

An Optimization Study for Flotation of Egyptian Phosphate Ore

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Abstract

Phosphate ores are highly used for phosphoric acid, fertilizers and animal feed production. Phosphate reserves in Egypt are present in three regions Red sea; New valley and Nile valley. These phosphate ores are found in different phases according to the nature of primary formation, such as sedimentary, metamorphic and igneous phosphate. This paper aims at studying the amenability of upgrading fine phosphate of Nile valley areas through application of froth flotation process. Such flotation technique is investigated to separate the associated gangues (silica and calcite) from the fine fractions of phosphate ores. The different operating conditions affecting on the efficiency of separation of phosphate mineral from its associated gangues are studied. These parameters, among others, are collector dosage, depressant dose, and pH. At the optimum conditions of flotation, a phospho-concentrate of about P₂O₅ of 29.5 % and 7.6 % A.I. is obtained from a feed sample containing about 21.13 % P₂O₅ and 19 % A.I.

1. Introduction

The demand for Phosphate ores is high all over the world because they are the main raw materials for the production of phosphate fertilizers and other chemicals [1]. About 191Mt of phosphate were produced in 2011 and the USGS predicts worldwide phosphate production to increase to 228Mt by 2015. Phosphate is also used for direct application to the soil [2]. Major fertilizers include diammonium phosphate (DAP), mono ammonium phosphate (MAP) and triple super phosphate (TSP). Sparingly soluble minerals are hydrophilic. Selective hydrophobization of the desired mineral by various reagents is critical in determining the effectiveness of the separation process. The separation of sparingly soluble minerals from oxide and silicate minerals has been successfully carried out by flotation method. However, separation of phosphate from carbonates (e.g., calcite, dolomite, etc.) is found to be difficult due to their similar surface properties [3]. The type of phosphate deposit affects the flotation performance. Sedimentary deposits of phosphate ores can be treated by flotation when the gangue consists essentially of siliceous materials, as the phosphatic sandstone in Central Florida. These sedimentary phosphates with high carbonates (e.g., Southern Florida and Mediterranean area), however, are not easily floated. Beneficiation of phosphate ores containing carbonate gangue is a worldwide problem and adequate technology for processing for such ores on an industrial scale does not exist at present [4]. Since most of the world's phosphate resources, approximately 80% or more, consist of carbonated sedimentary ores,

extensive researches at both laboratory and pilot-plant scales have been devoted to carbonate-phosphate separation by flotation. Poor amenability of non-weathered sedimentary phosphates to flotation is attributed to unfavorable texture and mineral distribution in ore particles [5]. This study to optimum parameters has different effect on flotation process include collector dose, depressant dose, pH and type of modifiers.

2. Materials and methods

2.1 Materials

A phosphate ore sample was collected from El-Sebaiya locality, Nile Valley, Egypt. Oleic acid was used as a collector and sodium silicate as a silica depressant. Collector was used as a mixture of oleic acid and fuel oil (1:1 ratio) while sodium silicate was used as 10 % solution. These reagents are of BDH grade. Analytical grade HCl, NaOH and Na₂CO₃ were used as pH modifiers.

2.2 Methods

2.2.1 Sample preparation

The phosphate sample was subjected to primary and secondary crushing leading to a product of 100% - 6.3 mm. Sampling of the crushed product was conducted by a 'Denver' Jones riffle to about 5 kg batches. One of these batches was ground using rod mills to reach the liberation size, at 0.208 mm. The ground product was deslimed at 0.045mm screen. The fraction - 0.208+0.045 mm was used as a feed for the flotation process. Another batch was finely

ground to - 200 mesh, in a laboratory analytical mill, for XRD and chemical analysis.

2.2.2 Chemical analysis

Complete chemical analysis of the sample was conducted by X-ray fluorescence (XRF). For routine chemical analysis, acid insoluble residue (A.I.) was determined using standard method of opening and dissolution of the samples (using HCl and HNO₃). Silica was determined using the standard gravimetric method while the filtrate solution was used for determining P₂O₅ content using the standard spectrometric method.

2.2.3 X-ray diffraction analysis

Identification of the mineral composition of the considered sample was conducted by X-ray diffraction (XRD), using the data of the powder pattern of the ASTM on cobalt radiation target with Fe filter at 30 kV and 20 mA. A 'Philips' X-ray diffractometer (PW 1730) was used. The scanning was limited from $2\theta=1$ to $2\theta=80$ degree range. Thin sections of samples representing the different varieties of the studied phosphorites were prepared and observed under the petrographic microscope to examine their grain composition and texture using Olympus Optical Microscope

2.2.4 Flotation experiments

The flotation tests were performed in a conventional "Denver D-12 sub-aeration" flotation machine with 1.0 liter capacity cell. The floated fraction was collected until the froth was barren. The reagents utilized were depressant (sodium silicate, doses from 0.5 -2 kg/ton); collector (oleic acid, doses from 1-3 kg/ton) and pH modifier (sodium carbonate). Conditioning of the pulp with reagents was performed for 2 min for the depressant and 3 min for the collector at 2000 rpm at about 50% solids by weight. Flotation process was performed at 1500 rpm. The flotation products (froth and sink) were collected, dried, weighed and analyzed.

3. Results and discussions

3.1 Mineral composition and characterization

Under the microscope, this phosphorite is composed of phosphatic grains with calcite, chalcedony, and detrital quartz (Fig. 1). No iron oxides were observed in these phosphorites. The contents of phosphatic grains range between 75 and 80 volume %. They are subdivided into

phosphatic mudclasts and bioclasts. Phosphatic mudclasts are generally well rounded to subrounded-spherical in shape, and lack discernible internal structure. Their size ranges from 40 to 90 μm in diameter, and they vary from colorless transparent through yellow to brown translucent. Although commonly spherical in shape, no concentric texture is observed. They are composed of a very fine-grained, cryptocrystalline, homogeneous matrix. Phosphatic bioclasts are composed of fragments of fish bones and sharks' teeth. The fish bone fragments are angular to subangular and prismatic or irregular in shape. Their size ranges from 90 to 110 μm . Generally, the fragments are colorless and transparent under the petrographic microscope. However, some show various shades of color ranging from yellow to grey. The fragments are generally anisotropic, but some show low birefringence and lamellar twinning. Elongated and prismatic bone fragments occasionally show extinction parallel to the elongated axis. In many cases, the phosphatic grains contain detrital quartz (Fig. 2). Detrital quartz grains are 70-80 μm in diameter, pale grey to pale brown, angular to subrounded, and generally show wavy extinction (Fig. 3). Chalcedony ranges from colorless transparent to brown translucent (Fig. 4). It fills 15-25 volume % of intergranular space. It sometimes replaces partially or completely the phosphatic grains (Fig. 5). Calcite occurs as pore-filling microsparite and sparite (Fig. 6), [6]. This is confirmed by XRD analysis, Fig. 7.

As noticed in Fig. 2, the phosphate sample is dominated by Francolite (Ca,Na,Mg)₁₀(PO_4)₆- $x(\text{CO}_3)$ - $y(\text{F,OH})_2$ associated with calcium hydrogen phosphate hydrate $\text{CaHPO}_4 \cdot (\text{H}_2\text{O})_2$, quartz, SiO_2 and calcite, CaCO_3 . Chemical analysis of sample, using XRF, is investigated the results of which are shown in Table 1. The sample contains lower content of P₂O₅ (~ 21.13 %) and higher amount of CaO (48.63 %) indicating the presence of other phases for calcium bearing minerals such as calcite and gypsum (2.43 % SO_3) in addition to apatite. This might explain the presence of higher acid insoluble (19.1 % A.I.) than the silica content (11.81 % SiO_2). The loss on ignition (LOI) is about 10.1% as a result of decomposition of apatite and calcite upon heating. The sample has about 2.77 % Fe_2O_3 and lower content of MgO (0.22 %).

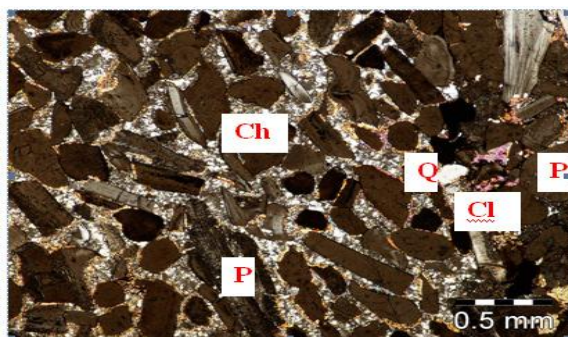


Fig 1. General photomicrograph of phosphorite from the Nile Valley shows the constituents of this phosphorite including phosphatic grains (P), chalcedony (Ch), calcite (Cl), and quartz (Q). PPL.

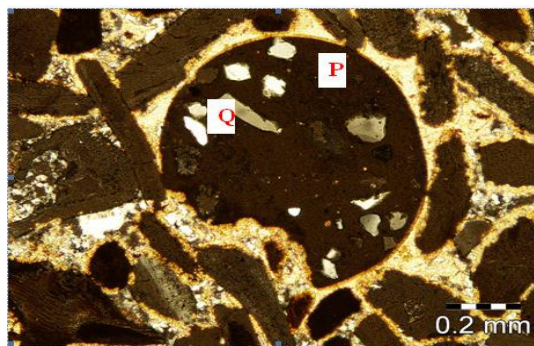


Fig 2. Photomicrograph of phosphorite from the Nile Valley shows the occurrence of fine detrital quartz grains (Q) inside the coarse phosphatic grains (P) that are cemented mainly by calcite (Cl). CN.

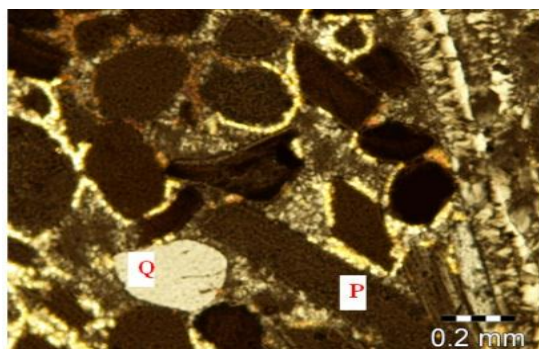


Fig 3. Photomicrograph of phosphorite from the Nile Valley shows the coarse detrital quartz grain (Q) within the phosphatic grains (P). CN.

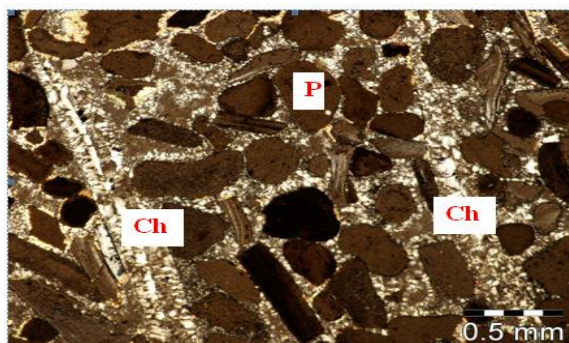


Fig 4. Photomicrograph of phosphorite from the Nile Valley shows that the phosphatic grains (P) are cemented mainly by chalcedony (Ch). PPL

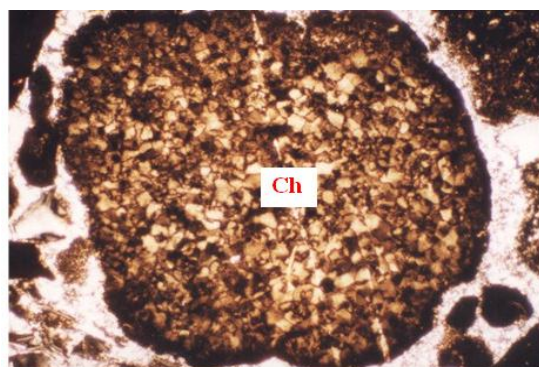


Fig 5. Photomicrograph of phosphorite from the Nile Valley shows that some phosphatic grains (P) are replaced completely by chalcedony (Ch). PPL

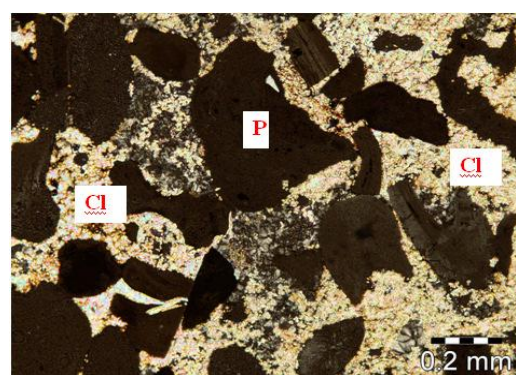


Fig 6. Photomicrograph of phosphorite from the Nile Valley shows that the phosphatic grains (P) are cemented mainly by calcite (Cl). CN.

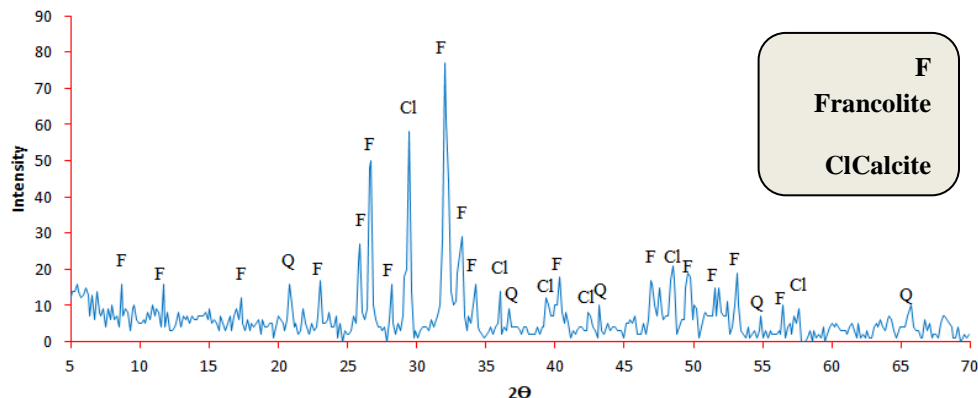


Fig 7. XRD pattern of phosphate sample

Table 1. Chemical Analysis of Phosphate Sample

Oxide	P ₂ O ₅ %	CaO %	MgO %	Fe ₂ O ₃ %	SiO ₂ %	SO ₃ %	F %	Al %	L.O.I %
%	21.13	48.63	0.22	2.77	11.81	2.43	0.75	19.1	10.1

3.2 Flotation of phosphate ore

3.2.1 Effect of collector dosage

Fatty acids are the most commonly used collectors in direct flotation of phosphate ores. The long chains of fatty acids and their salts are the most extensively used especially oleic acid or sodium oleate. The effect of oleic acid dosage on flotation performance of phosphate ore was evaluated and the results are given in Fig. 3. In these experiments, 0.5 kg/ton sodium silicate was used as a depressant for silica. As noticed, both the recovery and grade of P₂O₅ increases by increasing the collector dosage till reaching the critical value of oleic acid 1.5 kg/t where a concentrate of 28.17 % of P₂O₅ with the minimum amount of silica 9.87 % was obtained. Further addition of oleic acid increases of recovery at the expense of the grade (P₂O₅ 26.5%) fig 8. For effective separations, selective adsorption of the collector at mineral/ water interface is essential. The mechanism of the adsorption of fatty acid based collectors on the salt-type minerals, as phosphate, has been widely studied and a comprehensive review on this subject was published by [7]. In general, chemisorptions, surface precipitation and bulk precipitation are thought to be the important reactions in these systems. However, a clear understanding on the chemistry of fatty acid interaction does not exist. It was suggested that, based on adsorption and zeta potential

measurements of oleic acid on apatite, a bi-layer formation prior to the precipitation of calciumoleate [8].

It was concluded that oleate condenses two dimensionally with the carboxylate group on Ca-sites, followed by the association of hydrocarbon chains due to strong lateral bonds [8, 9]. Thus it is expected that the recovery of phosphate would increase by increasing the oleic acid dosage, due to its adsorption on the Ca-sites of phosphate mineral in addition to the flotation of silica particles, as shown in Fig. 3, up to certain dosage (e.g. 3 kg/t) leading to lower grade. Similar trends have been mentioned by the authors for phosphates from other localities [10]. From Fig. 3, it is clear that the optimum dosage of oleic acid is 1.5 kg/ton. Therefore this dose is used in the subsequent tests.

3.2.2 Effect of sodium silicate dosage

Figure 9 represents the effect of sodium silicate dosage on the flotation of phosphate sample. Different doses of sodium silicate were tested starting from 0.5 kg/ton till 2 kg/ton at a definite dose (1.5 kg/ton) of oleic acid. A lower dosage (0.5 kg/t) of sodium silicate was enough to get the best grade with suitable recovery. Further addition of sodium silicate did not improve the grade. It has been known that sodium silicate has a beneficial effect when used with fatty acid and fuel oil mixture due to its

ability of depressing silica that causes higher collector selectivity and enhancing the separation efficiency [11]. The mechanism of minerals depression is mainly due to the hydrolysis of sodium silicate solution which produces a number of monomeric, polymeric and colloidal species. The role of each species on the

depression mechanism was studied by some researchers [12]. These studies showed that the polymeric sodium silicate solution has more depression effect due to the ability of the polymer to cover larger surface of the silica mineral.

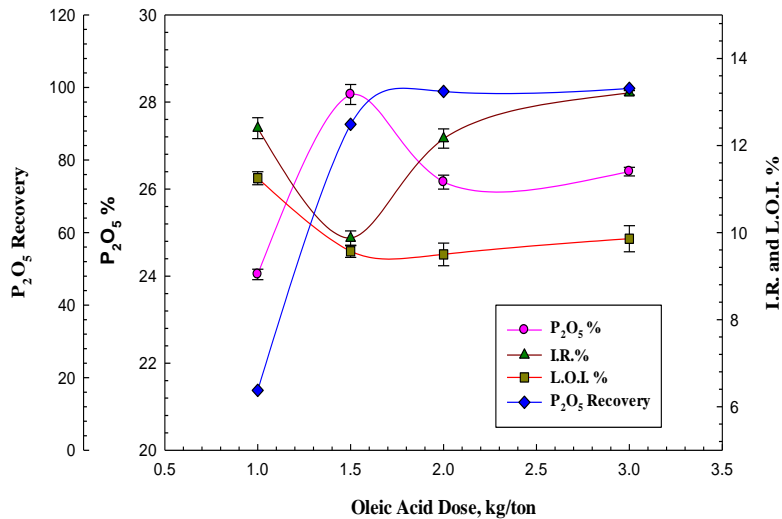


Fig 8. Effect of oleic acid dose on flotation

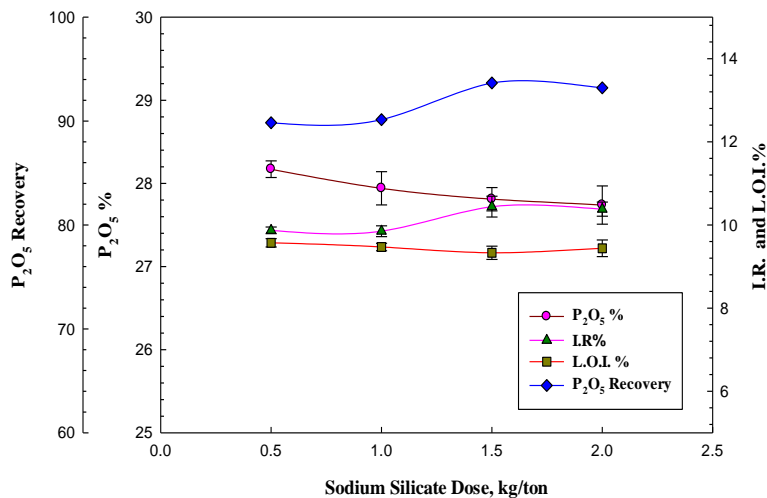


Fig 9. Effect of sodium silicate dosage on phosphate flotation

3.2.3 Effect of pH

Slurry pH value is considered as one of the important factors that has a highly effect on phosphate flotation, to establish the correct sequence of pH adjustment procedures, the optimum points, and the levels of additions. The solution pH determines the extent of ionization and hydrolysis of collector; this helps or hinders

the adsorption of the collector at the various ionized solid/liquid interfaces, contributing to greater or lesser selectivity of flotation [13].

Flotation tests were conducted to investigate the effect of slurry pH on the collector performance in apatite flotation by varying the pH from 8-11. Figure 10 demonstrates the effect of pH slurry in the presence of 1.5 kg/t of the

collector and 0.5 kg/t sodium silicate while using sodium hydroxide as pH regulator. It can be seen that the flotation efficiency increased with increasing pH values starting from pH 8. A concentrate with the best grade (P_2O_5 28.17 %

and 9.87 % A.I. with a recovery of 70.89%) was obtained at pH 9.5. Above such pH, the grade starts to decrease at higher pH range. This observation is in agreement with the previous studies [14].

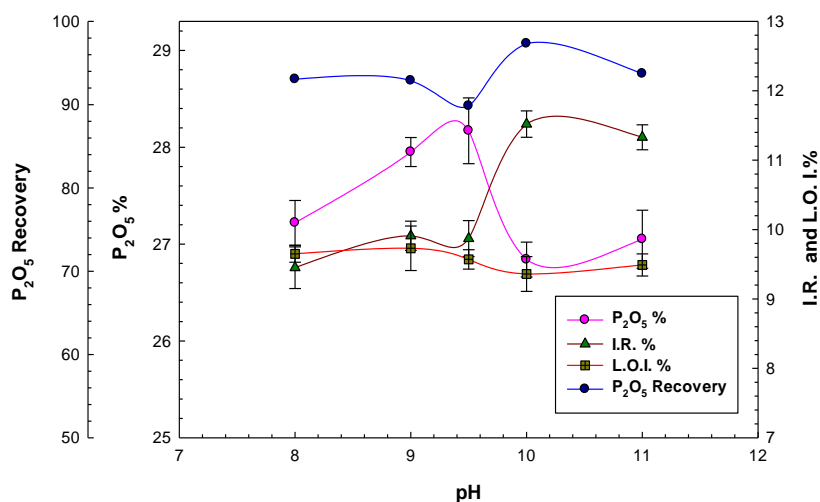
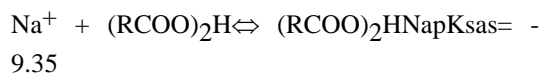
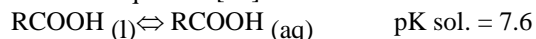


Fig 10. Effect of pH value on flotation using NaOH pH modifier

It is known that oleic acid as a fatty acid collector is a weak acid. It undergoes hydrolysis and forms complex species which exhibit markedly different solubilities and surface active characteristics according to the following chemical equilibria[15].



The concentration of the ionic species OL^- , $(OL)_2$, $(OL)_2^{2-}$, H^- and that of the molecular one $HOL_{(aq)}$ depend on the pH of the solution. For example, below pH 6 the predominant ones dissolved species is $HOL_{(aq)}$ while above pH 8, OL^- and $(OL)_2^{2-}$ are the predominant ones [16]. Rapid flotation occurs at the pH where the collector present in the hydrolyzed forms (OL^- and $(OL)_2^{2-}$), i.e. above pH 8. Under these conditions, significantly increased amounts of collector are present in the stern plane [17]. This probably explains the maximum grade obtained at pH 9.5. Below this pH range the neutral oleic acid, HOL , precipitates from the aqueous solution and, in turn, flotation is deteriorated.

Significant drop in the grade (i.e., lower P_2O_5 % with higher I.R. %) was noticed at highly alkaline medium (pH 10 - 11) probably due to the electrostatic repulsion between

the negative species OL^- and $(OL)_2^{2-}$ and that of similar charges of the phosphate surface. Also, the presence of calcium ions (derived either from the phosphate mineral or its associated calcite gangue) at such high pH values may lead to precipitation of oleate which, in turn, deteriorates flotation process [10].

3.2.4 Effect of type of PH modifier on phosphate flotation

The type of modifier used to control the pH is often of paramount significance, the economic aspect alone i.e. the price, is obviously not always the sole criterion to follow in deciding which pH modifier to use, since the ions derived from such modifier may play a very significant role in some systems [13]. On using sodium carbonate (Na_2CO_3) as pH modifier instead of sodium hydroxide (NaOH), the same trend was obtained as in case of sodium hydroxide within the pH range 8 – 11. The only change is that lower grade (P_2O_5 27.08% and I.R. 13.19%) is obtained in comparison to P_2O_5 % 28.17 % and 9.87 % A.I. with a recovery of 89.88% while using NaOH at pH 9.5. It can be concluded that NaOH is more favourable in phosphate flotation and can be seen that from fig 11 whereas at NaOH

selectivity ratio (SR $(P_{2}O_{5}/SiO_{2})$) lower than at $Na_{2}CO_{3}$.

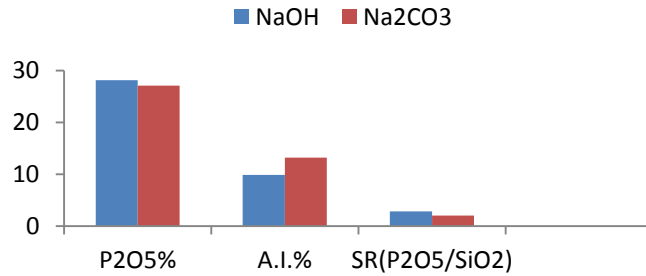


Fig 11. Effect types of modifier on grade of phosphate, SR(P₂O₅/SiO₂) and A.I.%

4. Effect of cleaning the rougher concentrate

In a trial to improve the grade of concentrate, the obtained rougher concentrate was subjected to a cleaning stage without adding further reagents. A final concentrate with 29.5 % P₂O₅ recovery of about 68.06 % and I.R. of about 7.65 % was obtained after such mechanical cleaning, Table 2 It is clear that cleaning of the rougher

concentrate can improve its grade due to reduction of the hydrophilic silica particles in the froth product which may be collected with hydrophobic phosphate particles by entrainment or/and entrapment. The specifications of such final concentrate satisfy the requirements for phosphoric acid and fertilizers production.

Table 2. Effect of cleaning rougher concentrate

Conc	Wt%	P ₂ O ₅ %	I.R.%	L.O.I%	Recovery P ₂ O ₅ %
Rougher	84.74	28.17	9.87	9.57	89.83
Cleaned	80.31	29.53	7.65	10.17	81.05

5. Tentative flow sheet of upgrading of Nile valley phosphate

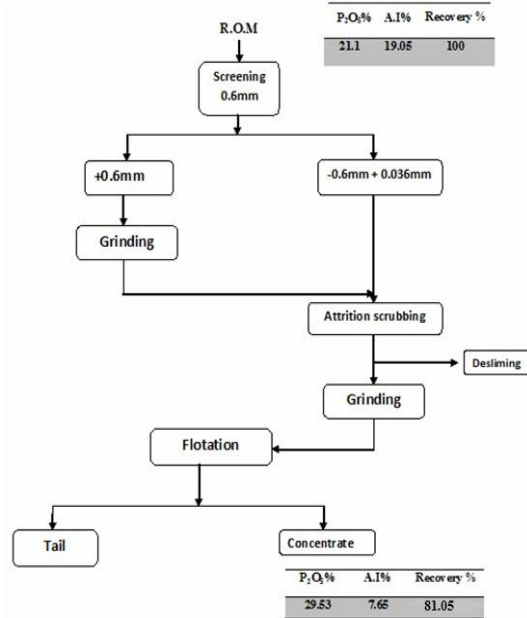


Fig 12. Flow sheet to upgrade phosphate ore from Nile Valley region

Fig 12 shows flow sheet to upgrade phosphate ore from Nile Valley region. It is clear that using such flow sheet; it is possible to get a concentrate assaying 29.5% P₂O₅ and 7.65% A.I with a recovery of 81.05% from a feed containing 21.1% P₂O₅ and 19.05 % A.I

4. Conclusion

Under the microscope, this phosphorite is composed of phosphatic grains with calcite, chalcedony, and detrital quartz. The petrographical and mineralogical investigations, the phosphorites from the Nile Valley area is composed of phosphatic grains (francolite) that occur as coarse-grained structureless grains and bone fragments that range in size from 70 to 80 μ m. These phosphatic grains are cemented by fine-grained (few microns) authogenic calcite and/or chalcedony. Few grains of coarse- to medium-grained detrital quartz are scattered with the phosphatic constituents.

It is expected that the recovery of phosphate would increase by increasing the oleic acid dosage, due to its adsorption on the Ca-sites of phosphate mineral in addition to the flotation of silica particles, as shown in Fig. 3, up to certain dosage (e.g. 3 kg/t) leading to lower grade. It is clear that the optimum dosage of oleic acid is 1.5 kg/ton. Therefore this dose is used in the subsequent tests.

The main role of sodium silicate in phosphate flotation is to depress the silica particles by the precipitation of sodium silicate polymeric species on silica particles. Also, sodium silicate interacts with calcium ions and precipitates them as calcium silicate in the solution, and on silica and phosphate particle which explain why extra sodium silicate dosage may significantly reduce phosphate recovery. NaOH is better than Na₂CO₃ as pH modifier in phosphate flotation. A concentrate with the best grade was obtained at pH 9.5 where the collector (oleic acid) is present in the hydrolyzed forms (OL- and (OL)-22). Cleaning of the rougher concentrate can improve grade due to reduction of the hydrophilic silica particles in the froth product which may be collected with hydrophobic phosphate particles by entrainment or/and entrapment.

The grade and recovery of concentrates are significantly affected by changing the studied parameters. On applying the optimum conditions (i.e., 1.5 kg/t oleic acid and 0.5 kg/t sodium silicate, pH 9.5 using NaOH) of flotation followed by a stage of cleaning, a final

concentrate with 29.5 % P₂O₅ and 7.65 % A.I with a recovery of about 68.06 % was obtained.

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