. 1990.

Figure 4.23 Simplified process flow diagram for University of Florida two-stage conditioning process

(i.e., the carboxylate anion ion chemisorbs to calcium sites on both dolomite and apatite; see Section 3.3.1). In addition, it was shown that a greater amount of oleate surfactant had absorbed to the dolomite than on the apatite at basic conditions. It was suggested that when the pH was shifted to acidic conditions (pH ~4), the higher adsorption of surfactant on dolomite surface remained, while the apatite experienced significantly lower flotation recovery. Furthermore, the authors indicated that some of the absorbed oleate surfactant transformed to the oleic acid species, which contributed to selective flotation of dolomite from apatite (Moudgil and Chanchani 1985a).

In the final stage of this process, the fine silica is removed from the phosphate concentrate with an amine flotation process. In lab-scale studies, Moudgil and Chanchani (1985b) demonstrated some selectivity using the two-stage conditioning process with an apatite/dolomite (95%/5%) mixed feed. However, the authors indicated several factors that could hinder the efficiency of the two-stage conditioning processes (Moudgil and Chanchani 1985b; Moudgil and Ince 1991):

1. Dolomite slimes
2. Dissolved Ca^{+2} and Mg^{+2} ions; and
3. Oleate depletion at alkaline conditions.

In attempts to increase the selectivity of the fatty acid collectors for this separation, many authors have investigated the use of phosphate depressants.

El-Shall et al. (1996) tested the two-stage conditioning process on a 35 × 150 mesh feed ore containing approximately 2.03% MgO. Caustic soda and sulfuric acid were used as pH adjusters, while fatty acid/fuel oil (FA/FO) was used as the phosphate collector. Results showed a phosphate concentrate containing 0.97% MgO with a 43.4% P_2O_5 recovery (from flotation feed). The authors noted that for the two-stage conditioning process, both the dolomite and silica flotation stages were very difficult to perform (El-Shall et al. 1996).

4.5.2 Tennessee Valley Authority Diphosphonic Acid Depressant Process

Hsieh and Lehr (1985) proposed a Tennessee Valley Authority (TVA) process that used a fatty acid carbonate collector and a diphosphonic acid for a phosphate depressant to selectively float dolomite from apatite. In this process, the carbonate is made selectively hydrophobic and floated from the

phosphate particles. The specific reagents used by the authors included a hydroxyethylidene diphosphonic acid ($C_2P_2O_7H_8$) (Figure 4.24) phosphate depressant and a fatty acid carbonate collector consisting of either isostearic acid or distilled tall oil. It was proposed that the phosphonic acid groups of the hydroxyethylidene diphosphonic acid selectively adsorb to the apatite surface, depressing the apatite by making it more hydrophilic. However, there may also be a tendency for the hydroxyethylidene diphosphonic acid to also adsorb to "calcite-type" carbonate mineral surfaces. This would hinder flotation of the carbonate minerals and make the process less effective (Hsieh and Lehr 1984).

For laboratory flotation trials, a 500-g Idaho dolomitic phosphate sample was first deslimed to remove slimes. The sample was then conditioned with the diphosphonic acid at 65% solids for approximately 1 minute. Next, the sample was conditioned with the fatty acid/pine oil collector for 2.5 minutes. The conditioned slurry was then transferred to a Denver float cell and diluted to approximately 18% solids with tap water. The tap water contained 32 ppm calcium, 6 ppm magnesium, and <1 ppm aluminum or iron. Dolomite was then floated from the phosphate and silica. After dolomite flotation was completed, dodecylamine hydrochloride was used to float silica from the remaining phosphate concentrate (Hsieh and Lehr 1985). There are no dedicated pH adjusting reagents used in this process, and the pH of the process typically ranged anywhere from 6.4 to 7.8.

Following the simplified process flow diagram in Figure 4.25, Hsieh and Lehr (1985) were able to achieve phosphate concentrates ranging from 0.7% to 1.3% MgO at P_2O_5 recoveries ranging from 70.7% to 78.0% from a 150 × 635 mesh feed that contained 3.0%–3.3% MgO. Reagent addition rates ranged from 0.5 to 1.5 kg/t fatty acid collector, 0.2 to 0.3 kg/t

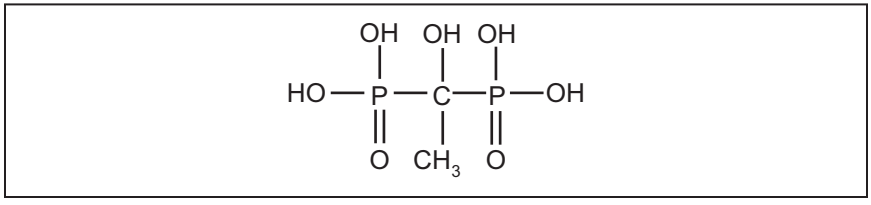
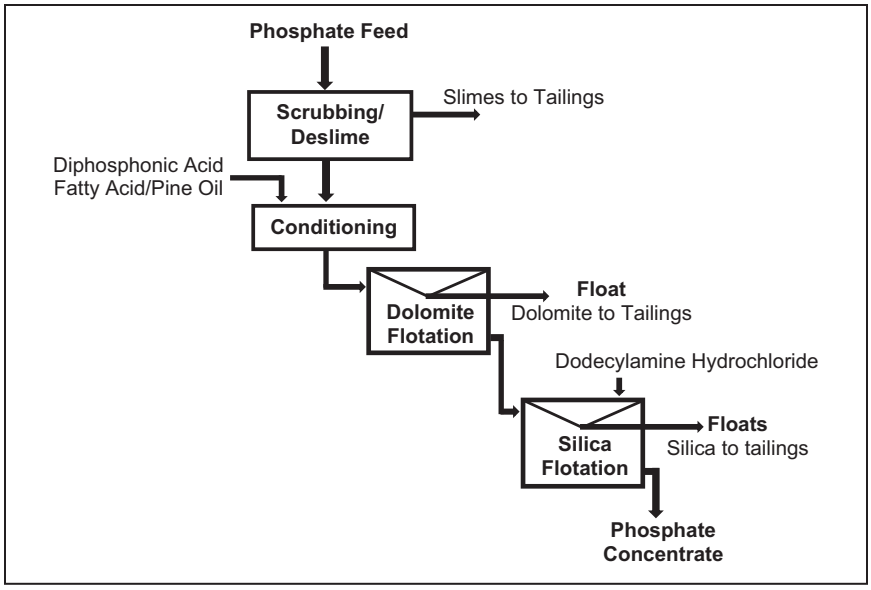


Figure 4.24 Chemical formula for hydroxyethylidene diphosphonic acid ($C_2P_2O_7H_8$)



Source: Adapted from Hsieh and Lehr 1985.

Figure 4.25 Simplified process flow diagram for TVA diphosphonic acid depressant process

hydroxyethylidene diphosphonic acid (phosphate depressant), and 0.15 to 0.2 kg/t dodecylamine hydrochloride (Hsieh and Lehr 1985).

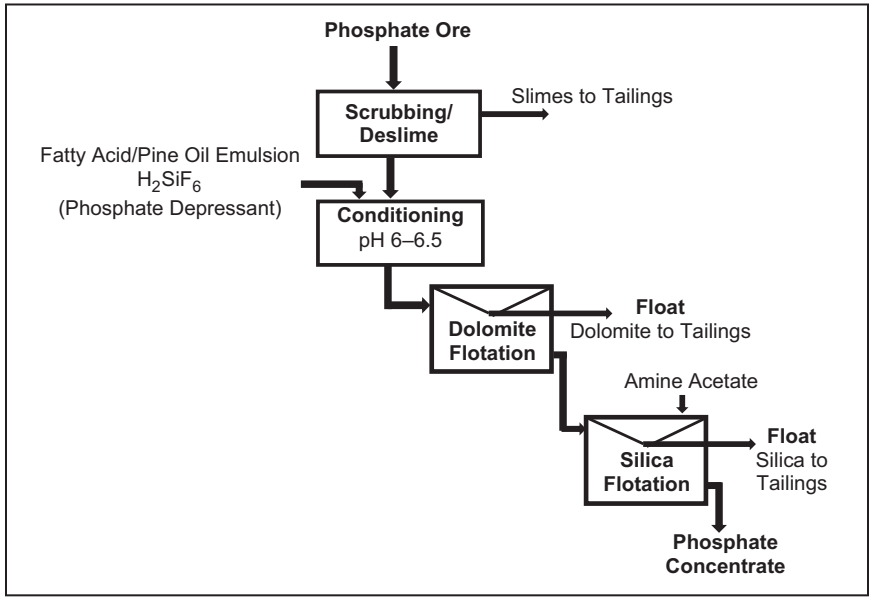
El-Shall et al. (1996) attempted to verify the TVA process using a 48 × 325 mesh phosphate sample containing approximately 2.03% MgO. Using very similar parameters, the authors achieved phosphate concentrates containing 1.40%–1.51% MgO at BPL recoveries of 96.6%–97.5%. Variations in results were attributed to differences in water hardness and feed properties (El-Shall et al. 1996).

4.5.3 U.S. Bureau of Mines Anionic Flotation Process

The U.S. Bureau of Mines (USBM) process uses a fatty acid/pine oil emulsion as a dolomite collector and hydrofluosilicic acid (H_2SiF_6) as a phosphate depressant. In this process, dolomite is first selectively floated from phosphate and silica using an anionic fatty acid collector and phosphate depressant. Amine flotation is then used to float the silica from the phosphate concentrate.

Figure 4.26 shows a simplified process flow diagram for the USBM process. First, the crushed and sized phosphate feed is scrubbed and deslimed to remove fines. Next, the phosphate ore is conditioned at pH 6–6.5 with a fatty acid/pine oil collector and H_2SiF_6 phosphate depressant. Carbonates are then selectively floated and sent to the tailings. Finally, an amine acetate collector is used to float the silica from the remaining phosphate concentrate. Rule et al. (1978) tested the USBM process on a western U.S. phosphate shale ore from Idaho. With a feed containing 24.8% P_2O_5 and 1.08% MgO, a phosphate concentrate composed of 30% P_2O_5 and 0.9% MgO was achieved at a 71% P_2O_5 recovery (Rule et al. 1978).

Rule et al. (1982) tested the USBM anionic flotation process with a scaled-up 60 lb/hour continuous flotation circuit. Reagents included hydrofluosilicic acid (1.0 lb/ton), fatty acid emulsion (1.3 lb/ton), and amine acetate (1.0 lb/ton). A phosphate concentrate containing 28.9%P_2O_5, 0.91%MgO, and 14.0%SiO_2 from a phosphate feed composed of 22.0% P_2O_5, 1.01% MgO, and 26.9% SiO_2 at a P_2O_5 recovery of 70.0% (Rule et al. 1982). The



Source: Adapted from Rule et al. 1978 and Prasad et al. 2000.

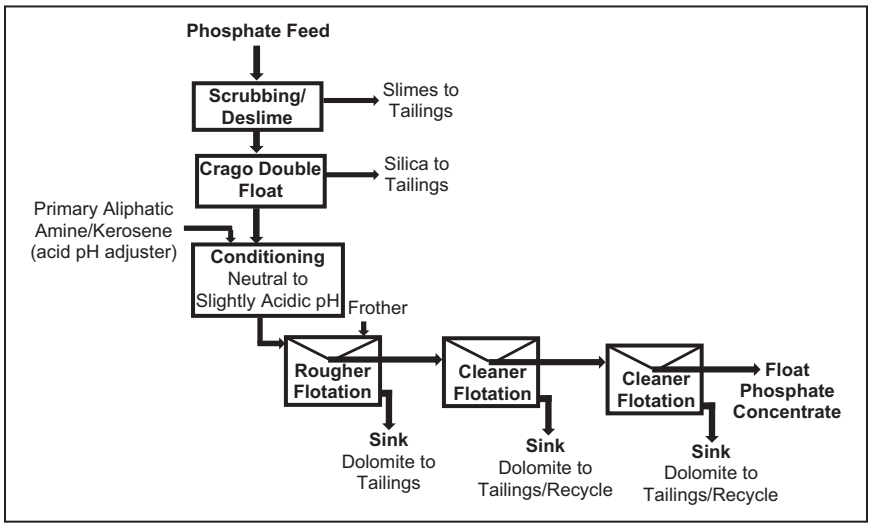
Figure 4.26 Simplified process flow diagram for USBM process for the anionic flotation of dolomite from phosphate ores

1.01% MgO in the feed is essentially at the 1% MgO minimum demanded for the wet process production of phosphoric acid. In order for this process to be considered feasible for current high-MgO sedimentary phosphate ores, it would need to be demonstrated on feeds containing considerably higher concentrations of dolomite (MgO).

4.5.4 IMC Cationic Flotation Process

Baumann and Snow (1980) described what is referred to as the International Minerals Chemical Corporation (IMC) cationic flotation process. The IMC cationic process first removes silica using the traditional Crago double float process (see Section 3.3 for details of the Crago process). Then a cationic amine collector is used to float phosphate from carbonates.

Figure 4.27 shows a simplified process flow diagram for the IMC cationic flotation process. In this process, a deslimed phosphate feed first goes through the conventional Crago double float process to remove silica. Next, the slurry is conditioned for less than 1 minute with a primary aliphatic amine/kerosene cationic collector at approximately 60%–70% solids. Conditioning is conducted at a neutral to slightly acidic pH. After conditioning, the slurry



Source: Adapted from Snow 1979, Baumann and Snow 1980, and El-Shall et al. 1996.

Figure 4.27 Simplified process flow diagram for IMC cationic flotation process

is put through a rougher–cleaner–recleaner flotation circuit to produce a final phosphate concentrate (Baumann and Snow 1980).

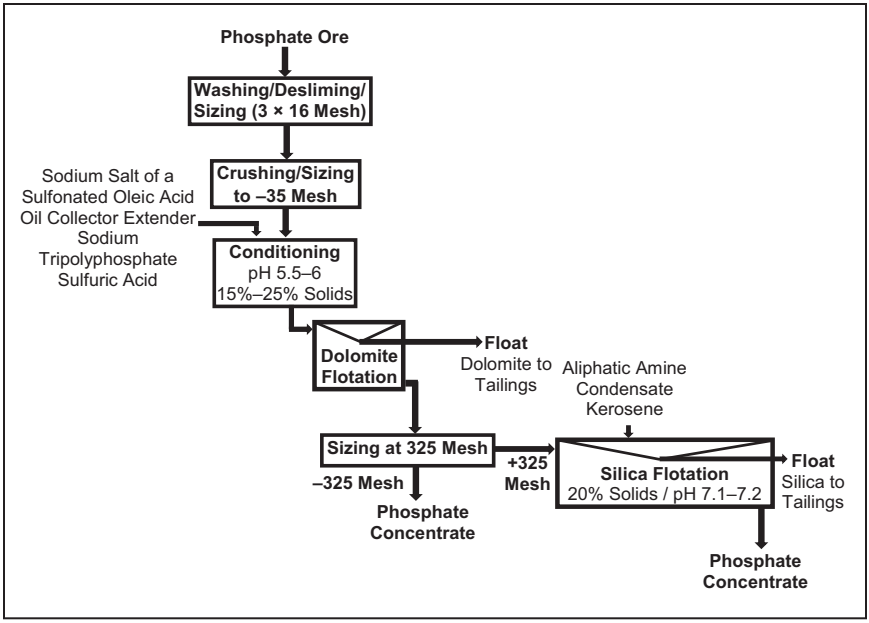
Snow (1979) also presented a cationic flotation process in which a primary tallow amine acetate salt was used as the phosphate collector. In this process, the phosphate ore is conditioned with a primary tallow amine acetate salt and fuel oil mixture at a pH of 5–6.5. Conditioning was completed at 55%–75% solids. Trials were conducted using hydrofluoric acid as a pH adjuster (1 lb/ton), with Armac T (1 lb/ton) as the cationic collector and kerosene (3 lb/ton). A phosphate concentrate containing 0.98% MgO was achieved from a feed containing 1.54% MgO at a BPL recovery of 95.2% (Snow 1979).

El-Shall et al. (1996) attempted to replicate the IMC cationic process using a tallow amine (Armac T)/diesel fuel collector with an acetic acid pH adjuster to condition a 28 × 150 mesh phosphate feed flotation feed. The feed was conditioned for approximately 20–30 seconds. The conditioned ore was then sent to rougher flotation where a frother and an additional surfactant (Tergitol NP-10) were added. Apatite was floated from the dolomite in a rougher–cleaner–recleaner flotation circuit. The resulting phosphate concentrate contained 0.74%–0.84% MgO at phosphate recoveries of 80%–90% for the dolomite flotation circuit. The head sample contained roughly 2.03% MgO. However, the actual MgO content when entering the dolomite separation circuit was not mentioned. The authors attributed the good agreement with previously reported results to the use of similarly sized feed ores and similar water chemistry (El-Shall et al. 1996).

4.5.5 IMC Anionic Flotation Process

Snow (1982) presented a dolomite flotation process that used a proprietary anionic dolomite collector, along with a phosphate depressant, to float dolomite from a high-MgO phosphate feed. Cationic amine silica flotation was then used to float silica from the phosphate concentrate.

Figure 4.28 shows a simplified process flow diagram for the IMC anionic flotation process. In this process, a −35 mesh phosphate feed is conditioned at a pH of 5.5–6, with sulfuric acid used as a pH regulator. Sodium tripolyphosphate is used as a phosphate depressant. The collector is a sodium salt of a sulfonated oleic acid, which has the general formula shown in Figure 4.29, where R=$CH_3(CH_2)_7$ and n=5-8. A collector extender consisting of fuel oil, kerosene, diesel oil, and other oils are recommended. The dolomite is then



Source: Adapted from Snow 1982.

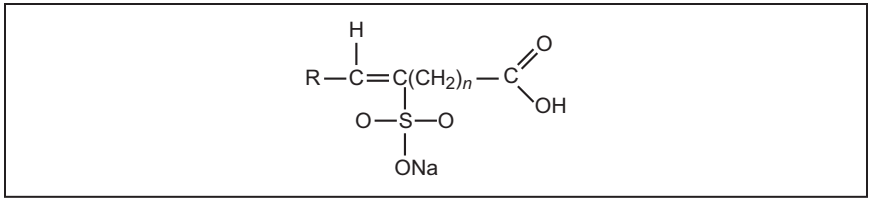
Figure 4.28 Simplified process flow diagram for IMC anionic flotation process

floated from the phosphate and silica. Next, phosphate and silica (sinks from the dolomite flotation stage) are sized at 325 mesh. The fine –325 mesh material is generally of high enough quality to be a phosphate concentrate. The +325 mesh size fraction is sent to silica flotation, where silica is floated from the phosphate concentrate using an aliphatic amine condensate collector and kerosene as an extender. Silica flotation is carried out at approximately 20% solids at a pH around 7.1–7.2 (Snow 1982).

In a trial using a –35 mesh central Florida phosphate feed containing 1.44% MgO, a phosphate concentrate containing 0.68% MgO was achieved at a BPL recovery of 83.05% (Snow 1982).

4.5.6 Summary of Flotation for Removal of Dolomite from Phosphate Ores

Developing an efficient flotation process for the removal of dolomite from sedimentary phosphate ores has proven to be difficult due to similar mineralogical properties between dolomite and francolite. More specifically, dolomite ($CaMg(CO_3)_2$) and apatite ($Ca_{10}(PO_4)_6F_2$) have similar cations (Ca^{+2}), which results in similar surface properties. To complicate things further, a



Source: Adapted from Snow 1982.

Figure 4.29 General structure of anionic collector (sodium salt of sulfonated oleic acid) used in IMC anionic flotation process

carbonate-rich apatite (francolite, $Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$), which is typically found in sedimentary phosphate ores, results in even more similar surface properties. Other unfavorable properties of sedimentary phosphate ores include

1. High slimes production,
2. Porous nature of sedimentary phosphate ores, and
3. Very fine liberation size (micron to submicron dolomite inclusions).

In particular, high slimes production leads to an increase in collector consumption and a decrease in collector selectivity. As for the very fine liberation size, removal of submicron- and micron-sized dolomite inclusions with flotation is impractical because grinding to such a fine size would drastically decrease the selectivity of the process. For these reasons, the effectiveness of a flotation process for removal of dolomite from phosphate ore depends significantly on the previously described mineral properties. Since these properties can vary significantly from reserve to reserve, development of a universal flotation scheme for this separation has not yet been accomplished.

4.6 SELECTIVE FLOCCULATION

Selective flocculation is a method used to separate finely ground minerals in a liquid suspension by addition of a flocculant that causes fine particles of one mineral to flocculate together into larger "flocs." The other nonflocculated minerals stay dispersed as fine particles suspended in the solution. The large flocs are then separated from the suspended fines by gravitational settling in a thickener, screening, or floc flotation. A simplified diagram of selective flocculation using a polymeric flocculant is shown in Figure 4.30.

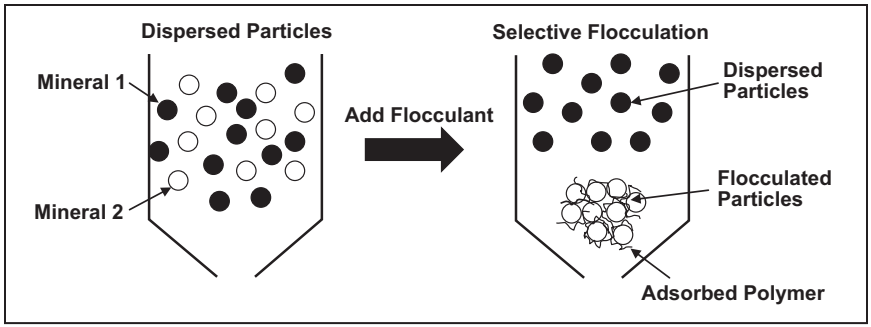


Figure 4.30 Selective flocculation using a polymeric flocculant

Separation efficiency during selective flocculation depends greatly on the selective adsorption of a flocculant onto the surface of one mineral. Adsorption of a flocculant onto an active site typically involves one of the following mechanisms (Mathur et al. 2000):

1. Hydrogen bonding,
2. Electrostatic attraction (ionic bond),
3. Hydrophobic interactions,
4. Chemical bonding, or
5. Van der Walls forces.

Selective adsorption based on electrostatic attraction is common when separating minerals with very different surface charges. In some instances, adjustments in pH can be exploited to give larger differences in zeta potential. Hydrogen bonding is often the most prevalent mechanism when using polymeric flocculants for phosphates because of the various functional groups typically present in polymers (Mathur and Moudgil 1998). Hydrogen bonding is particularly important in systems where the minerals have a very similar surface charge, such as the dolomite/apatite system. Overall, adsorption of flocculants onto particle surfaces will decrease the zeta potential of a mineral and cause the dispersed fine particles to flocculate together.

In addition to having a highly selective flocculant, dispersion of the inert particles is a critical part of an efficient selective flocculation system. As shown in Figure 4.30, it is desired that the initial solution be well dispersed and that the nonflocculating minerals (i.e., mineral 1) stay well dispersed after addition of the flocculant. Dispersion is often achieved by electrostatic

stabilization, where the surface charge of the dispersed mineral is either highly negative or highly positive. The high surface charge makes the fine particles repel one another and stay dispersed in the fluid medium. Reagents such as sodium silicate and sodium hexametaphosphate are often used as dispersants since they give a highly negative surface charge to the mineral they adsorb on.

4.6.1 Flocculants for the Apatite/Dolomite/Silica System

In the case of removing dolomite from sedimentary phosphate ores, the potential benefit to selective flocculation is its ability to separate very finely ground minerals. As discussed in Chapter 2, some MgO exists as fine micron-sized dolomite ($CaMg(CO_3)_2$) inclusions inside of phosphate pebbles. It may be possible to process fully liberated phosphate ore with selective flocculation, whereas fully liberated phosphate ore would be too fine for conventional separation methods such as froth flotation and gravity separation. The majority of available literature is focused on using polymeric flocculants such as polyacrylic acid (PAA) and polyethylene oxide (PEO) to separate mixtures of apatite ($Ca_{10}(PO_4)_6(F)_2$), silica (SiO_2), and dolomite ($CaMg(CO_3)_2$) (Pradip et al. 1991; Pradip and Moudgil 1991; Moudgil and Mathur 1994; Mathur and Moudgil 1995; Moudgil et al. 1995; Mathur et al. 1996; Mathur and Moudgil 1998).

Moudgil and Mathur (1994) investigated the use of PAA and PEO for selective flocculation of apatite/silica and apatite/dolomite/silica systems. Molecular structures for PAA and PEO are shown in Figure 4.31. Single mineral flocculation tests were completed to determine how well PAA and PEO of varying molecular weights flocculate apatite and dolomite. For apatite, they found that PEO (5 million MW) showed no flocculation at a pH of 9.5. When using a PAA (4 million MW), greater than 90% apatite flocculation was achieved at a dosage of 1 kg/t. For dolomite, strong flocculation occurred with PEO at a dosage of 1 kg/t. A PAA test gave 90% flocculation of dolomite. For silica, PEO and PAA both resulted in no flocculation. Based on these results, one could propose the following process for selective flocculation of a dolomite/apatite/silica system:

1. Remove dolomite by flocculating with PEO; and
2. Separate the remaining apatite from silica by flocculating apatite with a PAA flocculant.

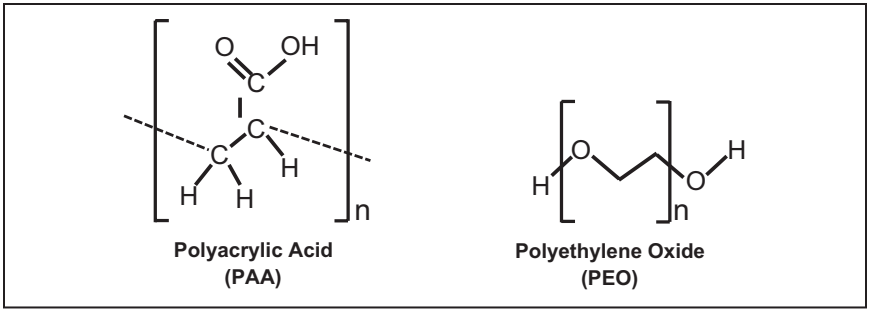


Figure 4.31 Molecular structures of PAA and PEO

However, single minerals systems often behave much different than mixed minerals systems. Furthermore, things become even more complicated when dealing with natural mineral systems (Moudgil and Mathur 1994; Mathur et al. 2000). Selectivity for an apatite/dolomite system was shown to be significantly lower because of heteroflocculation. Although apatite did not flocculate alone when using PEO, selectivity greatly decreased in a mixed apatite/dolomite system.

4.6.2 Factors Affecting Selectivity of Flocculation Processes

Many complications can hinder selectivity in multicomponent selective flocculation systems. Mathur et al. (2000) determined the major barriers to be

- Heterocoagulation,
- Charge patch neutralization,
- Dissolved ion interference,
- Slimes coating,
- Physical entrapment,
- Entrainment,
- Heteroflocculation, and
- Smearing during grinding.

Heteroflocculation, slimes coating, and smearing have been shown to be the most detrimental for the apatite/dolomite/silica system (Mathur et al. 2000).

Heteroflocculation of apatite and dolomite in a mixed apatite/dolomite system is a result of loss in selectivity of the nonionic polymer flocculant PEO. In some instances, the flocculant will adsorb to some active sites on the nonflocculating particles, which in a single mineral test would not be

enough to achieve flocculation. However, in mixed mineral systems, even minor amounts of flocculant adsorbed onto the inert particles may be enough for "bridging" with the active (flocculating) mineral to occur (Mathur et al. 2000). Moudgil and Mathur (1994) introduced the concept of site-blocking agents (SBAs) as a method of increasing flocculant selectivity. An ideal SBA would selectively block active sites on the nonflocculating particles (apatite) rendering them inert and minimizing heteroflocculation. Lower molecular weight PEO was proposed as an SBA for the following reasons: (1) Since the mechanism of adsorption is the same as the high molecular weight PEO, adsorption onto the active sites of the nonflocculation mineral would occur; and (2) the molecular weight should be low enough that it does not cause flocculation. For an apatite/dolomite (80:20) system, using a 5 million molecular weight PEO flocculant (1 kg/t) with a 1 million molecular weight PEO SBA (2 kg/t) at a pH of 10, a phosphate concentrate grade of 95.1% at 90.6% recovery was achieved (Moudgil and Mathur 1994).

Smearing occurs when a mixture of softer and harder minerals are going through dry crushing, such as an apatite/silica system. The softer particle (apatite) can "smear" the harder particle (silica), resulting in an apatite coating that makes the silica particle behave as if it was apatite (Moudgil and Mathur 1994). This effect can be reduced by the use of wet grinding and selective dispersants.

Slimes can have a significant effect on the efficiency of the selective flocculation process. Slimes of one mineral can coat the other, decreasing selectivity. Surface coatings can also come from minerals other than the major constituents of the ore. Moudgil et al. (1995) performed a detailed study on dolomites from three sources to determine why the Florida dolomite sample demonstrated flocculation with PEO while the others did not. With the use of X-ray diffraction, Fourier transform infrared radiation, particle size analysis, Brunauer-Emmett-Teller, and other analytical methods, they determined that a very small amount of palygorskite clay coating on the Florida dolomite sample was responsible for flocculation with PEO (Moudgil et al. 1995; Mathur and Moudgil 1998). The importance of a thorough sample characterization is crucial in determining the mechanism of adsorption involved in specific selective flocculation systems.

Another potential complication in a selective flocculation system is the interference of dissolved ions. For the apatite/dolomite system, this could be

particularly problematic because of the semi-soluble nature of dolomite and apatite. Some dissolved ions can interact with the surface of the minerals and significantly affect surface charge. This can potentially lead to loss in selectivity. Usually pH modifications and dispersants can be used to help control the amount of ions such as Mg^{+2} and Ca^{+2} present in the solution.

Scaling up a bench-scale process based on mixed components systems to a plant-scale operation using natural ores systems can be discouraging because of the many complexities involved with natural ores. The dolomite/apatite system is particularly problematic because of very similar surface chemistries of the minerals involved, the tendency for softer dolomite to produce slimes, presence of clays, and the semi-soluble nature of dolomite and apatite.

4.6.3 Selective Flocculation for the Removal of Dolomite from Phosphate Ores

Moudgil and Mathur (1994) found that PEO was an effective flocculant for the separation of dolomite from an apatite/dolomite/silica (30/10/60) sample (Moudgil and Mathur 1994). This PEO flocculant was later found to be effective for this specific Florida-based dolomite sample due to the presence of palygorskite on the dolomite surface (Moudgil et al. 1995; Mathur and Moudgil 1998). This makes the use of PEO as a flocculant limited to a very specific ore type.

PAA begins to flocculate dolomite at a molecular weight of approximately 450,000 and achieved almost complete flocculation at a molecular weight of 4 million for single-mineral tests. However, since the main mechanism of adsorption for PAA involves the formation of calcium carboxylate bonds on the dolomite surface, similar reactions will occur on the surface of apatite. Moudgil et al. (1995) attempted to minimize the flocculation of apatite in an apatite/dolomite (80:20) system by using a high dosage (20 kg/t) of sodium silicate dispersant. With a 450,000 molecular weight PAA flocculant (2 kg/t) and sodium silicate dispersant (20 kg/t), the following phosphate concentrates were achieved:

- For dolomite A (Florida dolomite sample), phosphate grades of 91.1% and 91.4% where achieved at phosphate recoveries of 62.8% and 59.7%, respectively; and

- For dolomite B (Ward's Natural Sciences sample), phosphate grades of 91.1% and 90.6% where achieved at phosphate recoveries of 69.7% and 71.6%, respectively.

All tests were done at a pH of 9.5 (Mathur et al. 1996).

Although some selectivity has been shown for dolomite/apatite mix mineral systems at a lab scale, scaling up to a natural ore system will greatly increase the complexity of the selective flocculation processes. Selective flocculation has yet to be proven for a natural high-MgO sedimentary phosphate ore system.

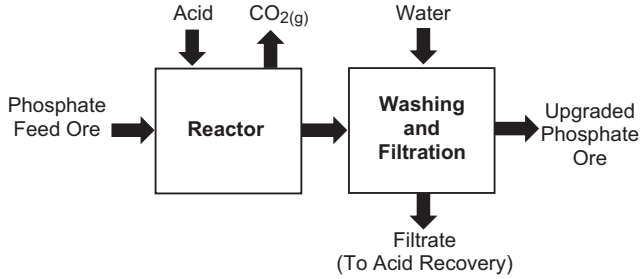
4.7 CONCLUSIONS FROM BENEFICIATION OF HIGH-MgO PHOSPHATE ORES

Beneficiation of phosphate minerals depends on mineralogy of the phosphate deposit, including the types of gangue minerals present and the origin of the deposit. In the case of siliceous phosphate deposits, current flotation technologies can be used to generate a salable phosphate rock product. However, in the case of high-MgO sedimentary phosphate rock deposits, finding a cost-effective beneficiation process is significantly more difficult because of very similar mineral properties of calcite/dolomite and francolite.

Dolomite ($CaMg(CO_3)_2$) is the most intolerable mineral found in carbonaceous sedimentary phosphate deposits because of its Mg content. In general, the phosphate industry demands that a salable phosphate concentrate contain less than 1% MgO. In high-MgO sedimentary phosphate deposits Mg is mainly present in three forms: discrete liberated dolomite particles, fine micron- to submicron-sized dolomite inclusions in apatite, and ionic substitution of Mg into the lattice structure of apatite (francolite, $Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$). This would indicate that there will be a minimum achievable MgO grade for a specific type (origin) of high-MgO sedimentary phosphate ore.

Organic acid leaching (summarized in Table 4.5) of carbonates from carbonaceous sedimentary phosphate ores is a promising method for phosphate beneficiation. Important parameters of acid leaching include acid type, acid concentration, liquid–solid ratio, particle size, reaction time, and reaction temperature. This process is capable of removing MgO in the form of discrete dolomite particles and the fine dolomite inclusions. One major downfall of

Table 4.5 Summary of organic acid leaching process for beneficiation of high-MgO sedimentary phosphates



Reactions

$$MCO_{3(s)} + 2HX_{(aq)} \rightarrow M(X)_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

where

M = Mg^{+2}, Ca^{+2}
X = acetate (CH_3COO^-), formate (CHOO–), lactate ($CH_3CH(CH)COO^-$)

Procedure

1. Weak organic acid is reacted with high carbonate phosphate ore in a stirred reactor.
2. The organic acid reacts with the carbonate minerals (as shown in above reactions).
3. The solid upgraded phosphate ore is filtered and washed from the resulting organic salt solution.

Process Considerations

- *Organic acid:* Acetic acid is the most cost-effective and widely available.
- *Particle size:* Finer sizes allow for more effective leaching but pose problems during washing and filtration.
- *Important parameters:* Acid type, acid concentration, liquid–solid ratio, particle size, reaction time, and reaction temperature.
- An efficient method for organic acid recovery is needed.

Advantages

- Good selectivity toward leaching of carbonates, resulting in lower phosphate losses than strong inorganic acids.
- Carbonates need only be exposed to the acid and not fully liberated.

Disadvantages

- Organic acids are relatively expensive.
- Recovery of organic acids could be difficult because of the production of soluble magnesium sulfate.

this process is the high cost associated with organic acids. To make organic acid leaching a feasible process, an efficient method of recovering the organic acid must be implemented.

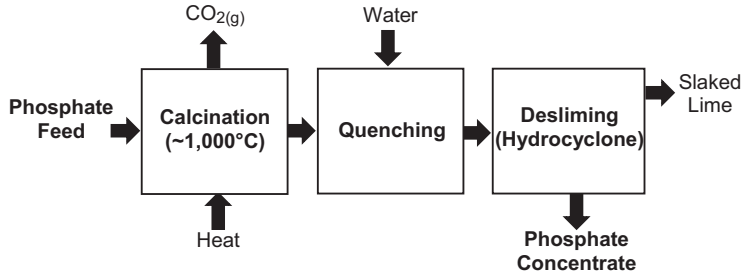
Calcination (summarized in Table 4.6) is a method used to beneficiate carbonaceous phosphate ores by thermally decomposing carbonates and removing the resulting CaO/MgO by quenching/desliming. Important parameters for calcination include temperature, retention time, particle size, and calcination unit. Calcination is capable of removing MgO associated with the discrete dolomite pebbles along with the fine dolomite inclusions inside the phosphate pebbles. The two main drawbacks associated with calcination are the high cost associated with the energy needed to heat the kiln, and undesirable loss in reactivity of the thermally treated phosphate product. For these reasons, calcination is generally only feasible in places where energy is cheap and water is scarce.

Physical separation methods are important in the processing of both siliceous and high-MgO sedimentary phosphate ores. In the case of the former, scrubbing and desliming of clays is necessary for the efficient operation of the Crago flotation process. In the case of high-MgO sedimentary phosphate ores, attrition scrubbing and desliming produce and remove significant amounts of fine dolomite slimes. Another benefit comes from the breaking down of softer dolomite particles, which are removed during attrition scrubbing and desliming.

Heavy-media separation (summarized in Table 4.7) has seen some attention in both the literature and at a plant level for removing dolomite from high-MgO sedimentary phosphate pebbles. Because of the narrow density difference between the dolomite and apatite pebbles, tight control of the fluid density is essential. Although heavy media have shown some success on both a lab and plant scale, separation efficiency can suffer greatly from the presence of interlocked dolomite/apatite pebbles. For these reasons, physical separation should be implemented as a preconcentration method, where further processing techniques are needed to produce a salable phosphate concentrate.

Although flotation has seen the most research interest, a universal flotation process for the removal of dolomite from high-MgO sedimentary phosphate ores has not yet been developed. This can be attributed to the very similar surface properties of dolomite and phosphates, along with the following mineralogical characteristics of high-MgO sedimentary phosphate ores:

Table 4.6 Summary of the calcination process for beneficiation of high-MgO sedimentary phosphates



Reactions

$$MgCa(CO_3)_{2(s)} \xrightarrow{\sim 500-750^{\circ}C} CO_{2(g)} + MgO_{(s)} + CaCO_{3(s)}$$

$$MgO + CaCO_{3(s)} \xrightarrow{\sim 750-1000^{\circ}C} CO_{2(g)} + MgO_{(s)} + CaO_{(s)}$$

Decomposition temperatures will vary based on sample mass, heating rate, partial pressure of CO_2, and particle size.

Procedure

1. High carbonate phosphate ore is heated at ~1,000°C (as shown in above reactions).
2. Calcined phosphate ore is quenched with wash water, and the calcium oxide (CaO) becomes slaked lime ($Ca(OH)_2$).
3. Slaked lime slimes are separated from the upgraded phosphate ore with a hydrocyclone.

Process Considerations

- *Calcination unit:* Rotary kiln, fluidized bed reactor, grate kiln, flash calciner, etc.
- *Particle size:* Finer feed particle sizes give more efficient calcination but also result in higher phosphate losses during quenching and desliming stages.
- *Important parameters:* Temperature, retention time, and bed depth.
- Dust control is important.

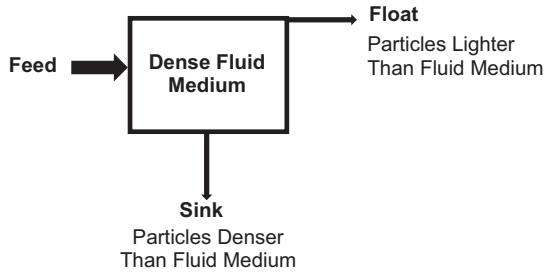
Advantages

- Provides complete removal of carbonates.
- Carbonates do not have to be completely liberated from phosphate.
- Low water demands.

Disadvantages

- Energy intensive.
- Produces a phosphate concentrate of low reactivity in the wet process.
- High capital costs associated with calcination plants.

Table 4.7 Summary of the heavy-media separation process for beneficiation of high-MgO sedimentary phosphates



Method

- Uses a heavy medium (fluid) with a density between the dense and light minerals.
- Less dense dolomite-rich pebbles float, while denser phosphate-rich particles sink.

Process Considerations

- *Separator:* Heavy-media cyclones are the most common separator device.
- *Heavy medium*: Fine particle suspensions (magnetite) or dissolved salt solutions ($CaCl_2$, $ZnCl_2$) are the most common.
- *Particle size:* Works with relatively coarser sized feeds (>0.5 mm) but suffers from liberation issues at coarser sizes.
- *Important parameters:* Cyclone diameter, inlet area, vortex finder diameter, cone angle, spigot diameter, feed pressure.

Advantages

- Capable of processing coarse feed sizes.
- Relatively high throughput.

Disadvantages

- Phosphate and dolomite pebbles have very similar densities, which results in low separation efficiencies.
- Coarse feed sizes tend to mean more dolomite impurities present within phosphate-rich pebbles.
- Most likely only useful as a preconcentration method, with other methods (i.e., calcination, acid leaching, flotation) being needed as a "cleaner" stage to reach the <1% MgO specifications.

high slimes production, the porous nature of sedimentary phosphate ores, and the very fine liberation size (the micron to submicron dolomite inclusions). All of the previously mentioned mineralogical properties significantly hinder selectively, while increasing reagent consumption and the total cost of the process.

5
Beneficiation of Igneous Phosphate Ores

Although sedimentary phosphate ores make up the majority of the phosphate reserves worldwide (~80%), igneous phosphate reserves are important in their own right, making up approximately (~15%–20%) of phosphate production (Abouzeid 2008). Igneous phosphates can have significantly different mineralogy than sedimentary phosphates, including associated gangue minerals. More information on the mineralogy of igneous phosphates can be found in Chapter 2. This chapter includes a discussion of the most relevant techniques for processing igneous phosphate ores. Also discussed are the mineralogy and general beneficiation processes of important igneous phosphate reserves around the world.

5.1 FLOTATION OF IGNEOUS PHOSPHATE ORES

Froth flotation has been the most widely used method for the beneficiation of igneous phosphate ores that contain silica and other gangue minerals (Houot 1982; El-Shall et al. 2004). The well-crystallized igneous phosphates are particularly advantageous to froth flotation because of their low porosity. In contrast, sedimentary ores suffer from high specific surface areas, high slimes production, and a high degree of substitution in the apatite crystal lattice structure (Baudet and Save 1999; Prasad et al. 2000). For these reasons, igneous phosphates are considered to be more easily beneficiated by means of froth flotation than sedimentary phosphates. Flow sheets for processing siliceous igneous phosphates are usually a simple direct flotation process, whereas more complex methods are needed for ores rich in barite, magnetite, or calcite impurities (Baudet and Save

1999). Reagents used in igneous phosphate flotation and beneficiation processes for specific igneous phosphate reserves are described in this chapter.

5.1.1 Collectors

Anionic fatty acid collectors have long been proven both theoretically and in plant practice to be highly efficient in the flotation of apatite ($Ca_{10}(PO_4)_6(F)_2$). At basic conditions (pH ≈10), the fatty acid is saponified, which results in a negatively charged carboxylate ion. The negatively charged carboxylate ion then reacts with calcium on the apatite surface to form calcium carboxylate. This chemisorption method is generally considered to be the primary method of fatty acid adsorption onto the apatite surface at alkaline conditions (Maltesh et al. 1996; Lu et al. 1998; Guan 2009a). More details on the flotation of phosphates with fatty acid collectors can be found in Section 3.3, where the Crago double float process is discussed. Traditionally, tall oil has worked exceptionally well as an anionic fatty acid collector and is used worldwide in the flotation of igneous phosphates. Tall oil is a by-product of the Kraft wood pulping process and typically contains significant amounts of fatty acids (oleic acid and linoleic acid).

However, in the case of Brazilian igneous phosphates, fluctuations in the quality of the local tall oil forced plant operators to look into alternative collectors. Brandao et al. (1994) investigated rice bran oil and soy bean oil as sources for vegetable lipid oils to produce saponified fatty acid collectors. Chemical analyses were completed in order to compare the vegetable sources to tall oil. Tall oil had high concentrations of oleic acid, with appreciable amounts of linoleic acid also present. Laboratory tests determined that linoleic acid and oleic acid (Figure 5.1) are both effective phosphate collectors. Rice bran oil has significant concentrations of linoleic and oleic acid,

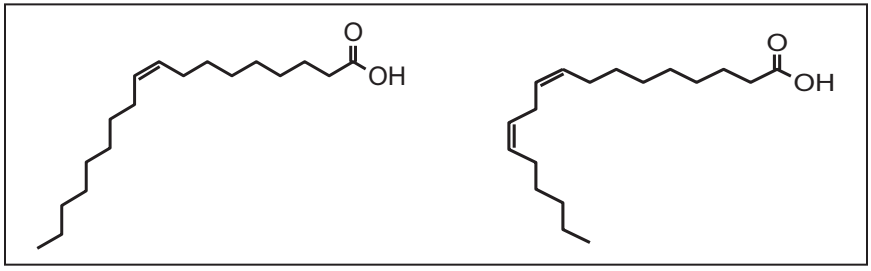


Figure 5.1 Chemical structure of oleic acid $C_{18}H_{34}O_2$ (left) and linoleic acid $C_{18}H_{32}O_2$ (right)

making it a desirable alternative to tall oil (Brandao et al. 1994; Guimaraes et al. 2005).

Amphoteric collectors are useful in phosphate flotation at concentrators in Cajati, Brazil, and Siilinjärvi, Finland. The amphoteric collector is from the sarcosinates family and acts as an anionic collector at basic pH values, making it suitable for flotation of apatite (Houot 1982; Guimaraes et al. 2005).

5.1.2 Depressants

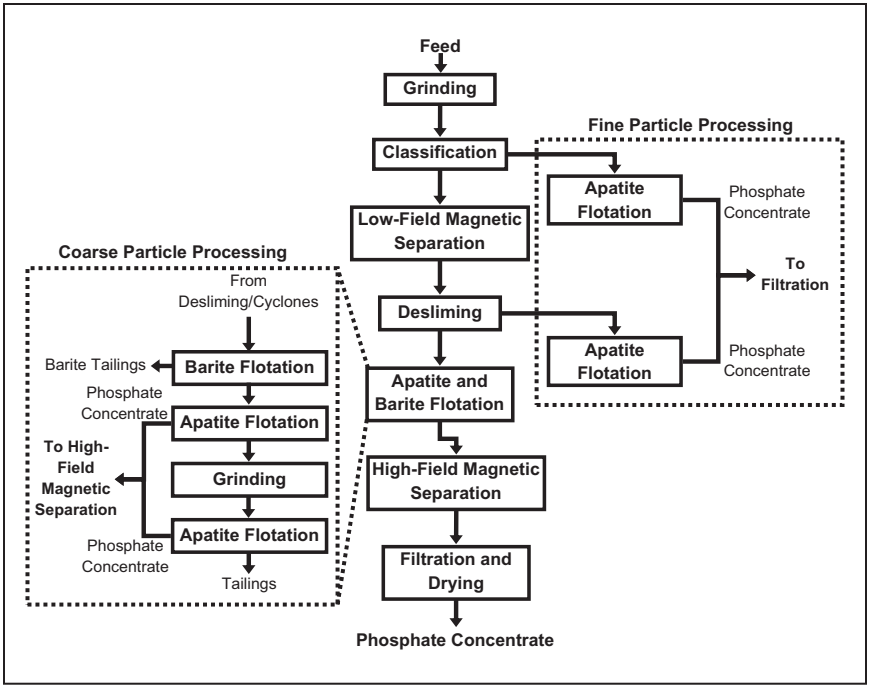
Starch is one of the most common depressants used in igneous phosphate froth flotation processes. In the case of Brazilian carbonatitic phosphates, modified starch is used to depress carbonates and iron oxides at a pH of 10 (Betz 1979). Modified (causticized) starch is used because it is soluble in water. Filho et al. (2000) attributed the selectivity of starch toward depressing calcite to steric compatibility. The "total fitting number" was developed to predict and compare steric compatibilities for different reagent/mineral combinations. In the case of starch, where the hydroxyl groups interact with calcium sites on the mineral surface, the fitting number is based on the distance between OH-OH sites in the starch and the Ca-Ca sites in the calcite (or apatite). The total fitting number for starch-calcite was considerably higher than starch-apatite, indicating a higher affinity of starch for calcite (Filho et al. 2000).

Sodium silicate is used in both igneous and sedimentary phosphate flotation, mainly for the purpose of removing calcium precipitates from the surface of quartz. This enhances the selectivity of the fatty acid collector toward apatite by suppressing silica (Dho and Iwasaki 1990).

5.2 BENEFICIATION OF MAJOR IGNEOUS PHOSPHATE RESERVES

5.1.1 Barreiro Carbonatite Complex, Araxá, MG, Brazil

The Araxá igneous phosphate deposit was first discovered in the early 1940s. Mining companies initially selectively mined the phosphate-rich portions to avoid the need for complex processing methods. However, many complications arose when attempting to process the whole deposit due to impurities such as magnetite and barite. In the 1960s, the Fosminas and Serrana processes were introduced to beneficiate the hard-to-process ores. These processes were the starting point for the current method of processing the Barreiro phosphate ore (Betz 1979).



Source: Adapted from Betz 1979 and Guimaraes and Peres 1999.

Figure 5.2 Simplified process flow diagram for processing of Brazilian igneous phosphate reserves that contain barite

The current process for the Barreiro igneous phosphate ore was outlined by Guimaraes and Peres (1999). Overall, the process can be simplified into the following steps:

1. Grinding,
2. Classification,
3. Low-field magnetic separation,
4. Desliming,
5. Apatite and barite flotation,
6. High-field magnetic separation, and
7. Filtration and drying.

As shown in Figure 5.2, the process is broken into fine and coarse particle processing to increase separation efficiency. In the fine particle processing, the natural fines and those generated from grinding are sent to apatite flotation.

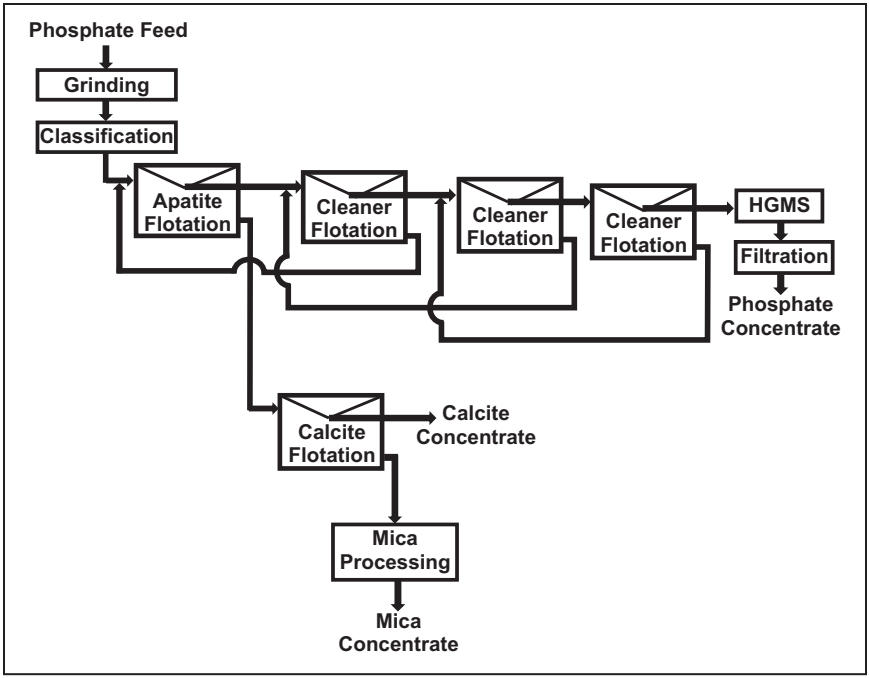
For the coarse particles, the ore is first put through a barite flotation stage, which is followed by two stages of apatite flotation. The ore is reground after the first apatite flotation stage to help increase phosphate recovery in the second flotation stage (Guimaraes and Peres 1999).

For the apatite flotation stages, the ore is typically conditioned at approximately 60% solids at a pH of 10–11.5 with a fatty acid collector (tall oil or rice bran oil). Depression of iron oxides is accomplished by adding gelatinized or causticized starch (Betz 1979; Guimaraes and Peres 1999; El-Shall et al. 2004; Guimaraes et al. 2005).

Barite flotation is needed during coarse particle processing when barite concentration in the run-of-mine ore exceeds 3%. Barite flotation is achieved using a cetyl or stearyl sulfate collector (Betz 1979). Guimaraes et al. (2005) noted that barite suppression could be accomplished at a pH of 12 with corn starch during apatite flotation. In some cases, this can be sufficient enough to eliminate the need for the barite preflotation stage. However, the high costs associated with the caustic soda demand make this option expensive (Guimaraes et al. 2005).

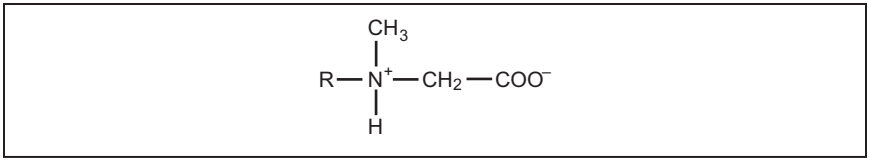
5.2.2 Processing Finnish Igneous Deposits

Igneous phosphate deposits in Finland, such as those located near Siilinjärvi, typically contain about 10% apatite, 22% calcite, 65% phlogopite, and 3% amphibole and other silicates (Houot 1982; Moudgil and Somasundaran 1986; Puustinen and Kauppinen 1989; El-Shall et al. 2004). A simplified process flow diagram for the Finnish phosphate concentrator plant is shown in Figure 5.3 (Remes et al. 2010). Apatite flotation is accomplished with the amphoteric collector N-sarcosine. The simplified formula for N-sarcosine can be seen in Figure 5.4. The amphoteric collector acts as an anionic collector to float apatite at a pH of 8–11 (Houot 1982). The rougher float concentrate goes through several cleaner stages, followed by high-gradient magnetic separation to produce a salable phosphate concentrate. The rougher tailings are sent to a calcite flotation stage where tall oil is used to float calcite that can be sold as a by-product. Tailings can be further processed to produce a mica concentrate. The Siilinjärvi plant produces 0.8 MT apatite concentrate, 0.8 MT calcite, and 10 kt mica per year (Remes et al. 2010).



Source: Adapted from Remes et al. 2010.

Figure 5.3 Simplified process flow diagram for Siilinjärvi (Finland) phosphate concentrator plant

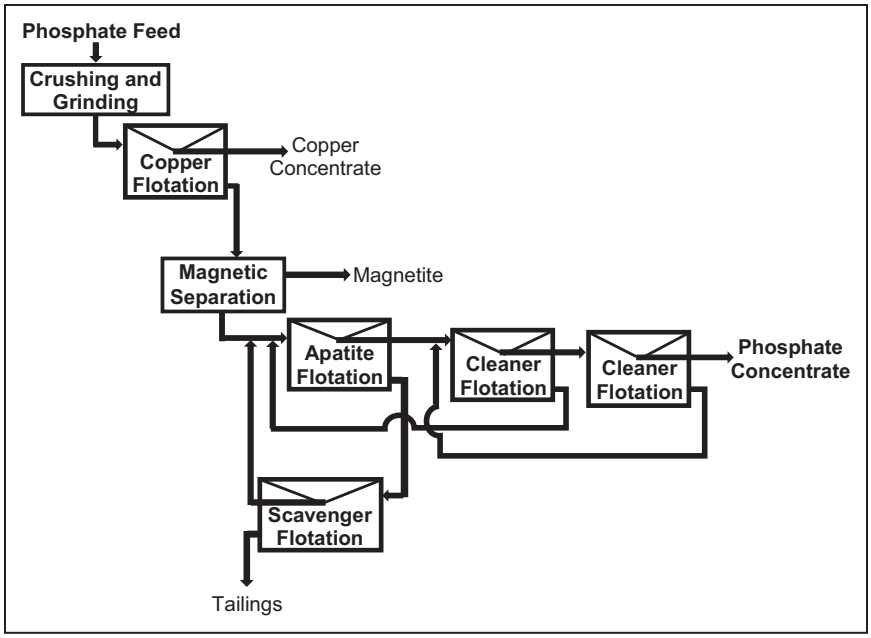


Source: Adapted from Houot 1982.

Figure 5.4 Simplified structure for the N-sarcosine collector used in the flotation of Finnish phosphates

5.2.3 Processing Phosphates of the Kola Peninsula, Russia

The Kola Peninsula of Russia is another very important source of igneous phosphate deposits. The Khibiny complex is one of the largest igneous complexes of the peninsula (Ilyin 1989). Apatite is present with gangue minerals consisting mainly of nephelinic syenites, which are composed of nepheline ($(Na,K)AlSiO_4$) and alkali feldspar (feldspar rich in potassium and sodium).



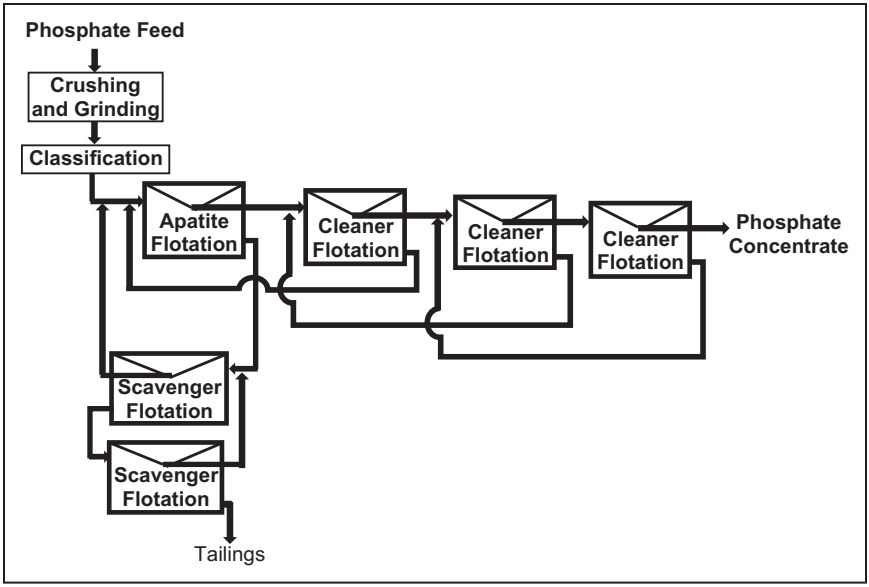
Source: Adapted from Woodrooffe 1972 and Houot 1982.

Figure 5.5 Simplified process flow diagram for beneficiation of Kola Peninsula (Russia) igneous phosphate ore

A simplified process flow diagram for beneficiation of Kola Peninsula igneous phosphate ores is shown in Figure 5.5. This process is relatively simple, consisting of a rougher float, followed by three cleaning and two scavenger stages. Flotation is accomplished using the following reagents: tall oil, oxidized petroleum, secondary oil gas tar, and sodium silicate. Caustic soda is also used to yield a basic pH for flotation. This process has been capable of upgrading a feed ore containing 18% P_2O_5 to a phosphate concentrate of approximately 39% P_2O_5, with recoveries around 94% (Houot 1982; El-Shall et al. 2004). Approximately 9 MT of apatite concentrate is produced annually from the Kola Peninsula (Glasby and Voytekhovsky 2011).

5.2.4 Processing South African Igneous Phosphate Ores

The Phalaborwa complex, previously called Palabora, is a significant igneous apatite reserve located in the northeastern region of South Africa (De Jager 1989). It is composed mainly of pyroxenite but has a core composed of carbonatite surrounded by a serpentine/magnetite/apatite ore known as



Source: Adapted from Houot 1982.

Figure 5.6 Simplified process flow diagram for beneficiation of Phalaborwa igneous phosphate ore

phoscorite (Lovell 1976). Apatite in this reserve is concentrated from three main sources:

1. **Phoscorite.** Apatite concentrations in the phoscorite are typically around 25%, with the apatite composed of approximately 70% fluorapatite and 30% hydroxyapatite. Impurities consist of approximately 35% magnetite and 30% dolomite.
2. **Pyroxenite.** Apatite concentrations are generally around 15%, with the apatite composed of a 50/50 split of hydroxyapatite and fluorapatite. Major gangues include pyroxene, phlogopite, and vermiculite. Notably, this apatitic source is free of magnetite and contains very little carbonates.
3. **Tailings from Palabora Mining Company (PMC).** The PMC processes an ore that contains 0.65% copper in the carbonatite and 0.4% copper in the phoscorite. After the copper has been removed, the tailings containing 15%–25% apatite are sent to the phosphate processing plant.

Before flotation is used to beneficiate the apatite, any iron and copper present are separated from the ore as by-products. A simplified process flow diagram is shown in Figure 5.6. After crushing and grinding, the copper is first removed by flotation using a xanthate collector. Next, the iron is separated by magnetic separation. Finally, apatite beneficiation is accomplished with a flotation circuit consisting of a rougher, scavenger, and two cleaners. Apatite flotation is carried out using a tall oil fatty acid collector. Caustic soda is used to sustain a pH greater than 8. Sodium silicate is added as a dispersant while nonyl phenyl tetraglycol ether is used as a calcite and dolomite depressant. Overall, the process is capable of producing a phosphate concentrate grade greater than 36% P_2O_5 at recoveries of 75%–80% (Lovell 1976; Houot 1982; Moudgil and Somasundaran 1986).

5.3 SUMMARY OF IGNEOUS PHOSPHATE PROCESSING

Beneficiation of igneous phosphates can vary significantly depending on the gangues present. One process common to all igneous phosphate concentrator flow sheets is the anionic fatty acid flotation of apatite ($Ca_{10}(PO_4)_6(F)_2$). Igneous apatite is more responsive than sedimentary phosphates to fatty acid anionic flotation because of its well-crystallized and nonporous nature (Baudet and Save 1999). Tall oil has been an effective anionic collector of apatite when used at basic conditions (pH 10–11.5). Rice bran oil is also an effective alternative for tall oil due to its high content of oleic and linoleic acids.

Additional processing techniques such as magnetic separation (iron removal), copper flotation, calcite flotation, and barite flotation are implemented when specific igneous phosphate reserves demand it. It some cases, these processes can result in valuable by-products.

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Note: *f.* indicates figure; *t.* indicates table.

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Beneficiation of Phosphate Ore

by S. Komar Kawatra and J.T. Carlson

Beneficiation of Phosphate Ore examines various methods for processing phosphate rock, an important mineral commodity used in the production of phosphoric acid. The majority of phosphoric acid is produced by the wet process, in which phosphate rock is reacted with sulfuric acid to produce phosphoric acid and gypsum (calcium sulfate dihydrate). This wet process demands a phosphate rock feed that meets certain specifications to produce phosphoric acid efficiently and economically.

Beneficiation of Phosphate Ore thoroughly explains the methods used in beneficiation of different types of phosphate ores for use in the wet process. The mineralogical properties of the two major types of phosphate deposits, sedimentary and igneous, are described along with the processing methods. The benefits and disadvantages of each process are discussed in detail.

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