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# CHEMICAL ENGINEERING

## On the Phosphate Rock Beneficiation for the Production of Phosphoric Acid in Saudi Arabia

**T.F. Al-Fariss, H.O. Ozbelge and H.S. El-Shall***
*Chemical Engineering Department, College of Engineering, King Saud University, P.O.Box 800, Riyadh 11421, Saudi Arabia and *Florida Institute of Phosphate Research 1855 W. Main St. Bartow, FL. 33830, U.S.A.*

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**Abstract.** The establishment of phosphate fertilizers and the phosphoric acid industries are expected in Saudi Arabia in the near future. This is an attempt to review the processes involved in the phosphate rock beneficiation. Existing processes are compared and contrasted, and the areas which need more study for better understanding are indicated.

### Introduction

With the expected commencement [1] of fertilizer facilities with TSP, DAP and NPK plants in 1990, the phosphoric acid needs of Saudi Arabia are expected to be around 250.000 tons $P_2O_5$ per year. A new phosphoric acid plant seems in prospect using the phosphate rock from the Sirhan Turayf region in the north and sulfuric acid produced as a by-product of the petrochemical industry in the east.

The first challenge in the phosphate industry is the reduction of impurities in the phosphate rock so that it is suitable for phosphoric acid production. This review addresses itself to this challenge: it considers the beneficiation methods for the phosphate rock.

Phosphate mineral, mainly of the apatite group, is found in the nature mixed with a wide variety of impurities such as clay, silica, calcite, dolomite, organic matter and various other inorganic compounds. Because of the adverse effects of these impurities [2] in the manufacture of phosphoric acid (See Table 1) they must be reduced to the lowest possible level. The beneficiation method which must be employed to achieve an efficient separation depends on the impurities present and the properties of the rock. Usually clay can be separated by simple washing and

**Table 1.** Effects of impurities in the manufacture of wet process phosphoric acid [2]

| Impurity | practical levels in rock fed to acidulation | Desirable properties | Undesirable properties | percentage of impurity passing into product acids |
|---|---|---|---|---|
| Aluminium | 0.2-3% $Al_2O_3$ | Reduces corrosion caused by fluoride ion | Forms gel-like phosphate complex which impair filtration, increase acid viscosity and excessive precipitation in the product | 70-90 |
| Iron | 0.1-2% $Fe_2O_3$ | In cases of excessive presence in the rock, recoverable as iron oxide | Forms complex phosphates which impede filtration. Strong influence on acid viscosity excessive sludge formation | 60-90 |
| Magnesium | 0.2-0.5% Mgo | May have nutrient value | Forms complex phosphates and fluosilicates, impairs filtration, increases viscosity and sludge in the product. | 90-100 |
| Fluorine | 2-4% F | Can be reacted and recovered as by-product | Liberated partly as HF part held by filter; part may contribute to sludge formation. More fluorine generated during concentration. If $H_2SiF_6$ formed by reaction with $SiO_2$ may modify cristal formation | 25-75 |
| Silica | 1-10% $SiO_2$ | To convert HF to less harmful $H_2SiF_6$ | In high proportions causes errosion problems in acidulation tanks and piping | 5-40 |
| Strontium and Lanthanides | 0-3% SrO |  | Inhibits recrystallization of hemihydrate gypsum. Forms insoluble compounds in 40% $P_2O_5$ acid | n.a. |
| Chlorine | 0-0.05% |  | Causes severe corrosion problems above 0.03% | 100 |
| Carbonates | 0.7-8% $CO_3^=$ |  | Increases sulphuric acid consumption | n.a. |
| Organics | 0.1-1.5% C |  | Foam formation during acidulation Impair filtration by blinding filter cloth. Dark colour in product acid. | 15-70 |
| Cadmium | up to 250 ppm |  | Toxic metal, accumulated in the soil treated with fertilizers containing $P_2O_5$ produced by wet process | 70 |
| Uranium | 35-400 ppm $U_3O_8$ | Recoverable from product acid and can be sold as by-product |  | 75-80 |

scrubbing. Separation of silica, calcite and dolomite may require more sophisticated beneficiation methods. Most frequently, flotation is used to separate the siliceous gangue. Application of this process to remove the carbonates (calcite, dolomite, etc.) is also under investigation by different research groups [2]. In addition to flotation, calcination has been proposed and is being used to beneficiate calcitic phosphate ores. A review of phosphate beneficiation techniques utilizing these two processes is given below.

## Flotation

For over 50 years flotation has been the most effective method in upgrading phosphate ores both of sedimentary and igneous origin [3-23]. Generally, igneous phosphates are of high-grade (37-38% $P_2O_5$) and are made up of crystalline apatite. In sedimentary deposits, however, the phosphate may be present in a wide variety of forms. The actual phosphate content is generally lower than that in igneous deposits.

Phosphate deposits in Saudi Arabia are of sedimentary origin. Even though these deposits are of relatively high grade, carbonate minerals (calcite) constitute the majority of the associated impurities. In this context, this review will concentrate on recent advances in beneficiation of phosphate ores containing carbonate gangue. However, a survey of beneficiation methods dealing with other types of ores are included also.

## Siliceous Ores

A large sedimentary deposit with high silica content is mined in Florida at a rate of one third of the annual world phosphate production. In the beneficiation of Florida phosphate rock, flotation plays a predominant role because it is the most economical way to separate the phosphate values from the sand and other impurities contained in the matrix. Typically, the matrix is washed and deslimed at 150 mesh. The material finer than 150 mesh is pumped to clay settling ponds. An estimate of 20-30% of the phosphate (contained in the matrix) is lost with these clays. The rock coarser than 150 mesh is screened to separate pebbles (−31/4 + 14 mesh) which are of high phosphate content. Washed rock (−14 mesh + 150 mesh) is sized into a fine (usually 35 × 150 mesh) which are treated in separate circuits. A two-stage flotation process is used in these circuits, where the feed is subjected to rougher flotation (fatty acids and fuel oils are used as collectors) to separate the phosphates from most of the sand. The rougher concentrate is scrubbed by sulfuric acid to remove the fatty acids and oils. Scrubbed material is then subjected to cleaner flotation (amine collectors are used) to float the sand. This stage of flotation is sensitive to impurities in water, so, fresh water is used instead of recycled water, the fatty acid circuit uses recycled water from the clay ponds.

Flotation of phosphates from the fine feed (35 × 150 mesh) presents very few difficulties and recoveries in excess of 90% are commonly achieved using conventional mechanical cells. On the other hand, recovery of the coarse phosphate feed is much more difficult and flotation by itself normally yields recoveries of just 60% or even less. In the past, hammer mills were used for size reduction of the coarse feed. However, due to high maintenance costs and loss of phosphates as fines (generated during milling) its use has been discontinued. The industry, however, has taken other approaches to circumvent the problem of low flowtability of coarse particles, for example, the use of gravitational devices such as spirals, tables, launders, silsluices and belt conveyors modified to perform a "skin flotation" of the reagentized pulp. Although, a variable degree of success is obtained with these methods, they have to be normally supplemented by scavenger flotation. In addition, some of them require excessive maintenance, have low capacity or high operating costs so performance is less than satisfactory, and in certain cases use has been discontinued.

The exact reasons that explain the low recoveries of coarse particles in conventional flotation machines are not clear. There have been several hypothesis about the behavior of such particles. For instance, the low flotability of large particles could be related to the extra weight per unit surface area that has to be lifted to the surface (usually under highly turbulent conditions) and then transferred and maintained in the froth layer. Factors such as density of the solid, turbulence, stability and height of the froth layer, tenacity of the particle - bubble attachment, depth of the water column, viscosity of the froth layer, and other variables that can indirectly influence these factors determine the flowtability of coarse particles.

In coal and sulfides industry some effort towards improving the flotation of coarse particles through stabilization of the froth layer, increasing froth height, improvement in froth density, etc., through the addition of fine particles or different frothers have been undertaken.

Changes in the design of the flotation cells presently used in the industry could constitute an alternative route to attack the coarse flotation problem.

Another important disadvantage of the existing beneficiation technology is its inability to separate impurity minerals containing MgO. Currently, almost all of the phosphate production is from the central Florida district. Such ores contain low levels of magnesium impurities. However, it is expected that the current deposits of lower MgO content will be depleted in the next few years. Unfortunately, the future phosphate reserves, located south of the present mining district, have a severe limitation in the form of high MgO content and would require innovations in the beneficiation technology.

The reagents used in beneficiation of Florida phosphates are listed below with typical consumption rates:

| Circuit | Reagent | Rate, kg/ton of Feed |
|---|---|---|
| Rougher | Fatty acid island | 0.4 - 0.8 |
| | Fuel oil | 0.75 - 1.5 |
| | Base (ammonia) | 0.2 - 0.4 |
| Deoiling | $H_2SO_4$ | 1.0 - 2.0 |
| Cleaner | Amine (tallow) | 0.125 - 0.25 |
| | Kerosene | 0.25 - 0.50 |
| | Caustic soda | 0.25 - 0.50 |

These usage rates are relatively low compared with those used in flotation of the siliceous ore from Senegal as listed below:

| | |
|---|---|
| Tall oil | 1.8 kg/ton feed |
| Diesel oil | 4/1 kg/ton |
| Sodium hydroxide | 0.6 kg/ton |
| Sodium carbonate | 0.1 kg/ton |

The difference in the consumption of reagents can be attributed to the fine size of the flotation feed since desliming is done with 30-40 micron particles. Nevertheless, the flotation separation of this ore is much simple (one stage-anionic flotation) because the high phosphate content of the Senegalese ore (30-31% $P_2O_5$).

## Carbonaceous Ores

The increase in demand for phosphate is accompanied by a rapid depletion of high-grade ores. Thus, the world attention is directed toward beneficiation of low-grade ores with carbonate gangue. The studies can be classified into several categories:

### Depressants for carbonates in igneous ores

In igneous ores, carbonate frequently occurs as calcite rather than dolomite. In many of these ores, it was found that apatite is somewhat more floatable than calcite.

Deppressants were investigated [24-28] in order to increase the selectivity of separation using the traditional collectors. Examples of these depressants include: starch (Brazil), tannin-based depressant "Totanim" (South Africa), and starch - ethoxylated carbonic acid (U.S.S.R.). All of these depressants are used with the traditional fatty-acid collectors together with added hydrocarbons such as oily gas-tars or kerosene. It is worth mentioning that, to obtain high flotation efficiency, favorable froth modifications are produced by the use of such reagents as nonyl phenyl polyglycol ether and ethoxylated alkyl phenol (U.S.S.R) [17].

## Highly selective collectors for apatite in igneous ores.

More recently, the emphasis in flotation research has changed from the use of depressants to the use of more selective collectors to replace the fatty acid-based reagents. For example, amphoteric sarcosine is used successfully in Finland [29] to float apatite from calcite. Another collector, amino-carboxylic acid reagent (Lilaflot 05-100), has been developed in Sweden and resulted in excellent separation of apatite from calcite, both in Swedish and Russian ores. Warren Springs Laboratories (U.K) have developed a new reagent of the immino bis methylene phosphoric acid class, which has given good selectivity in floating apatite from dolomite of igneous ores [30].

## Depressants for apatite in sedimentary ores

The bulk of the world's phosphate reserves is located in sedimentary deposits which also contain appreciable amounts of carbonate. Since these are the most difficult type to treat, initial mining has been confined to the limited number of deposits in which the carbonate is sufficiently friable as to be easily rejected, by sizing into a fines fraction. The increasing demand for phosphate and the depletion of the more amenable reserves, however, have steadily increased the pressure for treatment of these difficult sedimentary phosphate-carbonate deposits, and probably no other mineral processing topic has attracted so much reserach in recent years [19-31].

As already noted there is natural selectivity margin favoring apatite in igneous phosphate-carbonate ores. With sedimentary phosphate ores, however, this is reversed and tends to operate in favor of carbonate minerals. Consequently, when fatty acid flotation separation of these minerals was first adopted, the search focused not on carbonate, but on possible phosphate depressant systems. Examples include the use of orthophosphoric acid in the Karatou Process [32,33]. A pH of 6.0 is achieved by using 6.0 kg $H_3PO_4$/ton of ore. A synthetic fatty acid ($C_{10} - C_{16}$) is added at a rate of 0.3 kg/ton. After carbonate flotation the pH is raised to 7.6-8 using 1.5 kg/ton sodium hydroxide and a toll oil (1.7 kg/ton) is added to float phosphates, and sodium silicate at 0.5 kg/ton is used to depress the silica. The reported data [32,33] indicate that only 75% of the phophate can be recovered at a grade of 28.0% of $P_2O_5$ from a feed of 22.5% $P_2O_5$. In addition, the concentrate contains 1.3% MgO which is higher than the requirements by phosphoric acid plant (less than 1.0%). Moreover, the cost of reagents are excessive to make the process economically attractive. Aluminum sulfate, Rochelle salt, (sodium potassium tartrate), (E.N.S.C. Nancy - O.C.P. Morocco Process) are used as shown in diagram given in Fig. 1.

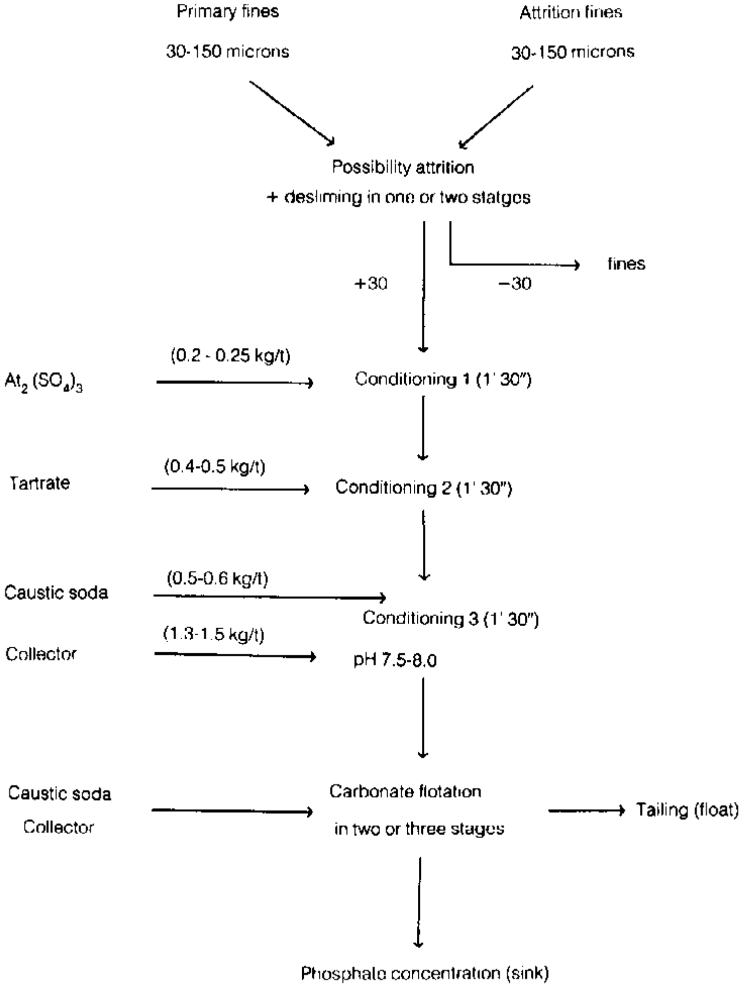

**Fig. 1. Diagram of the French-Moroccan [24].**

In this process, the selectivity of dolomite separation is reported to be very good with over 80% phosphate recovery [24]. However, the presence of clays due to imperfect desliming can reduce the efficiency of separation. Thus, good desliming is a prerequisite for success.

The use of silicofluoride either as sodium salt or hydrofluosilic acid has been reported to be effective as a depressant for phosphate minerals in their separation from the carbonates gangue [25].

Addition of alkylphosphoric acids alone or in combination with HF is found to be effective as apatite depressants as reported by TVA researchers [26]. However, the process was found to be ineffective in processing undeslimed flotation feeds or high MgO ores because high reagent doses are needed to achieve separation which renders the process uneconomical.

Water soluble salts or tripolyphosphates and hexametaphosphates were used by IMC's (International Minerals Company, U.S.A.) researchers to depress phosphate minerals [27,28]. Dolomite is floated with sodium salt of sulfonated oleic acid in the pH range of 5.5 to 6.0. Even though this process has been tested on a pilot plant scale, IMC is not proceeding with its application commercially. Instead, they are in the process of building a heavy media separation plant. The reasons for not using the above mentioned process are not known. Nevertheless, one may speculate that the cost of reagents as well as the increase of phosphate concentration in recycled water may depress apatite flotation in other circuits dealing with low MgO feeds. Also, the presence of high levels of sodium ions in process water stored in clay settling ponds could be objectionable since it can lead to clay swelling.

## Highly selective collectors for carbonates in sedimentary ores

As with the igneous apatite-carbonate ores, much research has been devoted to the possible substitution of the traditional fatty acids by a novel collector. For example, the family of reagents developed by the French researchers [34] involving alkalylaminopropionic and propionic acids have demonstrated good separation of MgO from Tunisian ore. These are amphoteric reagents that are used to float dolomite first at pH 7 then at 5.0 as shown in Table 2.

Even though the rates of reagents consumption are not reported and these types of reagents are quite expensive, it is worth testing their efficiency in separating carbonate gangue from the Saudi Ores.

In another process, the same workers have proposed bulk flotation of the phosphate and carbonate away from silica by using phosphoric ester - fuel oil mixture under moderately basic conditions. Phosphate is then depressed subsequently by $H_2SO_4$ at pH 6.0 and carbonate is refloated with a small addition of collector.

**Table 2.** **Separation of dolomite from tunisian phosphate ore by amphoteric reagents**

| Products | Weight | Content (%) | | | Distribution (%) | | |
|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | MgO | $SiO_2$ | $P_2O_3$ | MgO | $SiO_2$ |
| 1st Float | 22.7 | 14.52 | 6.11 | 6.85 | 12.3 | 87.8 | 25.5 |
| 2nd Float | 7.2 | 14.76 | 0.55 | 34.78 | 4.0 | 2.5 | 41.0 |
| Sink | 70.1 | 31.83 | 0.22 | 2.91 | 83.7 | 9.7 | 33.5 |
| composite | 100.0 | 26.67 | 1.58 | 6.10 | 100.0 | 100.0 | 100.0 |

## Other flotation separation techniques

Research into developing different techniques to separate dolomite from apatite has been pursued in various laboratories. Examples of such techniques are:

a) *IMC process* [34,35] in which dense media of phosphate pebbles by Dynawhirlpool to reject a dolomite-rich lighter fraction is followed by grinding of the sink pebbles and treatment by flotation in conjunction with the original fines. The classic two-stage flotation system is modified by addition of a third stage to float phosphate by an amine-kerosene mixture at slightly acidic pH. The process diagram is shown in Fig. 2 and summary of the process data is given in Table 3.

The process is quite complex. IMC is in the process of building a commercial plant.

b) *The U.S. Bureau of Mines process* involves scrubbing and desliming at 150-mesh to remove MgO-rich slimes. Fatty acid-fuel oil is used to float apatite and dolomite at pH 9.5 followed by two or three cleaner stages using sodium silicate as a dolomite depressant. The process is not successful in removing dolomite to less than 1.0% MgO in the concentrates in all situations.

c) *Two stage conditioning process:* In another process developed by Moudgil *et al.* [36], separation of dolomite from south Florida phosphate is achieved by first conditioning at pH 10 with a fatty acid, followed by reconditioning at a pH around 4.0 using either $H_2NO_3$ or $H_2SO_4$ as pH modifiers. The reconditioning pH and collector concentrations were found to be major parameters of flotation selectivity.

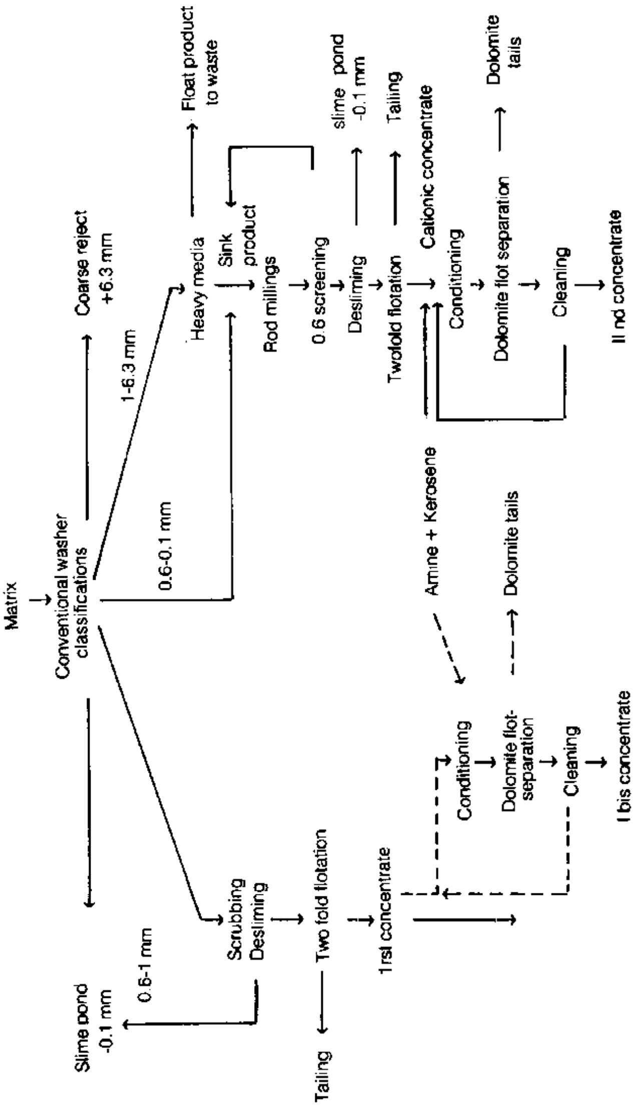

**Fig. 2.** Basic process diagram for IMC process

**Table 3. Results of IMC process [23]**

| Products | Weight | Analysis (%) | | | Distribution (%) | | |
|---|---|---|---|---|---|---|---|
| | (%) | BPL | Insol | MgO | BPL | Insol | MgO |
| + 6.3 mm reject | 1.0 | 12.25 | 14.75 | 14.00 | 0.6 | 0.3 | 3.5 |
| 1-6.3 mm pebble | 4.4 | 45.18 | 14.09 | 5.08 | 10.2 | 1.2 | 5.5 |
| 0.6-1 mm feed | | | | | | | |
| 0.6-0.1 mm feed | 58.2 | 22.65 | 66.33 | 0.36 | 67.6 | 75.9 | 5.3 |
| –0.1 slimes | 32.0 | 7.58 | 30.77 | 10.50 | 12.5 | 19.4 | 84.4 |
| Composite matrix | 100.0 | 19.49 | 50.85 | 3.98 | 100.0 | 100.0 | 100.0 |
| 0.6-0.1 Amine conc. | 17.7 | 68.88 | 3.86 | 0.83 | 62.6 | 1.3 | 3.8 |
| 0.6-0.1 Amine tail | 4.2 | 7.16 | n.d. | n.d. | 1.5 | - | - |
| 0.6-0.1 Rougher* | 35.6 | 1.20 | n.d. | n.d. | 2.2 | - | - |
| –0.1 Scrub. Slime | 0.7 | 37.77 | n.d. | 6.81 | 1.3 | - | 1.3 |
| Composite 0.6-0.1 | 58.2 | 22.65 | 66.33 | 0.36 | 67.6 | 75.8 | 5.3 |
| 1-6 mm float reject | 1.14 | 18.33 | 12.59 | 13.10 | 1.1 | 0.3 | 3.8 |
| 1-6 mm sink product | 3.26 | 54.56 | 14.70 | 2.28 | 9.1 | 0.9 | 1.7 |
| Composite 1-6.3 | 4.40 | 45.18 | 14.09 | 5.08 | 10.2 | 1.2 | 5.5 |
| 0.6-0.1 feed | 5.81 | 45.68 | 31.09 | 1.04 | 13.6 | 3.5 | 1.5 |
| -0.1 slimes | 1.85 | 48.93 | 15.72 | 3.50 | 4.6 | 0.6 | 1.5 |
| Composite R.M. feed | 7.66 | 46.47 | 27.37 | 1.64 | 18.2 | 4.1 | 3.0 |
| Amine conc. | 3.77 | 64.23 | 2.30 | 1.54 | 12.4 | 0.2 | 1.4 |
| Amine tail | 0.56 | 30.21 | n.d. | n.d. | 0.9 | - | - |
| Rougher tail | 1.48 | 4.35 | n.d. | n.d. | 0.3 | - | - |
| Composite feed | 5.81 | 45.68 | 31.09 | 1.04 | 13.6 | 3.5 | 1.5 |
| Phosphate conc. | 3.45 | 66.47 | 2.22 | 0.98 | 11.8 | 0.1 | 0.8 |
| Dolomite tail | 0.30 | 38.50 | 3.67 | 8.00 | 0.6 | 0.1 | 0.6 |
| Composite amine conc. | 3.77 | 64.23 | 2.30 | 1.54 | 12.4 | 0.2 | 1.4 |
| Directly floated conc. I | 17.70 | 68.88 | 3.86 | 0.83 | 62.6 | 1.3 | 3.8 |
| From H.M. + grinding con. II | 3.47 | 66.47 | 2.22 | 0.98 | 11.8 | 0.1 | 0.8 |
| Total Concentrate | 21.17 | 68.49 | 3.59 | 0.85 | 74.4 | 1.4 | 4.6 |

d) *The salt flotation process:* University of Florida, (U.S.A.) investigators [37] have demonstrated that sodium chloride acts as an apatite depressant during flotation at acidic pH values with oleic acid, while dolomite flotation is not affected. It was observed however, that dolomite particles larger than 48 mesh are difficult to float and they tend to remain in the sink fraction. The trends observed during Hallimond cell tests of single and mixed minerals were confirmed with mixtures of minerals and a natural ore at bench scale level. In the bench scale tests, MgO content of the mineral mixtures was reduced from 5% to 1% less with at least 90% recovery of $P_2O_5$ in the sink fraction.

As mentioned above, the latter two processes have been developed on the bench scale. Further testing on pilot scale is needed to answer very important questions regarding practicality of the process (*e.g.* pH and reagent addition control within specified narrow ranges). Also, the cost of reagents as well as residual concentration of NaCl in the process water which may constitute environmental problems.

e) *MRI no conditioning process:* Recently, a new selective flotation technique for processing dolomitic and calcareous-siliceous phosphate ores, without the use of a depressant, has been developed by Hanna, *et al.* [38]. The process uses standard flotation equipment and conventional fatty acid collectors for carbonate/phosphate separation. It involves a unique procedure of applying conventional fatty acids as collectors for selectively floating the carbonate minerals under slightly acidic pH's of 4-6.

The flotation results obtained to date have demonstrated that the MRI "no-conditioning" process (see Table 4) is effective for selectively floating the carbonate minerals from a high MgO phosphate matrix. In the following phosphate flotation step high quality phosphate concentrates containing about 31.5% $P_2O_5$, 0.7% MgO, and 3% insolubles are obtained using a unique phosphate flotation procedure. Reagent requirements for the process are modest being of the order of about 1.5-1.75 kg/t (3.3-3.8 lb/t) oleic acid, 0.66 kg/t (1.3 lb/t) $H_2SO_4$ and 0.5 kg/t (1.1 lb/t) sodium silicate, for both carbonate and phosphate flotation steps.

The distinct advantage of this new processing approach is the elimination of both collector and pH regulator conditioning steps normally required for carbonate flotation, while achieving high separation efficiency and selectivity. Considering the potential advantages of this process, bench scale testing of removal of carbonates form the Saudi ores warrant consideration.

Another new method of flotation [30] involves the treatment of the ore suspension with copper and zinc ions followed by the addition of an alkali sulfide solution to cover the surface of the apatite particles with copper sulfide and zinc sulfide which in turn are floated by using xanthate type collectors.

**Table 4.** **Results of carbonate/phosphate flotation using the MRI process**

| Product | Weight, % | Analysis, % | | | Distribution, % | | |
|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | Insol | MgO | $P_2O_5$ | Insol | MgO |
| Carbonate froth | 6.4 | 11.55 | 39.81 | 12.53 | 7.3 | 4.0 | 76.4 |
| Rough. phos. conc. | 28.9 | 30.49 | 5.58 | 0.75 | 86.1 | 2.5 | 20.5 |
| Clean. phos. conc. | 27.3 | 31.41 | 2.92 | 0.70 | 83.8 | 1.2 | 18.2 |
| Middling | 1.6 | 14.66 | 51.59 | 1.54 | 2.3 | 1.3 | 2.3 |
| Rough. silica tail | 64.78 | 1.05 | 92.98 | 0.05 | 6.6 | 93.5 | 3.1 |
| Composite feed | 100.0 | 10.22 | 64.33 | 1.05 | 100.0 | 100.0 | 100.0 |
| Carbonate froth | 5.6 | 10.81 | 7.39 | 12.57 | 6.0 | 0.7 | 73.1 |
| Rough. phos. conc. | 30.0 | 29.73 | 5.69 | 0.74 | 87.8 | 2.7 | 22.9 |
| Clean. phos. conc. | 27.9 | 30.68 | 2.80 | 0.75 | 84.4 | 1.2 | 21.6 |
| Middling | 2.1 | 16.80 | 45.02 | 0.59 | 3.4 | 1.4 | 1.3 |
| Rough. silica tail | 64.4 | 0.98 | 96.58 | 0.06 | 6.2 | 96.7 | 4.0 |
| Composite feed | 100.0 | 10.15 | 64.33 | 0.97 | 100.0 | 100.0 | 100.0 |
| Carbonate froth | 6.7 | 9.06 | 10.79 | 13.11 | 6.6 | 1.1 | 76.3 |
| Rough. phos. conc. | 26.7 | 30.20 | 4.56 | 0.88 | 87.6 | 1.8 | 20.2 |
| Clean. phos. conc. | 25.0 | 30.76 | 2.89 | 0.88 | 83.6 | 1.1 | 19.0 |
| Middling | 1.7 | 21.83 | 29.30 | 0.81 | 4.0 | 0.7 | 1.2 |
| Rough. silica tail | 66.6 | 0.80 | 97.24 | 0.06 | 5.8 | 97.1 | 3.5 |
| Composite feed | 100.0 | 9.20 | 66.68 | 1.16 | 100.0 | 100.0 | 100.0 |

The economic feasibility of a flotation process is highly dependent on the efficiency of comminution, amount and the price of the flotation reagents, flotation equipment and the amount of water needed. For grinding phosphate rock, the energy used is about 25-35 MJ per tonne and the process water needed is around 13 $m^3$ per tonne while the average values for ore flotation units are 62.5 MJ per tonne and 5.3 $m^3$ per ton [31] for energy and water use, respectively. So far the challenge in the flotation of high carbonate containing sedimentary phosphate rock has been to find the method which is reliable and low in cost. It seems that because of the changes in impurities each rock has been treated as a special case and until a reliable and general method is devised accumulation of data and experience are needed.

Another significant development in the phosphate flotation is the introduction of the flotaire cell [39] which can process rock with larger particle sizes to reduce the cost of grinding. It also has a more favorable grade-recovery relationship. Column flotation is recently receiving increased interest [40-45], especially in cleaning flotation, so application to phosphate flotation should be studied.

### Recovery of phosphates by non-flotation techniques [19]

Although much of the discussion so far has been concerned with flotation, it is by no means the only process to be considered. Indeed, almost every known beneficiation technique has been seriously tested or considered for the upgrading of more difficult phosphate deposits. For instance:

a) *Test work in the U.S.S.R.* showed that use of a two-stage dense medium cycloning operation can result in the production of a final phosphate sink product of acceptable quality. It produces an intermediate-density product which is combined with fines from dense medium separation and requiring grinding and carbonate flotation only.

b) *Low-intensity magnetic separation* has always been used in the treatment of igneous apatite deposits (U.S.S.R) which contain appreciable amounts of ferromagnetic minerals, such as magnetite or titanomagnetite. Recently, however, such operations have been extended to the use of high-intensity magnetic separation to effect the rejection of complex ironbearing silicate minerals from new development areas. Magnetic treatment of the + 100 mesh fraction yields a nonmagnetic apatite concentrate (less than 37% $P_2O_5$) fines (-100 mesh) which are treated by flotation.

c) *Selective leaching* of the carbonate mineral with careful control of pH (3.0) by $H_2SO_4$ can be used to purify hig-grade sedimentary ores containing limited amounts of dolomite (Warren Springs Laboratories, U.K). The process is technically feasible, but practical implementation would depend largely on economic considerations such as acid cost.

d) *High-tension separation* is reported to be successful in upgrading Egyptian ores containing dolomite, silica, significant amounts of pyrite, organics and water soluble alkali. After careful dry size reduction, the ore is wetted and classified to eliminate fines and reduce the alkali content. A low-temperature roast at 650°C eliminates organics and converts the pyrites into magneticallyd rejectable oxides. Advantage is then taken of the high sand temperatures to reject silica and carbonates in high-tension separations at 200°C and 80°C. During cooling the phophate particles regain moisture films and reach the surface much faster than the carbonates, so permitting the second separation. Pyrite is rejected by induced-roll magnetic separation.

e) *Treatment of carbonate-phosphate rock* by selective magnetic coating (Warren Springs Laboratory, U.K). The principle of the process is the selective adsorption of fine-grained magnetic material on mineral surfaces in a mixed pulp, which renders the coated grains amenable to recovery by conventional high-intensity magnetic separation.

f) *Calcination* (in the range 800-900°C) has been proposed in the past to treat carbonate-bearing sedimentary phosphate ores followed by slaking and rejection of the calcined oxide by desliming and classification operations [46-53]. The high cost of energy required for calcination has always acted against the implementation of such proposals. It is interesting to mention that China is building a calcination plant using the abundant supply of cheap coal. The interesting feature of the process is the proposed reconversion of the milk of lime and magnesium to solid carbonates by reaction with kiln gases in a carbonation tower. The resulting solid carbonates are be much easier to dump and will greatly reduce the pollution caused by the tailings. Control of the pressure and $CO_2$ concentration during the carbonation stage may also permit the production of a magnesium carbonate by-product [46].

It seems that calcination can be a feasible alternative method of beneficiation under the circumstances which apply in Saudi Arabia where water is scarce and oil is plentiful. However, research is needed to study the kinetics of calcination and the effects of process parameters on the quality (*e.g.* specific surface area, porosity, reactivity, $P_2O_5$ content, sludge formation, etc.) of the beneficiated rock produced. More energy efficient designs [54] and the advances in the understanding of the fluidized bed behavior [55-57] can also contribute to the competitiveness of this method.

## Conclusions

1) Beneficiation of the sedimentary phosphate rocks found in Saudi Arabia are still unresolved. Various methods of flotation are still need to be investigated.

2) Flotation poses further problems in Saudi Arabia because of the scarcity of water.

3) Calcination, although expensive in other circumstances must therefore be regarded as a serious alternative in Saudi Arabia given abundant energy sources. To reduce the calcium and magnesium content of the ore, water is nevertheless needed but in smaller quantities than for flotation (for slaking after calcination).

4) Flotation and calcination characteristics of Saudi phosphate ore must be studied in order to obtain the data on which feasibility studies can be based.

5) Explorations for the water resources in the northern Saudi Arabia must be started and water recycling must be incorporated into flotation process so that it is economically more comparable with calcination.

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# مسح مرجعي لتركيز خام الفوسفات وصناعة حامض الفوسفوريك في المملكة العربية السعودية

**طارق فارس الفارس، حلمي أوندر أوزبلجه وحسن السيد الشال***

*قسم الهندسة الكيميائية، كلية الهندسة، جامعة الملك سعود، ص.ب ٨٠٠،*
*الرياض ١١٤٢١، المملكة العربية السعودية*

**ملخص البحث.** نظرًا للنهضة الزراعية في المملكة العربية السعودية، فإنه من المتوقع إنشاء صناعات للأسمدة الفوسفاتية ولحامض الفوسفوريك بالمملكة في المستقبل القريب. ومن ثم، فإن هذا البحث يشمل دراسة مرجعية لكل الطرق التقنية المستخدمة في تصنيع حامض الفوسفوريك، وكذلك الأساليب المختلفة لتركيز خام الفوسفات. وقد عنيّت الدراسة بتحليل هذه التقنيات المختلفة ومقارنتها ببعض لاختيار الأنسب منها مستقبلاً لتركيز الخام السعودي. كما أظهرت الدراسة بعض الثغرات البحثية التي لابد من دراستها في المستقبل.

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* معهد فلوريدا لأبحاث الفوسفات، ١٨٥٥ شارع ويست مين، بارتو، فلوريدا ٣٣٨٣٠، الولايات المتحدة الأمريكية.