Nonsulfide Flotation Technology and Plant Practice

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INTRODUCTION

Minerals are often placed in categories according to mineral characteristics rather than chemical composition. Common definitions used in the industry are "metallic minerals," "nonmetallic minerals," and "mineral fuels." The common metallic minerals are the mineral sulfides, such as pyrite and chalcocite, and the native metals, gold and copper. The mineral fuels include coal and oil sands. The nonmetallic mineral term is essentially synonymous with the term "industrial minerals." Probably the best definition of industrial minerals is "any rock, mineral, or other naturally occurring substance of economic value, exclusive of metallic ores, mineral fuels, and gemstones." For a comprehensive overview of industrial minerals, the reader is referred to the SME book *Industrial Minerals and Rocks*, the 5th and 6th editions. In this regard, the category of nonsulfide minerals includes industrial minerals, energy minerals, and nonsulfide metallic minerals.

There are hundreds of nonsulfide mineral flotation plants throughout the United States, and most have a plant design that depends upon the specific ore characteristics and the market specifications for their product. There is no common thread of technology between the design and processing of different nonsulfide minerals, or even between processing minerals of the same kind.

Although most nonsulfide processing plants utilize flotation, other mineral separation techniques are often necessary to yield a marketable product. Typical beneficiation techniques used in conjunction with flotation include gravity separation, magnetic separation and chemical leaching. Sometimes several different flotation systems are used in the same processing plant, such as the flotation of mica, quartz and feldspar from pegmatite ores.

Usually there is a primary material produced at a nonsulfide processing plant with other mineral products sold as by-product material. Often the economics of a facility is dependent upon the by-products and sometimes the by-products become the most profitable commodity produced at a plant.

The stone, sand and gravel industry is the exception and is not included in this chapter. This nonsulfide mining industry is huge, exceeding all the metals industry and fuel industry tonnage combined. These mining operations do not beneficiate their material by flotation nor do they normally use any other mineral separation process. This industry mines a one-component deposit that only requires removal of fines and clays to produce a saleable product.

The field of nonsulfide minerals is so varied and so large that to encompass the topic in this chapter is impractical, if not impossible. Some nonsulfide minerals are processed in very large tonnages in numerous plants, and some nonsulfide minerals are processed in only one or two small tonnage plants. These latter plants are so unique and so specialized that including them in this chapter would be of little use to most mineral engineers. Therefore the best this chapter can accomplish is to show the great diversity of nonsulfide flotation technology and provide several examples of actual nonsulfide plant practice.

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General Aspects of Nonsulfide Flotation

The dimensions of nonsulfide flotation technology extend in many different directions, as might be expected from the diversity of the mineral classes, which include soluble salt minerals (potash, borax, and trona), semi-soluble salt minerals (phosphate minerals, fluorite, calcite, and barite), insoluble oxides/silicate minerals (mica, quartz, and feldspar), and energy minerals (coal and oil sands). As a consequence, some flotation separations are accomplished from saturated brine, while other separations are achieved in solutions of rather low ionic strength. Also it is worth noting that certain nonsulfide minerals are naturally hydrophobic, such as talc, graphite, and coal. But in general, the nonsulfide minerals are hydrophilic and require relatively high levels of collector addition on the order of 1 lb/ton to establish a hydrophobic surface state. Further, the nonsulfide collectors generally are anionic or cationic surfactants, having hydrocarbon chains of ten carbon atoms or greater. In many instances, the collector is sufficiently insoluble that a distinct collector phase is present in the system, existing as a dispersion or as a collector colloid. This situation further complicates the analysis of nonsulfide flotation chemistry, and in view of the foregoing, it is evident that the flotation chemistry is distinctly different from the flotation chemistry of sulfide minerals.

Nonsulfide flotation technology also differs from sulfide flotation technology with respect to particle size. In many nonsulfide systems, but not all, flotation is accomplished with deslimed feed and a particle size that extends up to several millimeters in diameter (coal, phosphate, and potash). On the other hand, some nonsulfide flotation systems involve flotation of micron-size particles (taconite and kaolin).

With respect to flotation rate, again, the variation is great, with long retention times (even one hour) required for the flotation of impurities (anatase, etc.) from kaolin, whereas rather rapid flotation (a few minutes of retention time) is required for phosphate flotation.

Advances in flotation technology, including nonsulfide flotation, have been documented in a recent publication (Parekh and Miller, 1999).

The Nonsulfide Mineral Industry

Before the design and operation of a nonsulfide plant, it is imperative to understand the industry. In almost all cases, the plant design parameters and processes used for beneficiation are dependent upon a specific marketable product and the quality of the mineral in the deposit. The importance of this fact cannot be under estimated.

Quartz is a prime example of this fact. In a sand (quartz) deposit there are several potential economic markets. If the deposit is located near an urban area, the sand quality will probably be acceptable for general construction, such as concrete, and find a market within 10 to 15 miles. Processing (crushing and sizing) cost would be minimal and the selling price of the sand would be in the range of 3 to 5 $/ton plus about 5 $/ton delivery by truck to a local market. If the sand could be processed by flotation and magnetic separation to yield glass sand quality, then the sand could sell for about 15 to 20 $/ton if there was a glass manufacturer within 100 to 150 miles. Yet, if the sand was of exceptional quality and could be processed to yield high-purity quartz, the product could be shipped anywhere in the world. Of course, other factors are involved in determining if the deposit is economic, but usually the overriding factors are (a) product quality, (b) market conditions and (c) location.

Product Quality. The nonsulfide minerals industry usually produces a commercial product that remains a "mineral", whereas the final product of the metals industry normally is a "metal", produced from a mineral. Further, it should be noted that nonsulfide minerals have highly variable natural characteristics. Not all mica found in nature has equal economic value. The "aspect ratio" (diameter to thickness of the particles) of a mica crystal structure cannot be altered by processing, yet this mineral characteristic dictates its value, Two mica concentrates can be exactly equal with 98% pure mica, yet a concentrate with a bulk density of 10 lb/cubic foot would make an excellent filler material at a very good price but the other mica concentrate may have a bulk density of 25 lb/cubic foot with limited, if any value, in the marketplace.

Other mineral characteristics influencing the value and marketability of nonsulfide process plant design include the following.

* Particle Size (not necessarily for liberation and beneficiation but for market specifications): If the ore requires a 100-mesh grind for liberation during processing, but the size specification is 28×100 mesh for the marketable product, then the material cannot be sold. If an ore is coarse liberating, after beneficiation the concentrate may have to be fine ground for sale.
* Particle Shape: The shape (round or angular, platy, fibrous, etc.) of a mineral can define a market and the mineral value. This is shown in the previous example of mica.
* Color: Color becomes a critical factor in some nonsulfide mineral markets. Kaolin, marble, limestone, mica, and quartz become more valuable with greater whiteness. Whiteness may depend not on the mineral concentration in a product but on the impurities contained within the crystal structure, and processing cannot modify these minerals.
* Chemical Composition: Feldspar and other nonsulfide minerals can have a variable chemical composition. Feldspar contains calcium, sodium and potassium in the crystal. A feldspar from a deposit can be classified as a soda (Na) feldspar or a potash(K) feldspar depending upon the amount of these elements in the structure. This will define what commercial market is potentially available and at what price.
* Concentrate Grade: The grade of a specific mineral in a concentrate from a nonsulfide processing plant can define the market potential and the sales price. A concentrate with a grade of 30% tantalum can be sold at 80 $/lb but if it is upgraded further, the sales price may be much higher. The minimum potash grade for the market is 60% K_2O, but if the grade drops to 58.8% K_2O there is a substantial reduction in the sales price – if the material can be sold at all!

Market Demands. The size of nonsulfide mineral markets tends to be more restrictive and limited than those in the metals industry. This is because the markets are more specialized and directly connected with the consumer. The use of fillers (nonsulfide minerals such as calcite, mica or kaolinite) is expanding with the increased use of plastic in automobiles and with an expanding economy. The market for fertilizers (potash and phosphate) is cyclic because of weather and world economics. Barite is used for drilling mud in exploration and its demand is dependent upon the price and supply of world oil.

The design and operation of nonsulfide plants must be flexible to adjust to the variations in market demands. These variable market demands may be tonnage (such as happens in the case of the demand for fertilizer in a wet weather in the planting season.) or quality (such as when more restrictive particle size specifications as specified for construction sand used in the "Super Highway" concrete). New industrial technologies can alter an industrial mineral market significantly and rapidly.

Location. Location of the deposit is important because most nonsulfide products are high-volume, low-price material; therefore, transportation cost will have a major impact in the economics of the deposit. For example, even an excellent high-grade ore deposit of feldspar using a proven processing technique may not be economic because of its location. The ore deposit is likely to be discovered in a remote geographical area, but the glass manufacturing plant is probably located near an urban location. Transportation of bulk products is costly and often exceeds the cost of mining and processing the ore. Salt produced from the Utah Great Salt Lake can be loaded on a unit train for less than $5/ton and yet the cost of shipping to a caustic chlorine producer in Nevada may be greater than $15/ton.

Consistency. An important factor in marketing most industrial minerals is to maintain product consistency. This is especially critical when attempting to enter a new market with an untried product. For example, glass manufacturers produce large batches using a specific mix of materials, (quartz, feldspar, limestone, soda ash and gypsum) and companies are very resistant to changing the mix. Specifications for feed mix limits are usually not the same for all glass manufacturers. Variations in the quality of the glass components can cause serious and expensive problems in their operations. Suppliers of industrial minerals must establish reliability with a client before sale contracts are made.

Evaluation of Deposits and Products.   The design, construction and operation of an industrial mineral facility are considerably different from a metallic processing plant. This is because the mineral products are market driven with specialized specifications and usually result in long-term contracts with the client. The metallic industry (copper, iron, gold, zinc, etc.) products are usually sold at published prices on the open market plus the processing technology is relatively uniform across the entire industry.

A critical market study and product evaluation must be carried out before spending capital money to develop a nonsulfide property. The importance of a comprehensive market study cannot be over emphasized. The study should be one of the first things to be considered in developing a new property and should include (a) a survey of the potential use of the mineral, (b) size of the market, (c) price of the commodity, (d) transportation, (e) estimating the profitability or margin on sales, (f) potential by-products and (g) competition, not only competition from other companies but also competition from other types of material.

In determining the capital and operating costs of a new industrial mineral plant, marketing is again important and the operating cost must include a sales staff or group. Process technology and marketing cannot be separated in the industrial minerals industry.

Product quality and consistency are important in the evaluation of a new deposit and in the development of a new product from an existing plant. A market evaluation of the product is usually necessary in order to obtain a sales contract, and usually this requires a substantial quantity of material to test. Laboratory or batch testing to design the industrial mineral plant is always required but a large quantity of the material usually is needed to provide to the potential client for testing in their operation. This can be as little as several hundred pounds but often is 20 to 50 tons of test material. Continuous pilot plant testwork is normal when starting an industrial minerals operation not just to obtain engineering design and process criteria for constructing the plant but also to obtain acceptance of the material to the clients.

MICA

Mica is a complex hydrous aluminosilicate with a varying chemical composition. There are several types of mica. Muscovite mica is commercially mined because of its unique characteristics, especially its color, laminated structure and insulating power. Phologopite mica is dark stained and is used in large volumes for sound deadening and fillers where color is not an issue. Biotite mica has a high bulk density and contains significant quantities of iron in the crystal (can be almost black in color), therefore, it has very limited use and generally are not considered of economic value.

Mica uses include paint fillers, plastic extender, joint compound, surface coating, insulation board and numerous other industrial applications. Important mineral characteristics of the mica that dictate the market potential and selling price are (a) aspect ratio or bulk density, (b) color or whiteness, and (c) particle size. Most commercial applications require that the product be finely ground. Product grinding can be either wet or dry.

Analytically determining mica is difficult because it is not a true mineral but a family of minerals with varying chemical composition. Potassium is the predominate element in muscovite but because of the variability of its composition, chemical analysis cannot be used to determine the mica content of samples. Usually commercial mica is not sold on chemical analysis but on specifications of its physical properties. Methods used in industry to evaluate mica flotation efficiency are vanning, magnetic separation and bulk density.

Mica is easily floated because of its flake like crystal structure and can be floated in two systems: (a) an acid system using a cationic collector and (b) a basic system using an anionic collector. Both systems are used industrially but the acid flotation system is more common. Flotation selectivity in both systems is quite good and the flotation concentrates usually contain 90% mica or higher. Mica flotation is fast and produces a thick heavy froth. Further information on mica and the processing thereof can be found in the literature (Chapman 1983; Tanner, 1994; Tippin et al., 1999).

Feed Preparation

After crushing, either wet ball and/or rod mills are used to grind the ore in preparation for flotation. Grinding conditions should minimize the formation of fines which are a detriment to the flotation process. Most ores are coarse liberating. Both the acid and the basic mica flotation system require desliming prior to flotation. One or two stages of desliming (at about 150 mesh) are generally required. The first stage of desliming follows grinding and removes primary slimes in the ore. The second stage of desliming follows scrubbing and removes the secondary slimes. Scrubbing and desliming is not absolutely necessary for mica flotation but the fines (clays) left in the flotation feed can cause a significant increase in reagent consumption and adversely effect selectivity.

It is usually advantageous to precede flotation with a scrubbing step to clean the mineral surfaces and remove slimes from the surface of the mineral. The intensity, retention time and pulp density of scrubbing is not critical to flotation. Typically the ore is scrubbed for 3 to 8 minutes at 55 to 70% solids. Depending on the weathered characteristics of the feed, scrubbing can immediately follow grinding or after the first stage of desliming.

Flotation in both the acid system (using amine) and the basic system (using petroleum sulfonate) have a conditioning step. The basic flotation system usually requires more conditioning time that the acid system. Here the pH is set, the collector added and the pulp density adjusted for flotation. Consumption of reagents for pH adjustment is dependent upon the minerals in the ore. High solids-high intensity and a long retention time during conditioning are not required and can actually be detrimental. Neither system is highly sensitive to the conditioning step. However, there is a saying that flotation is easy if the feed preparation is correct.

In the acid system, conditioning time is very short, less than two minutes are needed. Since the cationic bond to the mica surface is not strong and the amine is slime sensitive, too much conditioning in this system can be detrimental. Typical amine collector usage is 0.3 to .06 lb/ton. The collector can be added as a chloride or an acetate amine. The pH for flotation ranges between 3.0 to 4.0 using sulfuric acid.

Conditioning time in the basic system is five to ten minutes in two stages at a pH between 8.0 and 9.0. Usually caustic is used to adjust the pH but other chemicals have been used. Flotation at the ore's natural pH may be possible but this is usually less efficient and not worth the small savings of the caustic needed to adjust the pH. Typical reagent consumption is 1.0 to 1.5 lb/ton of petroleum sulfonate.

Mica Flotation

The acidic and basic flotation systems are quite similar. The major difference is that the basic system has a tendency to float more of the gangue minerals, especially in the fine sizes and the concentrate is more difficult to clean. The acid circuit has a more tenacious froth that has a tendency to entrap fines. The decision as to which system is used, sometimes is a matter of preference and experience.

A typical system consists of a rougher (5 to 8 minutes), one cleaner (3 to 5 minutes) and a scavenger (3 to 5 minutes). Depending upon the ore and the market specifications, sometimes a second cleaner is used and the scavenger may not be necessary. The middling from the cleaner circuit are recycled back into the rougher circuit.

Pulp density in the flotation feed (conditioner discharge) ranges between 20% and 30% solids. A frother, such a MIBC or a commercial frother reagent is normally added (0.1 to 0.2 lb/ton) to the rougher cell to loosen up the froth. Small frother dosages may also be added to the cleaner cells.

Plant Practice

Many industrial minerals are produced in multi-component plants, including mica. Mica is often a co-product or a by-product in an ore processing plant. Few mica-bearing deposits have the content and quality to be economic by selling only mica unless there are unique market conditions. It is common to have mica, quartz and feldspar in a deposit and to have a plant that beneficiates all three minerals commercially.

Mica is beneficiated both by gravity and by flotation techniques in plant practice. Coarse mica can be concentrated by flotation but it is more economic to use gravity methods. Spirals, tables and screens are most commonly used. Because of the unique shape of the particles, pre-concentration of mica from an ore is sometimes done using a hydraulic classifier. Several stages of gravity concentration steps may be used to yield the grade of mica desired. Gravity techniques can be effective down to about 40 mesh. Very often the tailings and/or middlings from the gravity circuit are ground to minus 30-mesh and sent to the flotation circuit. Gravity methods also have an advantage in that the mica product does not have any residual reagent on the surface. Some markets require a chemical free mica product.

Typically the ore is ground and sized to 30 × 150 mesh before flotation. Due to the unique shape of the mineral, selective grinding naturally occurs during grinding. Because of this, mica plants often have spirals installed ahead or in the grinding circuit to recover the coarse mica. Gravity concentration is more effective and less costly than flotation for plus 10 mesh mica. Below 150 mesh, flotation selectivity is reduced as the platy nature of the mineral is reduced.

Mica flotation is effective down to about 150 mesh but below this size the concentrate grade diminishes. Flotation selectivity in the finer sizes is usually better in an acid system than a basic system. Standard mechanical flotation cells are more common than column cells in mica flotation.

Depending on the beneficiation process and the sales market, sometimes the dry mica flotation concentrate is further upgraded by magnetic separation or screening. To meet size specifications, the final mica concentrate from the beneficiation plant is often wet or dry ground to ultra-fine sizes before shipment. Wet ground mica is a higher value product than the dry ground product.

The coarse mica concentrate may be combined with the fine mica concentrate or each can be sold separately depending on the commercial market. Typically mica products sold from a beneficiation plant are 95% mica or higher.

QUARTZ/FELDSPAR

Quartz and feldspar are among the most abundant minerals on earth, occurring almost everywhere. Depending on the chemical composition, physical characterization and ore location, these minerals have similar commercial usage. They also generally occur in the same deposit and are often recovered jointly as a feldspathic sand (a mixture of quartz and feldspar). Therefore, this section of the chapter considers quartz/feldspar flotation technology together for the production of (a) feldspathic sand and (b) the quartz/feldspar concentrates.

The market for feldspar and quartz minerals is quite large, and includes glass, glass fiber, whiteware, tile, dinnerware, paint, adhesives and plastics. Glass and glass fiber are the largest tonnage market (68%). The quartz and feldspar products are sold under private contracts to individual users and there is no published national price. In general the quartz products can be sold at a price between $5 and $120 per ton and the feldspar products between $40 and $200 per ton. Feldspathic sand prices vary between $20 and $40 per ton. The wide range of prices for various usage results in transportation becoming an important factor in the economics of these two minerals

The important characteristics for commercial feldspathic sand and quartz/feldspar concentrates are (a) chemical purity, (b) whiteness or color, and (c) particle size. Also, the sodium to potassium ratio is an important factor in selling feldspar products.

Flotation is the primary recovery process for these two minerals, excluding construction material usage. However, there is no known flotation plant in the United States that recovers only feldspar. Feldspar is recovered as a feldspathic sand (a mixture of quartz and feldspar) or as a result of a feldspar/quartz separation that yields both a feldspar concentrate and a quartz concentrate. Both flotation systems use a first stage of flotation to remove impurities.

The option of producing a feldspathic sand or quartz/feldspar concentrates is both technical and economic. The technical factors are mineral liberation size between the quartz and feldspar crystals and the potassium:sodium ratio of the feldspar. The economic factors are product use, market tonnage, and end user location. If a plant is designed to produce quartz and feldspar concentrates, it is a simple matter to change the process to produce feldspathic sand. However, converting a

feldspathic sand plant to one that produces individual concentrates is more difficult and requires capital investment for an additional flotation circuit. Further information on quartz and feldspar and the processing thereof can be found in the literature (Rogers and Neal, 1983; Kauffman and Van Dyk, 1994; Zdanczyk and Linkous, 1994; Ibrahim, 2002; Tippin et al., 1999).

Feed Preparation

After crushing, either wet ball and/or rod mills are used to grind the ore in preparation for flotation. Typically the ore is ground to 30-mesh to be applicable for most markets. Most ores are coarse liberating, up to 20-mesh, but the glass industry does not want any material over 30 mesh. Even though many applications for the minerals have a maximum iron specification grinding is done in a standard rod/ball mill with metal liners. The grinding mills are in closed circuit with cyclones, screens or hydraulic classifiers.

After grinding, one or two stages of cyclone desliming (at about 150 mesh) are required. The first stage of desliming follows grinding and removes primary slimes in the ore. The second stage of desliming follows scrubbing and removes the secondary slimes. Desliming is not absolutely necessary but the fines (clays) left in the flotation feed can cause a significant increase in reagent consumption and adversely effect selectivity.

It is usually advantageous to precede flotation with a scrubbing step to clean the mineral surfaces and remove slimes from the mineral surface. This improves flotation selectivity. The intensity, retention time and pulp density of scrubbing is not critical to flotation. Typically the ore is scrubbed for 3 to 8 minutes at 55 to 70% solids. Depending on the weathered characteristics of the feed, scrubbing can immediately follow grinding or after the first stage of desliming.

Flotation

Often the mined ore contains varying amounts of mica. Then the first beneficiation step is the removal of the mica by gravity methods and/or flotation. (see mica section of this chapter for details). Depending on the quantity and quality of the mineral, the mica will be sold as a by-product or rejected as a tailing waste. If a mica flotation is used, the tailings from the cells are dewatered to remove any excess reagents and increase the pulp density for the next flotation step (iron removal).

To remove the contaminating iron minerals from the ore, a separate flotation system is used. A conditioning step precedes iron flotation where the pH is adjusted to about 3.5 with sulfuric acid, the collector added and the pulp density adjusted. High solids-high intensity and a long retention time during conditioning are not required as the iron flotation is rapid and effective. Conditioning time is short, less than two minutes at 60% to 65% solids. Typical collector usage is 0.3 to 0.6 lb/ton. Consumption of acid is dependent upon the minerals in the ore.

Although the flotation time for iron flotation may be as much as five minutes, very little material (less the 2%) is actually removed in this process step. Sometimes it appears that the froth doesn't contain any solids. However, this flotation step is very important to remove as much of the iron mineral as possible. Because of the small amount of material being floated, a frother is added to form a manageable froth. The iron concentrate is discarded as tailings waste and the underflow from the iron flot is dewatered. If a feldspathic sand is the desired product, the flotation cell underflow becomes a final product. If a feldspar product and a quartz product are desired, then another flotation step is necessary to separate the feldspar away from the quartz.

A conditioning step precedes quartz-feldspar flotation step where the pH is adjusted to about 1.5 with hydrofluoric acid, an amine collector is added and the pulp density adjusted. Conditioning time is short, less than two minutes at 50% to 65% solids. Typical collector usage is 0.2 to 0.5 lb/ton. If needed, a frother is added to the feed immediately ahead of flotation.

The feldspar/quartz separation requires the use of the fluoride ion to activate the feldspar and to depress the quartz. The fluoride ion is a very effective depressant, and an excellent separation of quartz (cell underflow) from feldspar (cell froth) is obtained. Flotation time is three to five minutes. Sometimes the initial feldspar concentrate is cleaned once to recover any entrained quartz in the froth and to improve recovery. The middlings are usually recycled back to the rougher feed. A scavenger flotation circuit is almost never required.

Plant Practice

Hydrofluoric acid is a hazardous and dangerous acid that requires special safety conditions in the plant. Fluoride discharge from process water is strictly controlled and limited. Several research studies have been made to find a replacement system. These have shown limited success but none have been used in actual plant operation.

Flotation is the preferred method to remove the major amount of iron-contaminating material from feldspathic sand, quartz, and feldspar products. Dry magnetic separation is used as a final iron removal step on the flotation concentrates before shipment. However, one plant in Egypt has successfully replaced the iron flotation circuit with magnetic separation in a quartz-feldspar operation. This technique is not practiced in the United States.

Many industrial minerals are produced in multi-component plants, including quartz and feldspar. It is common to have mica, quartz, and feldspar contained in a deposit and to have a plant that beneficiates all these minerals commercially. The flowsheet in Figure 1 shows the processing strategy for such a multi-component plant. Other saleable products from industrial minerals plants producing quartz/feldspar include crushed stone, sand, clay, spodumene and beryl. In the multi-component plants, it is often difficult to determine the primary product and the by-products. The design and operation of multi-component plants must remain flexible to alter the flowsheets to meet changing market situations.

The feldspathic sand and feldspar concentrates from various mineral processing plants differ in chemical composition and physical characteristics. The sodium and potassium content make some flotation concentrates better suited for certain markets.

After flotation, the feldspathic sand, quartz and/or feldspar are filtered, dried and stored for shipment. Most operators use hi-intensity dry magnetic separators as the final clean-up step before bulk shipment or bagging. Depending upon the market and specifications, most of the quartz/feldspar produced is sold as ground material. Grinding is usually below 325 mesh and accomplished in ceramic ball mills to prevent iron contamination. The quartz products are sold with at least 99.5% silica. Typical iron specifications for quartz, feldspar and feldspathic sand are

Insulating Fiberglass	Can be greater than 0.080% Fe_2O_3
Glass Industry	Typically between 0.080 and 0.065% Fe_2O_3
Ceramics Industry	Typically less then 0.05% Fe_2O_3

High Purity Quartz Technology. Quartz and/or silica sand (SiO_2) has enjoyed a multitude of industrial uses. Today's technology has enabled the mass production of quartz to various levels of purity, depending on the end use. With the growth of the modern electronics and computer industry there has arisen a demand for very high purity natural quartz. Very few deposits have the purity of the natural quartz to meet the market specifications in these industries. The Spruce Pine area of North Carolina produces over 90% of the high purity quartz used in the country. High Pure quartz (Quintas Grade) is produced primarily from physical beneficiation techniques, including grinding, scrubbing, flotation, and magnetic separation. Ultra High Pure quartz (Iota Grade), typically produced from the High Pure products, receives additional beneficiation, commonly in the form of intense acid leaching and chlorination processing. Details of the technology are proprietary, and very little data is available.

Because of the advances in many of the high tech industries, the use and price of the high pure and ultrahigh pure grades have grown accordingly, thus creating a higher level of interest in finding suitable raw material deposits of quartz. Therefore, the evaluation process, although highly objective in the initial phases, can become rather complex and time consuming. Once the material has been initially qualified and performance determined, furnace trials must be conducted with potential customers to certify the raw material for their use.
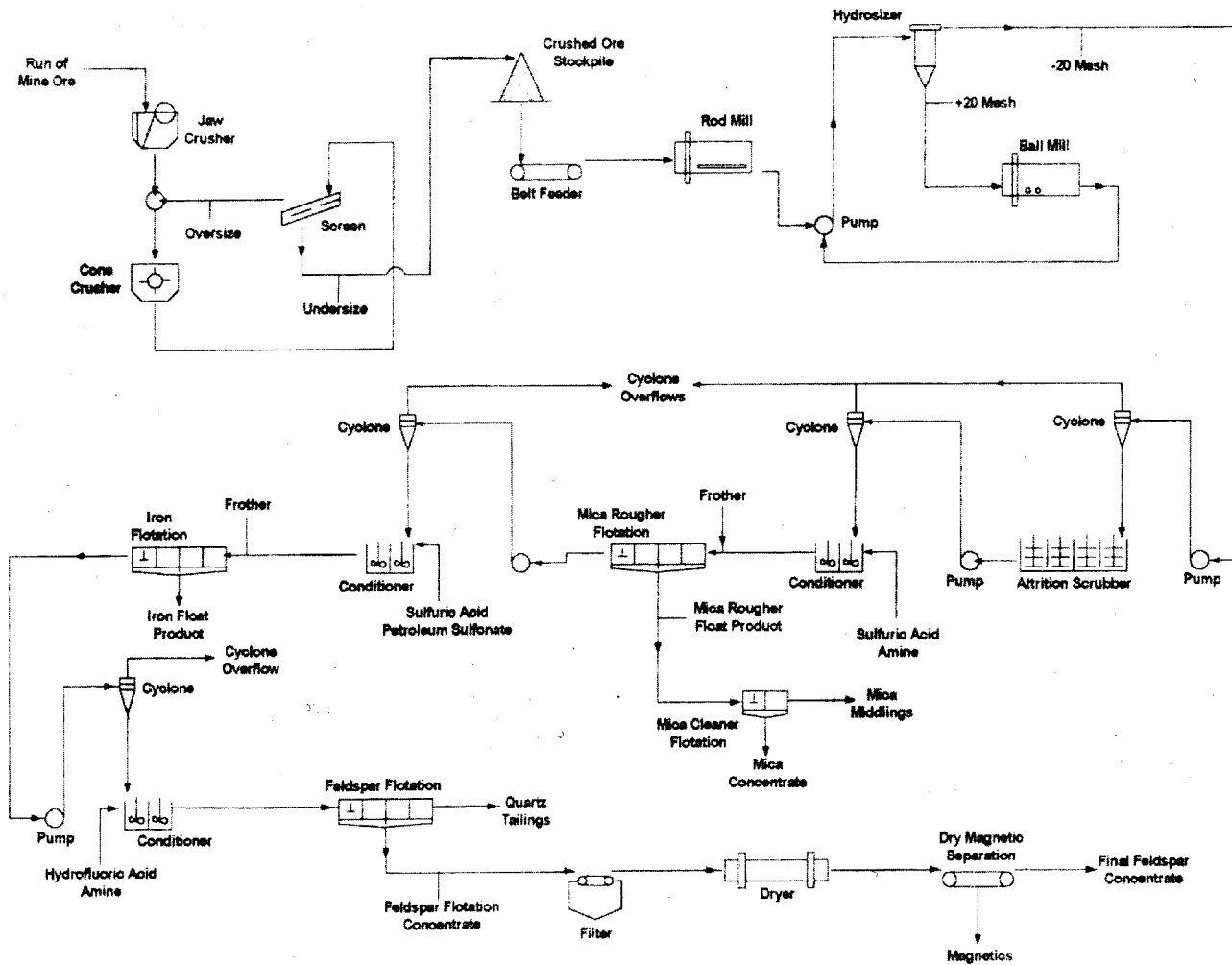
Figure 1. Schematic flowsheet – Typical Alaskite **flotation.** Mica, quartz, and feldspar flotation.

Because of the variety of end uses for the quartz products, it is difficult to assign exact product specifications, and quality is ultimately defined by performance. However, some typical guidelines can be applied to initially evaluate the quartz and/or to control the process. Typical limits on contaminants are as follows.

High Pure Quartz (PPM)

Fe	20 ppm max.	Al	200 ppm max.	K	50-80 ppm max.
Na	100 ppm max.	Ca	50 ppm max.	Li	2 ppm max.
Mg	30 ppm max.	Ti	5 ppm max.		

Ultra High Pure Quartz (PPM)

Fe	1.0 ppm max.	Al	15 ppm max.	K	2.0 ppm max.
Na	2.0 ppm max.	Ca	2.0 ppm max.	Li	0.5 ppm max
Mg	0.5 ppm max.	Ti	1.0 ppm max.		

It should be noted that the above do not include all of the elements that could possibly disqualify a quartz, but are instead listed as a basis for further evaluation. It should also be noted that while many describe the purity of quartz in terms of % SiO_2, this could be somewhat misleading, especially in the Ultra High Pure grades. A quartz product could be described as containing 99.999% SiO_2, but still contain trace elements on a ppm level that could hinder the performance of the quartz for end use in electronics or computer applications.

Once chemistry has been determined, actual performance must be evaluated to fully define the materials commercial viability, and this phase of the evaluation is almost always market specific. A common method is to produce a fused quartz product (e.g. crucibles) and examine the product for any flaws. This requires the production of bulk concentrates, sometimes ten tons or more, of the final quartz product on a pilot-plant scale under very controlled and noncontaminating conditions.

The High Pure processing plants are costly to construct, operate, and maintain due to the special considerations required to prevent contamination. Because the High Pure markets are relatively low volume operations, unit costs for processing can be high. A High Pure quartz plant almost always produces both High Pure quartz and Ultra-High Pure quartz. Development of markets for the High Pure grades is almost essential for the economic survival of a high-grade quartz facility. The production of a High Pure grade quartz material with a price of $500 to $1500 per ton can create a steady cash flow while the Ultra High Pure markets are being developed. High Pure quartz is also a much larger market as compared to the Ultra-High Pure quartz, consisting of many low-volume niche uses. The Ultra-High Pure grade price ($2000 to over $10,000 per ton) can then create a nice profitability once fully developed and proven. Most plants producing High Pure quartz material also produce the lower grade quartz products also.

KAOLIN

Kaolin is a white-to-near-white clay that contains kaolin minerals. The majority of kaolin particles have an equivalent spherical diameter less than two microns in products sold for coating pigments. Kaolin products sold as functional fillers or extenders have particle diameters less than 45 microns. Kaolin minerals are hydrous aluminum silicates that include the minerals kaolinite, dickite, nacrite and halloysite. Kaolinite, $Al_2Si_2O_5(OH)_4$, is the kaolin mineral of most importance for application as a white pigment in paper coating, paper filling, paint, plastics, rubber and a long list of other applications. Iron substitution for aluminum up to 2% on a number basis causes defects in the kaolinite crystal structure that is measured by the Hinckley Index.

Kaolin deposits are classified as primary and secondary. Primary deposits are formed through the *in situ* kaolinization of rock-forming minerals, namely feldspar and mica. Secondary deposits are formed through the erosion, transport and deposition of kaolin mineral-bearing sediments. Sedimentary kaolin is a kaolin deposit hosted in sedimentary rock that contains kaolin minerals that

are detrital, authigenic or both. Kaolin ore bodies show a continuum of kaolin mineral content that ranges from 10% to >95% by weight. The continuum of kaolin ore types with increasing kaolin mineral contents includes hydrothermal kaolin, residual kaolin, kaolinitic sandstone, sandy kaolin, and kaolin clay. The kaolinite particles in these ores have a particle size distribution that is different from deposit to deposit and show a particle size range from two millimeters to sub-micron.

Flotation may be used to concentrate kaolin from ores that have high gangue content such as hydrothermal or residual kaolin. Quartz, mica, feldspar and tourmaline are common gangue minerals in primary kaolins having low kaolin mineral content. Flotation can be used to concentrate kaolin minerals when the size of gangue minerals is forty-five to five microns and separation from kaolin minerals by gravity settling or hydrocylones is not practical.

Kaolin products are divided into several grades based on particle size, brightness or value-added processing. Standard grades are specified by percentage of particles by weight below two microns equivalent spherical diameter (ESD) as measured by a gravitational settling method for particle sizing. A #2 coating clay has 80 wt. % of particles below two microns, a #1 coating clay has 90 wt. % of particles below two microns, and a fine #1 coating clay has 95 wt. % of particles below two microns. Regular kaolin grades have GE brightness between 84 and 89, and high brightness grades have GE brightness greater than 89. GE Brightness is a measure of visible light reflectance made at 457 nm relative to a MgO standard on dried and pulverized kaolin compressed into a cake with 30 psi. Highly processed grades include delaminated, calcined, aggregated or engineered. Other important properties for kaolin pigments are shade, residue content measured on a 325-mesh screen, hard and dark particle counts, abrasion, moisture content, pH of slurry, Brookfield (low-shear) viscosity of clay-water slurry, and Hercules (high-shear) viscosity of clay-water slurry.

Flotation or selective flocculation may be used to beneficiate any kaolin grade that has a brightness or shade specification. Common minerals that harm kaolin brightness are iron oxides (hematite, goethite), iron sulfides (pyrite and marcasite), titania minerals (anatase, pseudorutile, rutile, brookite) and mica. Most kaolin operations located in Georgia use flotation or selective flocculation to remove titania minerals, which are difficult to remove by size fractionation or by high-intensity, wet magnetic separation (HIMS).

Feed Preparation

Kaolin used for pigments and additives is wet processed. Unless the kaolin is extracted from the wall of an open pit using a monitor, blunging is used, where kaolin ore is made-down into slurry with water in a range between 35% and 70% solids (Murray, 1980). The kaolin blunger is a tank with an impeller located near the bottom to provide mechanical work input. Chemicals are introduced during the blunging process to disperse particles liberated during blunging.

There are two facets to dispersion of kaolin particles: pH adjustment to induce a negative charge on both the edge and face of kaolinite particles to enable deflocculation, and the use of a dispersant chemical to increase the negative charge on mineral surfaces and thereby increase particle-particle repulsion. The choice of pH used to disperse the kaolin slurry is partly dependent on downstream processes utilized for beneficiation. Generally pH is adjusted to around 6.5 or 7.0 using sodium carbonate (soda ash) for clay slips transported by pipeline and beneficiated using a HIMS or selective flocculation. When flotation is used for beneficiation, the pH may be adjusted to between 8.0 and 9.5 using ammonia or sodium hydroxide. Primary dispersants used during blunging may include sodium silicate, sodium hexametaphosphate, sodium polyacrylate or a combination of dispersants. Dispersant dose depends on several parameters such as particle size, surface area, organic matter content and mineral content. Dispersant doses typically range from 0.1 wt. % to 0.5 wt. % on a dry basis. Care must be taken to select a dispersant chemistry that does not interfere with selection or extraction of impurities.

Flotation

Froth flotation is used to recover kaolinite in rejects from kaolin-refining operations. The rejects from hydro separators used for processing primary kaolins in Cornwall and Devon may contain upwards of 60% kaolinite (Pemberton, 1989). The kaolinite from these rejects can be recovered using flotation with chemistry selective for kaolinite that permits a separation from quartz, feldspar, tourmaline and other nonclay minerals.

Reverse froth flotation was introduced to kaolin processing in the early 1960s (Greene and Duke, 1962; Grounds, 1964).

Flotation of kaolin can operate with or without carriers. Greene and Duke (1962) used a ground limestone carrier. Their approach to kaolin flotation comprised adding the carrier to a dispersed kaolin slip, conditioning the kaolin-ground limestone slurry with a collector and frothing agent, and floating out the ground limestone with attached anatase. Cundy (1976) avoided the use of carriers by dispersing the kaolin slip at pH 9, introducing divalent ions such as calcium or barium to aggregate anatase particles, introducing a fatty acid such as oleic acid to coat the anatase particle surfaces, and aggregating the conditioned slip in the presence of air bubbles to separate of the anatase. Yoon and Hilderbrand (1986) developed a noncarrier flotation process using hydroxamate collectors instead of fatty acids.

Selective Flocculation

The basis of selective flocculation is to flocculate one or more minerals and leave the other minerals in a dispersed state to permit separation by gravitational settling in a thickener . Selective flocculation of kaolin can entail flocculation of kaolinite and removal of impurities in the overflow from a thickener or entail flocculation of specific impurities such as anatase and collecting a kaolin product from the thickener overflow.

A common selective flocculation process used by Georgia producers flocculates anatase out of a dispersed kaolin slip (Maynard et al., 1969). The process developed by Maynard (1968, 1974) requires that the blunged kaolin slip at pH 6.5 and dosed with sodium hexametaphosphate and sodium silicate, be conditioned with sodium chloride, and aged to aggregate anatase. A water-soluble, strongly anionic, high molecular weight ($>10^6$) polyacrylamide polymer is then added which acts to form anatase flocs that settle in a thickener. Other developments in selective flocculation were made by Shi (1986), who used an ammonium salt conditioning agent, and Behl et al. (1996) who used calcium salt and fatty acid to accomplish the titania aggregation. Garforth et al. (2000) further improved the process by adding sodium polyacrylate, a dispersant, in conjunction with addition of the high molecular weight polyacrylamide polymer flocculating agent. Although counter-intuitive for a flocculation process, this patented technology promotes the formation and separation of anatase- and mica-bearing flocs from the dispersed kaolin slip to increase floc settling rate and increase overall process recovery.

Plant Practice

Kaolin flotation and selective flocculation are practiced at wet process plants that produce white pigments. These plants are typically very high volume and have multiple process steps. After the kaolin has been extracted from the ore body and made down into slurry, the kaolin is transported by pipeline to a degritting operation. Grit is defined as particles >45 microns in size. Degritting is the removal of grit particles from the kaolin slip using dragboxes, spiral classifiers, hydrocyclones, and screens. Flotation and selective flocculation typically follow degritting or HIMS. HIMS is used to remove iron-bearing paramagnetic impurities that are harmful to brightness. HIMS may be used before or after flotation or selective flocculation in a kaolin plant. Some kaolin operations using gray kaolin containing organic matter have an ozone process before HIMS. Ozone gas is reacted with the organic matter in the kaolin in contact towers. The ozone breaks complex organic molecules into simpler and lower molecular weight organic compounds that can be removed with further processing and that do not absorb visible light, thereby increasing kaolin brightness.

Fractionation is the size classification of particles using solid bowl decanter centrifuges to make particle size cuts in the clay that are appropriate to grade. Fractionation may occur after titania impurities and other discoloring impurities have been removed. The coarse centrifuge rejects from fractionation that contain kaolinite stacks are typically ground using an attrition grinder. The attrition grinder delaminates the coarse kaolinite stacks into component platelets.

Following fractionation, kaolin is reduce-acid leached. The kaolin slip is acidified with sulfuric acid to pH in the range pH 2 to 4; alum may be added to help flocculate the kaolinite particles, and sodium hyposulfite is added to reduce ferric to ferrous iron. Ferrous iron absorbs less visible light in the blue wavelengths, thereby increasing brightness. The flocculated kaolin slip is then dewatered using a rotary vacuum filter to remove soluble salts that are inherent in the crude or were added during processing. The filter cake from the rotary vacuum filter is then dispersed again in a repulper with pH increased to a range between pH 6.5 and 7.5 using soda ash and a dispersant such as sodium polyacrylate.

The dispersed kaolin slip typically gets some chemical treatment with biocide to prevent bacteria and mold growth that may spoil the product. Higher biocide dosages are needed where process chemicals such as fatty acids are used. The clay slurry is further dewatered to a slurry shipping solids near 70% or is dried for shipment as bulk or bagged product. Drying is typically done using a spray dryer that yields a kaolin product form of small beads.

COAL

The processing and/or disposal of fine coal is of significant importance to the coal industry. In the US about half of the more than 1 billion tons of coal produced annually is processed in preparation plants. More than 300 plants in 20 states process as much as 3700 tph in one case, average plant capacity about 700 tph (Dorsett, 1995). Most of the clean coal production comes from coarse and intermediate particle sizes by gravity separation at a low cost ($1.50-2.50/ton). It is reported that 65% of the plants use heavy media. In almost one third of the preparation plants in the US, froth flotation is used for fine coal recovery (-0.5 mm), which amounts to about 10% of the total clean coal production. In this regard, it is estimated that 30 to 50 million tons of fine coal are discarded each year. Fine coal recovery is impeded by higher preparation costs ($4.50-7.00/ton) and dewatering costs ($2.00-6.00/ton).

Flotation

Coal, which consists of complex hydrocarbon molecules derived from the anaerobic alteration of plant matter, tends to be naturally hydrophobic and is associated with other inorganic mineral matter, including clay, quartz, and gypsum. Sulfur occurs as sulfate sulfur, pyrite sulfur, and organic sulfur chemically incorporated into the complex hydrocarbon molecules. Coal is ranked as anthracite, bituminous, sub-bituminous, and lignite, according to its carbon content, volatile matter, and energy value. Not unexpectedly, the coal hydrophobicity as revealed by contact angle and flotation response varies with coal rank and its petrographic composition, maceral type (Aplan, 1976; Arnold and Aplan, 1989; Laskowski, 2001). In fact, on this basis, resin macerals can be separated from other coal macerals by flotation (Miller and Ye, 1989; Miller et al., 1993). Of course the natural hydrophobic surface state of coal can be altered by oxidation processes which lead to an increase in polar oxygen groups at the surface, making flotation more difficult. Also, the naturally hydrophobic surface state is influenced by solution chemistry phenomena. For example, the adsorption of water-soluble macromolecules (organic colloids) such as dextrin can cause the coal surface to become hydrophilic (Haung et al., 1978; Miller et al., 1984). Such phenomena are the basis for the reverse flotation process in which pyrite is floated from coal (Miller, 1973; Miller and Lin, 1986).

Plant Practice

The general strategy is to float coal from the mineral matter, relying on the natural hydrophobicity of coal. Typically the feed, minus 0.5 mm, is conditioned with an oily collector, fuel oil, at a dosage of about 1.0 lb/ton as necessary and pH 6 to 8. For unoxidized high-rank bituminous coal, collector

addition may not be necessary, and flotation can be achieved with just a frother. In most other cases, an oily collector is required. The critical issue then is distribution of the collector and the selective wetting of the coal particle surfaces. In this regard the use of surfactants for dispersion/emulsification facilitates the distribution of the fuel oil collector and enhances its wetting of the coal particle surfaces (Yu et al., 1990). As a result, even difficult-to-float subbituminous coals can be floated if the oil emulsion is prepared properly.

Of course frother is required to develop a froth phase to carry the coal, and this is most commonly accomplished with MIBC (methyl isobutyl carbinol) at a level of addition which varies from 0.1 to 0.5 lb/ton (Aplan, 1976). Although a number of dispersants/depressants can be used to depress the mineral matter, generally this practice is not necessary. However, for feed material containing a high content of clay, contamination of the clean coal product can be a problem, and, in this regard, a dispersant might be added. Alternately, the feed can be deslimed or a split feed strategy can be practiced, in which case the slimes (minus 100 mesh) are separated by classifying cyclones and floated in a separate flotation circuit.

The use of column flotation cells has become quite popular in the coal industry. With the use of wash water, a clean coal product containing 5 to 6% ash can be achieved, as compared to 10 to 12% ash as might be achieved in single-stage flotation with mechanical flotation cells. In this way, improved coarse coal yield can be achieved with columns and the yield optimized to meet ash specifications. The key is to maximize the incremental ash. A most recent review of coal flotation technology and practice is given by the set of five papers published in *Advances in Flotation Technology* (Parekh and Miller, 1999).

PHOSPHATE

World fertilizer production from phosphate continues to be a crucial factor for the efficient growth of crops to feed the peoples of the earth. Phosphate is an essential ingredient of fertilizer, and the world production of phosphate rock is around 140 million tons per annum with reserves of 12,000 million tons. It should be noted that the U.S. is the world's largest producer of phosphate with most of its ~40 million tons per annum coming from the vast sedimentary deposits of Central Florida. In the U.S. phosphate rock was mined by 10 firms in 4 states, and upgraded into an estimated 39.7 million tons of marketable product valued at $1 billion, f.o.b. mine site in 2000. Florida and North Carolina accounted for 85% of the total domestic output, with the remainder produced in southeastern Idaho and northeastern Utah. However high-grade phosphate ores, particularly those containing few contaminants, are being progressively depleted and production costs are increasing. As discussed at the International Engineering Foundation Conferences on Phosphate Beneficiation, December 1993 and 1998, Palm Coast, Florida, and more recently at the Engineering Foundation Conference Beneficiation of Phosphate III, December 2001, St. Pete Beach, Florida, many technological problems must be solved if we are to continue to produce phosphate rock at our current rate of consumption. Proceedings of the first two conferences have been published (El-Shall et al., 1993; Zhang et al., 1999). The 2001 conference is scheduled to be published in 2002.

There are two main types of phosphate deposits, igneous and sedimentary, which have widely differing mineralogical, textural and chemical characteristics. Igneous rock is often associated with carbonates and/or alkalic intrusions and is generally quite crystalline and low in grade. Most phosphate rock production comes from sedimentary marine phosphates. Sedimentary deposits account for the majority (87%) of the phosphate reserves and resources. Consequently it is not surprising that 80% of the world production of phosphate rock comes from the mining and concentration of sedimentary phosphate ores. Most of the sedimentary phosphates are earthy in appearance, cryptocrystalline, and associated with gangue minerals which may include appreciable amounts of dolomite, quartz, hematite, aluminosilicates and clay minerals. The phosphate content in currently mined rocks can range from over 40% to below 5% P_2O_5. The biggest technical problem facing the Florida operations is lower grade resources with an increasing content of MgO. As the mining operations progress to the south, the overburden and clay slimes increase significantly. Disposal of the slimes is a serious environmental problem that has yet to be solved.

Flotation

The chemistry fundamentals of fatty acid flotation of phosphate minerals have been studied extensively, and this research provides a basis for the understanding of industrial practice. However, there is still much unknown regarding the collector adsorption and oil wetting phenomena which occur in the actual flotation of phosphate rock at plant sites. Important issues include water quality as well as structure and composition of phosphate minerals. For example, the significance of composition is revealed in oleate adsorption studies for different apatites as shown in Table 1 (Yehia et al., 1993).

Table 1. Comparison of Adsorption Density, Contact Angle, and Flotation Recovery for Apatite Minerals with Oleate as Collector at 5×10^{-4} M and pH 10.

Mineral	Adsorption Density, mg/m^2	Surface Coverage	Contact Angle, degrees	Flotation Recovery, %
Fluorapatite	1.08	0.49	55	88.7
Carbonatapatite	0.86	0.39	43	71.3
Hydroxylapatite	0.52	0.24	38	62.5
Chlorapatite	0.34	0.20	No Attachment	53.2

It is evident that the adsorption density, hydrophobic surface state, and the flotation recovery decrease in the order fluorapatite, carbonatapatite, hydroxylapatite, and chlorapatite. Certainly it is to be expected that similar variation would be expected for the flotation of phosphate rock in plant operations. In any event, it has been well-established that oleate will chemisorb at the apatite surface, forming a calcium oleate surface species (Lu et al., 1998). Unlike other semi-soluble salt minerals, the adsorption generally is limited to monolayer coverage, or less, apparently due to solubility considerations and the calcium site density at the apatite surface. Nevertheless, it seems that this chemisorbed fatty acid at the apatite surface provides sufficient hydrophobicity to allow for the spreading of fuel oil typically used in plant operations.

Plant Practice

Conventional plant practice for the siliceous sedimentary phosphate resources involves the double float process, also known as the "Crago process", as shown in Figure 2. This flotation process is used around the world, and has been practiced for at least 60 years. A number of useful references exist which discuss the flotation technology for phosphate (Wiegel, 1999a and 1999b; Zhang, 1993; Davis and Hood, 1993; MaHeesh et al., 1996; Lu et al., 1997 and 1998). The phosphate ore is classified into four size fractions, the pebble (+16 mesh), the coarse (16×35 mesh), the fine (35×150 mesh), and the slime (-150 mesh). The pebble product, containing over 28% P_2O_5, is one of the final products. The slime, containing a significant amount of ultra fine clay mineral particles, is discharged to tailings due to difficulties in the separation of phosphate minerals from the very fine clay particles. Typically the coarse and fine size fractions, containing substantial quartz, are fed to the plant for beneficiation by froth flotation with an insoluble oily collector consisting of a mixture of fatty acid and fuel oil. The coarse and fine feeds are conditioned separately at 70% solids with fatty acid and fuel oil at alkaline pH. After conditioning the phosphate minerals (such as francolite, a cryptocrystalline carbonate fluorapatite) are generally floated in mechanical cells. The flotation concentrates are further upgraded by reverse amine flotation to remove the entrained quartz particles after being scrubbed with sulfuric acid to remove the adsorbed fatty acid and fuel oil. Both mechanical and column flotation cells are used in the Florida operations. Interestingly the columns have been used for rougher flotation of coarse feed. In most applications in other industries, columns have been used for fine particle flotation.

High solids conditioning (>70% by weight) with fatty acid/fuel oil mixtures is used extensively in the double float process as practiced for sedimentary ores to improve the phosphate recovery and reduce collector consumption. Some research has been carried out to investigate the phenomena involved and to optimize the conditioning parameters. It has been found that the phosphate recovery
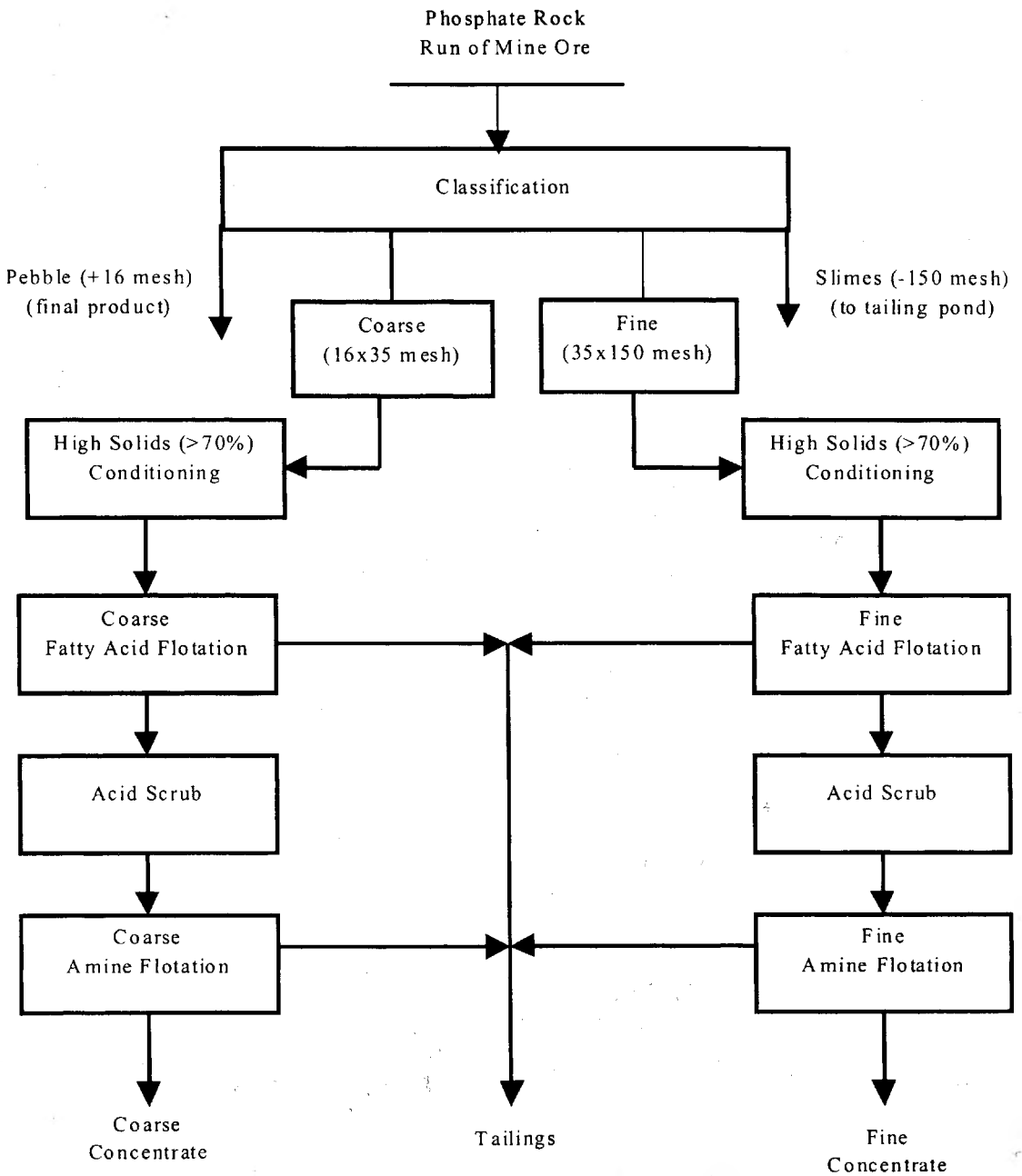
Figure 2. Flowsheet for the processing of Florida phosphate rock.

increases as the energy input for conditioning increases up to a critical value and then decreases as the energy is increased further. At a higher level of energy input, recovery decreases due to the generation of slimes under extremely strong agitation. In view of the mechanisms of anionic collector adsorption, reducing the water content during conditioning has the dual effect of increasing the concentration of collector in the aqueous phase and reducing the quantity of activating ions. As is the case for most systems that involve insoluble oily collectors, the distribution of the collector is an important consideration. In addition to high solids conditioning, the use of certain nonionic surfactants significantly increase the recovery of coarse phosphate apparently due to improved froth stability and improved dispersion/attachment/spreading of the fatty acid/fuel oil collector.

Recent research relates the improved flotation with high solids conditioning to the selective wetting of phosphate minerals by the fatty acid/fuel oil mixture (Lu et al., 1997). Results from an experimental study with a high-speed video system clearly show the preferential transfer of oil to a francolite surface (carbonate fluorapatite) and helps to explain the high solids conditioning mechanism. When a quartz particle with an attached oil drop interacts with a francolite particle, the oil drop will spread at the francolite interface. When these two particles are forced apart, a major portion of the oil drop is transferred to the francolite surface. A small portion of the oil drop may remain at the quartz surface. This procedure happens again and again during high solids conditioning, and the fatty acid/fuel oil collector which initially may be at quartz surfaces will ultimately be transferred to the surfaces of francolite particles. In this way, flotation selectivity is improved. Therefore, both recovery and selectivity in phosphate flotation with fatty acid/fuel oil are improved by high solids conditioning.

POTASH

The world production of potash, which exceeds 30 million tons of equivalent K_2O annually, comes primarily from Canada, Russia, and the Ukraine. U.S. production of potash from New Mexico and Utah has diminished significantly because of low grades and high clay content. The important potash ores typically contain sylvite, halite, and insoluble gangue minerals, including clays and carbonates. Other common potash minerals are listed in Table 2.

Table 2. Common Potash Minerals (Zandon, 1985)

Mineral	Formula	Specific Gravity	% K_2O
Sylvite	KCl	1.99	63.17
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$	1.60	16.95
Kainite	$KCl \cdot MgSO_4 \cdot 3H_2O$	2.13	18.92
Langbeinite	$K_2SO_4 \cdot MgSO_4$	2.83	22.70
Leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	2.25	25.69
Schoenite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$	2.15	23.39
Polyhalite	$K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 4H_2O$	2.78	15.62

Flotation is used to separate the potash minerals, particularly sylvite from halite, in about 70% of the operations. Alternately, evaporation and crystallization are used in certain instances. The unique feature of potash flotation is that the separation is accomplished from a saturated brine, typically using long-chain alkyl amines for flotation of the sylvite. Almost all potash flotation plants have a crystallization step to maintain a brine balance and reduce potash losses. In addition to sylvite flotation, other potash minerals that are recovered by flotation include schoenite, carnallite, and langbenite.

Flotation

In general, soluble salt flotation with both cationic (alkyl amines) and anionic (alkyl sulfates) collectors can be explained based on hydration phenomena at the salt surface (Hancer et al., 2001).

Some salts tend to promote water structure, and these salts, which are extensively wetted by their saturated brines, cannot be floated with either alkyl amines or alkyl sulfates. Such is the case for halite, NaCl. On the other hand, some salts tend to be water-structure breakers, and these salts, which are not wetted completely by their saturated brine, can be floated with either alkyl amines or with alkyl sulfates. Such is the case for sylvite, KCl. For example, the brine contact angles for sylvite and halite are compared in Table 3 in the absence of collector. In view of the foregoing, it is not unexpected that sylvite flotation will be sensitive to brine composition, and, for example, the presence of magnesium (a structure maker) in the brine depresses the amine flotation of sylvite.

Table 3. Advancing Contact Angle Measurements for Saturated Brine at the Surface of KCl and NaCl (No Collector Present)

Salt	Contact Angle, degree
KCl	7.9 ± 0.5 ($12.0 \pm 1.4*$)
NaCl	$0*$

*Measured on the natural cleavage plane of a single crystal.

In addition to the salt properties and the brine composition, the presence of clay slimes is an important factor which can impede flotation (Laskowski, 1994). This is particularly true in the case of sylvite flotation. Generally in potash flotation, the slimes must be blinded or the feed deslimed prior to sylvite flotation with amines. It is well established that amine flotation of sylvite occurs when the amine precipitates from the brine. In this regard, is appears that such a similar event occurs at the sylvite surface, leading to the hydrophobic surface state.

Finally, the effect of temperature in sylvite flotation with amine is worth noting. It has been established that higher temperatures result in a decrease in sylvite flotation with amine collectors. Such an effect is even seen in plant operations where the potash recovery decreases during the summer season. This temperature effect might be due to the increased solubility of the amine at higher temperatures. Also, the behavior of KCl may change with temperature, from a water-structure-breaking salt at lower temperatures to a structure-making salt at temperatures above 30°C.

Plant Practice

One of the major concerns in flotation operations is the presence of slimes and their elimination prior to sylvite flotation from halite. A number of process strategies are used, and these include:

* mechanical desliming with classification cyclones
* flocculation-flotation desliming

In the case of desliming by classification, intensive scrubbing is required, and this treatment may contribute to sylvite loss to the slimes product. To avoid this loss of sylvite by abrasion during scrubbing some operations flocculate the clay slimes and remove them by flotation with low levels of collector addition prior to the flotation of sylvite (Tippin et al., 1998).

For feed containing a low level of clay slimes or for treatment of feed with residual slimes, slime depressants, polymers, can be used to prevent amine adsorption by clay. These polyelectrolytes include both anionic and cationic polymers as well as nonionic polymers, and carboxy methyl cellulose. Considerable savings in collector consumption can be achieved with the use of such polyelectrolytes with improved selectivity in the flotation of sylvite from halite and clay slimes.

Finally, it should be noted that frequently potash flotation plants have both fine and coarse flotation circuits, split feed, not unlike the practice in phosphate plants and in some coal plants. In the case of the flotation of coarse sylvite, oil is frequently used to promote the flotation response (Laskowski, 1997). Again, the use of oil is similar to the strategy used in phosphate and coal flotation.

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