Beneficiation of Abu Tartur phosphate rock by leaching with dilute acetic acid solution

G.F. Malash

Chemical Eng. Dept., Faculty of Eng., Alexandria University, Alexandria, Egypt

Dilute acetic acid solutions have been used for the leaching of free carbonates contained in Egyptian Abu Tartur phosphate rock by their partial acidulation from the rock.. Acetic acid is a weak organic acid, which when applied to phosphate rocks containing free carbonates as impurities under controlled experimental conditions , can react with the calcium carbonate impurities found in the rock accompanied by a small attack on phosphate minerals. The effect of acid concentration, its quantity measured as a percent of the stoichiometric amount required to react with the carbonate, and the reaction time were studied. It was found that upon treatment of ground Abu Tartur phosphate rock with dilute acetic acid the % P_2O_5 can be raised to 28.6% from an original value of 25.6 % P_2O_5 with a phosphate recovery of 97.2%. These results were obtained at certain experimental conditions , which are an acid concentration 0.9 M , an acid quantity 60% of the stoichiometric amount , and a reaction time of 30 minutes.

تم استخدام حامض الخليك المخفف لازالة شوائب الكربونات الموجوده في خام فوسفات أبو طرطور و ذلك بطريقة التحميض الجزئي للخام. يعتبر حامض الخليك حامض عضوي ضعيف و عند اضافته لخام الفوسفات المحتوي على الكربونات الحره كشوائب يستطيع الحامض أن يتفاعل مع تلك الشوائب دون أن يتفاعل بشكل يذكر مع الفوسفات نفسه. و تم دراسة تأثير تركيز الحامض، و كميته محسوبه كنسبه مئويه من الكميه النظريه الكافيه للتفاعل فقط للتفاعل مع الكربونات، و زمن التفاعل. و كانت نتيجة هذه الدراسه كالآتي: تم رفع نسبه خامس أكسيد الفوسفور من ٢٥,٦% الى ٢٨,٦% بنسبة استرجاع قدرها ٩٧,٢% و هذه النتائج قد تم الحصول عليها عند الظروف الآتيه: تركيز الحامض ٠,٩ مولار، كمية الحامض ٦٠% من الكميه النظريه اللازمه للتفاعل مع الكربونات، و زمن تفاعل قدره ٣٠ دقيقه.

Keywords: Phosphate rock, Beneficiation, Leaching, Recovery

1. Introduction

Phosphate rock is one of the abundant and most important minerals in Egypt. It is situated in different locations, namely Nile Valley area, Western desert, Red sea shores, and central Sinai [1, 2]. Phosphate rock is considered as the basic raw material upon which several important chemical industries are established. An example of which is phosphatic fertilizers and detergents. Owing to the continuous consumption of high grade ores, depletion of such ores necessitates the consumption of lower grade ores containing different quantities and types of impurities [3] such as, free carbonates, silica, iron and aluminium oxides and so on. Certainly impurities will impose several problems during the different stages of dealing with the rock in industry. Therefore, impurities should be kept as close to a minimum in the rock prior to its processing. Thus a concentration step is important.

1.1. Some methods used for the concentration of phosphate rock containing carbonate impurities

The basic beneficiation technology of phosphate rock consists of two steps, the liberation, and separation. Liberation is usually effected by size reduction or particle detachment to create free particles of the desired minerals so that they can be separated by one of the following methods: calcination [4-6], flotation [7-12], and leaching with dilute acids [13-18].

In this study Abu Tartur phosphate rock containing free calcium carbonate impurities is concentrated by leaching off the fore mentioned impurity using dilute acetic acid solution.

1.2. Disadvantages of calcium carbonate impurities

The presence of free carbonates in

phosphate rocks usually requires additional acidulent during the manufacture of phosphoric acid and the superphosphates by the wet process. In addition the carbon dioxide produced during acidulation causes more foaming and results in the production of smaller size gypsum crystals that may bind the downstream phosphgypsum filters and a low quality phosphoric acid is produced. In addition carbon dioxide also dirts the equipment and pollutes the atmosphere. An antifoam can be added but if carbon dioxide exceeds a certain limit, it will have negative effects on the economy of the whole process [2].

1.3. Beneficiation of phosphate rock by acid leaching

The idea of beneficiation of phosphate ores by acid leaching is based on the fact that the reactivity of the different minerals in phosphate rock towards acids are not the same; some minerals react more rapidly than others. This phenomenon may be used to selectively dissolve the impurities from the rock leaving the phosphate matrix in the solid residue.

The rate of reaction of calcium carbonate impurities in phosphate rock with acids is much higher than the rate of reaction of tricalcium phosphate. This leads to the conclusion that under controlled conditions of acid concentration quantity and time of contact, the calcium carbonate can be removed from the rock with a very small loss in phosphate.

Not all phosphate rocks have the same potential for upgrading their phosphate values by acid leaching of the carbonate impurities. This mainly depends on the particular composition of their apatite component, where the degree of upgrading increases with increasing the carbonate substitution in the apatite composition.

Advantages of leaching off the carbonate impurities with dilute acids:
*Low energy consumption:* it requires less energy than does calcinations and slaking
The utilization of waste acids: It offers a possible way of utilizing spent acid which otherwise would pose a disposal problem

A smaller reactor volume in the subsequent digestion: With a partial acidulation step prior to the full acidulation, most of the calcium carbonate impurities found in the phosphate rock are removed. Hence excessive foaming during the full acidulation is avoided and the chemical reaction vessels volume requirements are not large. In this way the added construction costs and the rigorous control of the digester are avoided.

1.4. Acid leaching of the carbonate impurities in phosphate rocks with dilute acetic acid

Several studies [19-24] have been carried out for the purpose of beneficiation of phosphate rock using dilute acetic acid. It has been found out that acetic acid is one of the most promising leaching agents used for partial acidulation. The reaction between acetic acid and calcium carbonates can be written as follows;

$$CaCO_3 + 2CH_3COOH = Ca(CH_3COO)_2 + CO_2 + H_2O$$
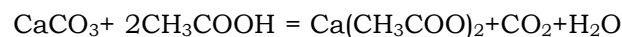
The carbon dioxide is evolved as a gas while the calcium acetate is highly soluble, and can be removed by filtration from the solid phosphate residue.

2. Experimental procedure

Abu Tartur phosphate rock was finely ground until the whole sample passed through 150 um sieve. The ground phosphate rock was thoroughly mixed so that each amount taken as a sample to carry an experiment on it would represent a representative sample.

The representative samples of the ground phosphate rock were dried in an electric oven at 110 ºC for 24 hours, cooled and then stored for further use. This phosphate rock was analyzed for P_2O_5, CaO , and acid insolubles.

A 2 gram sample of this finely ground phosphate rock was put in a 100ml. beaker containing dilute acetic acid of known concentration and quantity. The reaction mixture was agitated using a mechanical stirrer at a low speed for a predetermined time. After which the mixture is filtered on a sintered glass, washed several times with

distilled water to remove any soluble materials. The washings are added to the filtrate. The washed solid residue was then dried in an electric oven at 110 ºC until a constant weight is obtained. The filter cake was analyzed for the P_2O_5 content and the combined filtrate and washings were analyzed for the lost P_2O_5.

3. Results and discussion

3.1. Effect of acid concentration

3.1.1. Effect on the % P_2O_5 recovery

As seen in figs. 1-5 that at lower acetic acid concentrations, there is a greater chance for the reaction between the tricalcium phosphate and the acetic acid leading to lower values of P_2O_5 recoveries, but as the concentration of the acid increases, the polarity of the OH bond will increase leading in a decrease in the acid reaction with the phosphate with a corresponding increase in the % P_2O_5 recovery.

3.1.2. Effect on the % P_2O_5 in the treated rock

As seen from figs. 6-10, that at lower acetic acid concentrations, there is a greater probability of the reaction between calcium carbonate and the acetic acid with a result of an increase of the P_2O_5 grade in the treated rock. Then as the concentration of the acetic acid increase there is a corresponding increase in the polarity of the OH group, the acid will react with the calcium carbonate to a lesser extent and hence more calcium carbonate will remain with the solid residue remaining after the experiment, and therefore the P_2O_5 grade in the treated rock will decrease again.

3.2. Effect of acid quantity

The quantity of acetic acid used calculated as a percent of the stoichiometric amount required to react with calcium carbonate is considered as the most important factor influencing the acid leaching process of the carbonate impurities.

3.2.1. Effect of acid quantity on the % P_2O_5 recovery

As shown in figs. 1-5, the increase in the quantity of acid added during partial acidulation, leads to decrease in % P_2O_5 recovery. This can be explained as follows. As the quantity of the acid increase, there is a greater chance of its reaction with the tricalcium phosphate found in the phosphate rock leading to greater P_2O_5 losses with a result in the decrease in the % P_2O_5 recovery.

This happens because the reaction of the acid with the phosphate rock begins at the surface of the phosphate rock particles, and as the quantity of the acid increase it begins to penetrate to the inner layers leading to increased attack of acetic acid on tricalcium phosphate, and hence more P_2O_5 losses.

3.2.2. Effect of acid quantity on the % P_2O_5 in the treated rock

As shown in figs. 6-10, that as the quantity of the acid increases from 40%-60%, there is an increase in the P_2O_5 grade in the treated rock. A further increase in the quantity of the acid leads to more P_2O_5 losses with a corresponding decrease in the P_2O_5 in the treated rock.

3.3. Effect of time of reaction

3.3.1. Effect of reaction time on the % P_2O_5 recovery, and on the % P_2O_5 in the treated rock

It can be deduced from the figs. 1-10, that as the reaction time increase, the P_2O_5 content in the concentrate increase, then decrease then increase again. This is due to the fact that dilute acetic acid can react with the calcium carbonate and tricalcium phosphate in two parallel reactions, but the rate of reaction of the dilute acetic acid with the calcium carbonate is much more quicker than the rate of reaction of the acid with the tricalcium phosphate. Therefore calcium carbonate dissolves faster in the early stages of the reaction, and on longer contact i.e at 15 and 20 minutes the acid reacts with the tricalcium phosphate forming monocalcium phosphate which is soluble and can be easily
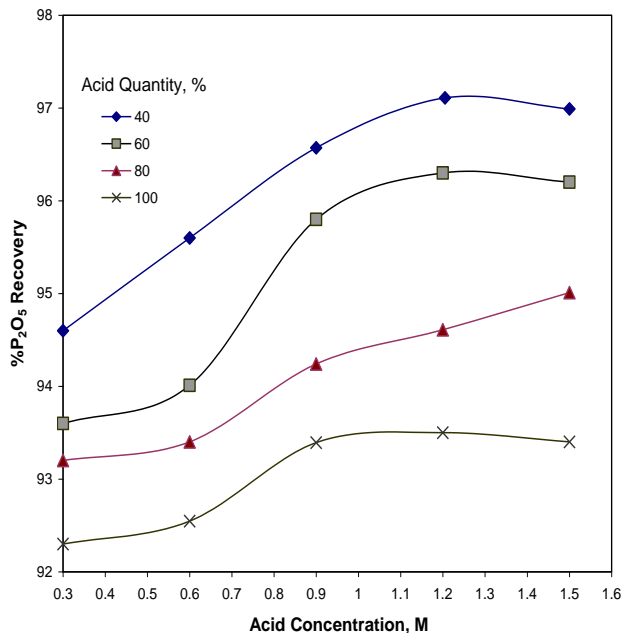
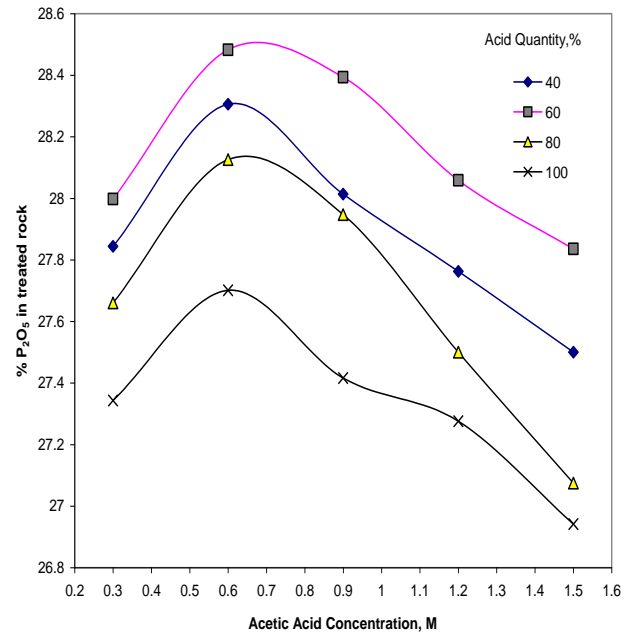Fig. 1. Effect of acetic acid concentration on % P2O5 recovery, (time = 5 min).

Fig. 3. Effect of acetic acid concentration on % P2O5 recovery, (time = 15 min).

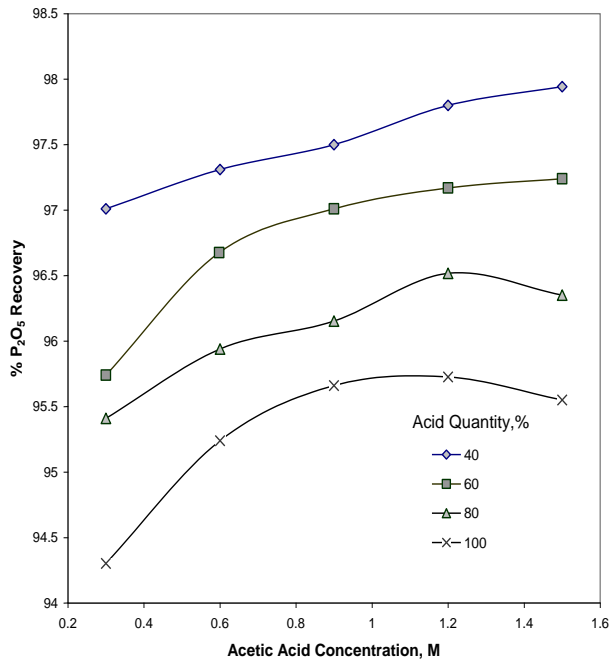Fig. 2. Effect of acetic acid concentration on % P2O5 recovery, (time = 10 min).

Fig. 4. Effect of acetic acid concentration on % P2O5 recovery, (time = 20 min).

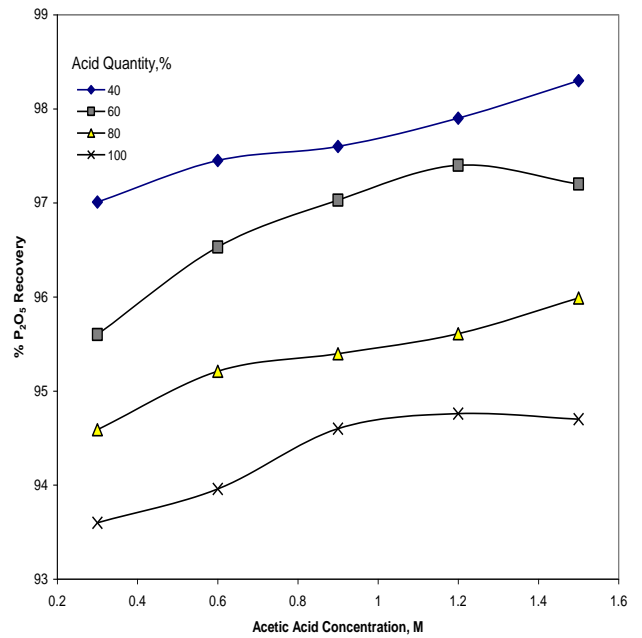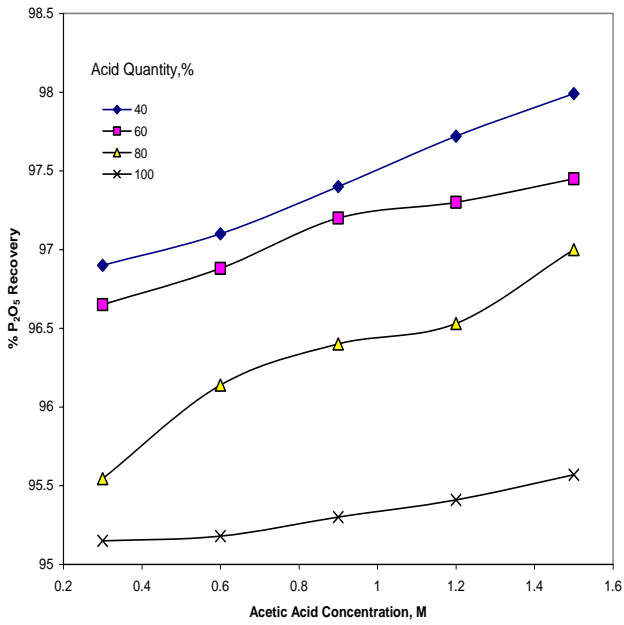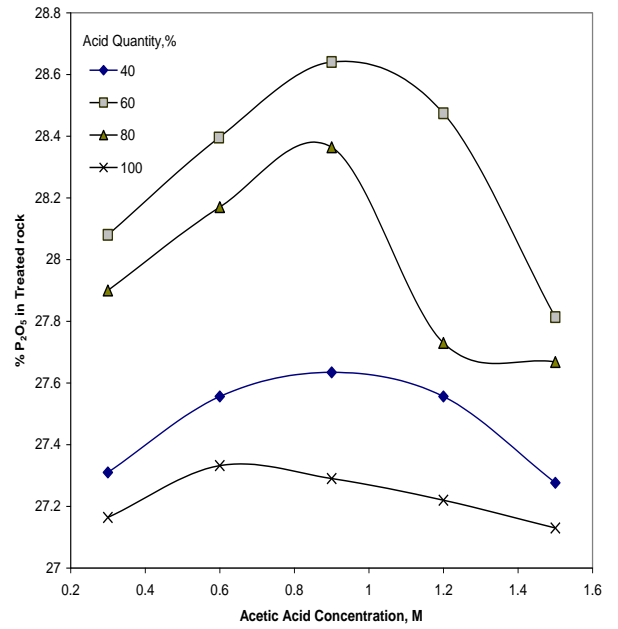Fig. 5. Effect of acetic acid concentration on % P_2O_5 recovery (time = 30 min).

Fig. 7. Effect of acetic acid concentration on % P_2O_5 in treated rock (time = 10 min).
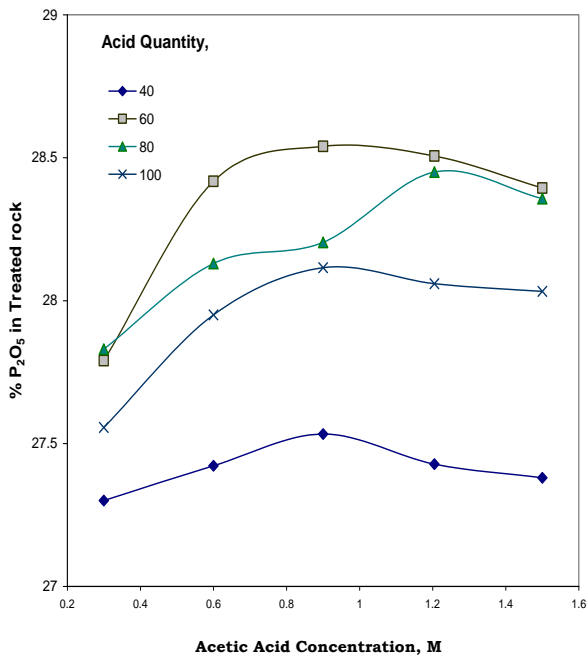
Fig. 6. Effect of acetic acid concentration on % P_2O_5 in treated rock (time = 5 min).
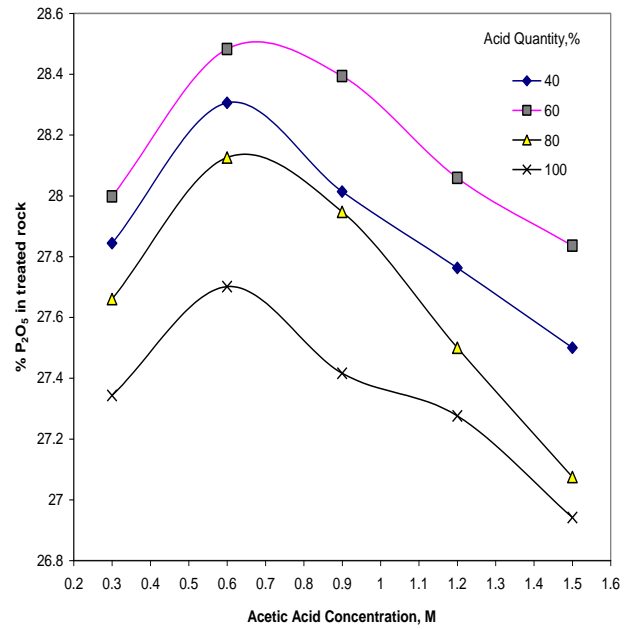
Fig. 8. Effect of acetic acid concentration on % P_2O_5 in treated rock (time = 15 min).
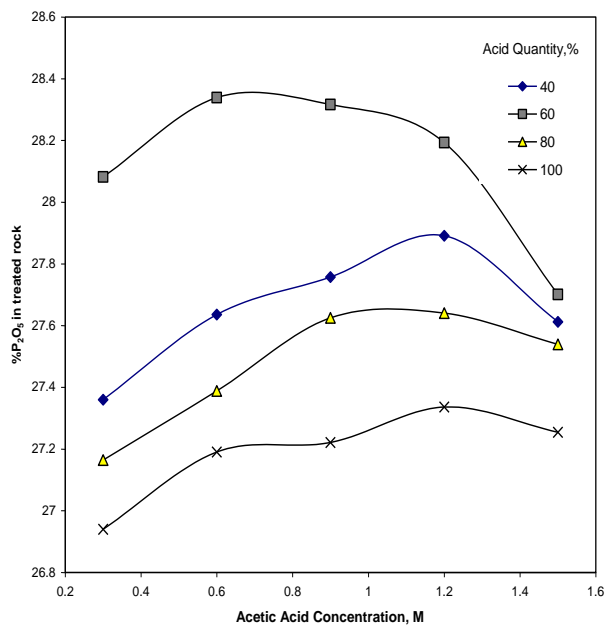
Fig. 9. Effect of acetic acid concentration on % P$_2$O$_5$ in treated rock (time = 20 min).
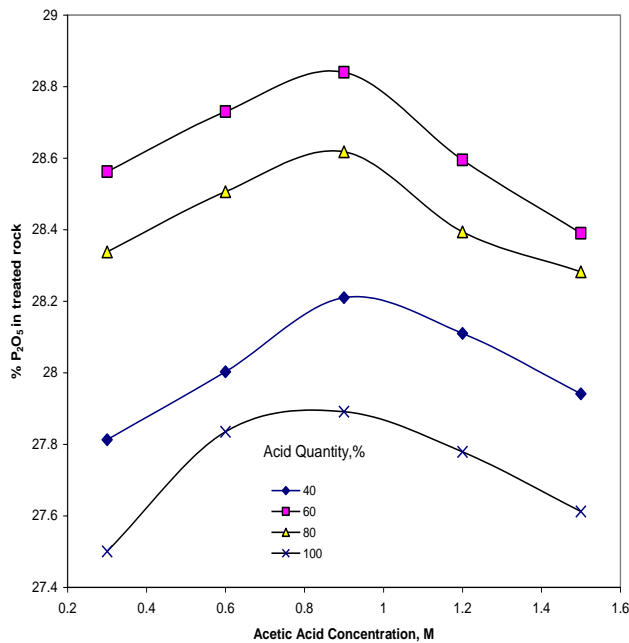

Fig. 10. Effect of acetic acid concentration on % P$_2$O$_5$ in treated rock (time = 30 min).

lost in the filtrate, which leads to a decrease in the % P$_2$O$_5$ grade and %P$_2$O$_5$ recovery. But as the contact time increase further to 30 minutes dicalcium phosphate forms (denning

phenomena) which is not soluble in the filtrate with a corresponding decrease in the P$_2$O$_5$ losses which leads to the increase in the %P$_2$O$_5$ grade in the treated rock and also an increase in the %P$_2$O$_5$ recovery.

4. Conclusions

Abu Tartur phosphate rock can be beneficiated by leaching it with dilute acetic acid. This is due to the fact that dilute acetic acid used in leaching has the ability to react with the calcium carbonate impurity found in the phosphate rock while its attack on the tricalcium phosphate is small. The calcium acetate formed is highly soluble and can be removed by filtration, leaving a solid residue enriched in the phosphate.

The factors that were studied and were found to have an effect on the leaching process were:
1-Acid concentration
2-Reaction time
3-Quantity of the acid as a percent of the stoichiometric amount required to react with the carbonate.

It was found that the best conditions for the leaching process according to this study were an acid concentration of 0.9 M, reaction time of 30 minutes, and an acid quantity of 60% of the stoichiometric amount required to react with the calcium carbonate at room temperature.

References

[1] J.G Arthur, "Phosphate Resources in the Mediterranean (Tethyan) Phosphogenic Province: A progress report", Sci Geol., Mem., Vol. 77, pp. 9-21 (1985).
[2] Abd El Gawad, Preface of the scientific conference about, "Chemical Engineering and Fertilizer Manufacture", Faculty of Engineering Dept., Minia University, pp. 1-17 (1990).
[3] G.H. McClellan and L.R. Gremillion, "The Role of Phosphorus in Agriculture", Chapter 3 Evaluation of Phosphate Raw Materials, pp. 49-78 (1980).
[4] Z. Iqbal, M.M Anwar, D.W Pritchard, "Optimization of Thermal Beneficiation of a Low Grade Dolomitic Phosphate Rock",

Int. J. Miner Process, Vol. 43, pp. 123-131 (1995).

[5] Tiit Kaljuvee, Rein Kuusik, "Enrichment of Carbonate- Phosphate Ores by Calcination and Air Separation" Int. J. Process, Vol. 43, pp. 113-121(1995).

[6] I. Galal, A. Mabrouk, "Upgrading of Abu Tartur Phosphate Ore", Arab Gulf J Sci Res, Vol. 10 (3), pp. 57-79 (1992).

[7] K.A. Matis, A.I. Zouboulis, "An Overview of the Froth Flotation Process", Flotation Sci Eng., pp. 1-44 (1995).

[8] Recovery of Phosphate from Florida Phosphatic Clays, FIPR Publication Number 02-096-179 October (2001).

[9] Development of New Technology for Beneficiation of Florida Phosphate Resources, FIPR Publication Number 02-129-167 April (1999).

[10] X. Zheng, and R.W. Smith, "Dolomite Depressants in the Flotation of Apatite and Collophane from Dolomite", Minerals Engineering, Vol. 10 (5), pp. 537-545 (1997).

[11] M. Prasad, A.K. Majmudar, T.G. Rao, "Flotation Studies on a Low Grade Cherty Calcareous Rock Phosphate ore from Jhabura India", Trans. Soc. Min., Metall Explor, pp. 92-96/section 3, 298, 1995 published (1996).

[12] D.A. ElGillani, A.Z.M. Abouzeid, "Flotation of Carbonates from Phosphate Ores in Acidic Media", Int. J. Miner Process, Vol. 38 (3-4), pp. 235-56 (1993).

[13] A.T. Sdoukos, E. Economou, "Development of a Method for Studying Selectivity in Ca5(PO4)3F- CaCO3-H3PO4 System", Journal of the Applied Chemistry of the USSR, 38 (3-4), Vol. 58 (9), pp. 1785-1791 (1985).

[14] A.T. Sdoukos, E. Economou, "Kinetic Study of the Selectivity and Chemical Enrichment of Phosphorites from the Epirus in Greece", Journal of the applied chemistry of the USSR, Vol. 58 (9), pp. 1792-1797 (1985).

[15] G.H. McClellan, A. Roy, T. Lawendy, "Some Characterization and Beneficiation Data on a Phosphorite from Kaiyang Area of Guinzhou China", Sci-Geol. Mem, Vol. 77, pp. 125-134 (1985).

[16] H.L. Douglas, "Magnesium Separation from Dolomitic Phosphate by Acid Leaching" FIPR publication No 01, pp. 113-138 August (1997).

[17] M.E.H. Shalabi, O.A. Mohamed, and N.A. El-Hussiny, "Granulation and Partial Acidulation of Low Grade El Sebaiya West Phosphate Fines by Phosphoric acid", Journal of the Institution of Engineers (India), Vol. 83, pp. 55-60 (2003).

[18] A. Demirbas, Y. Abali and E. Mert, "Recovery of Phosphate from Calcined Bone by Dissolution in Hydrochloric Acid Solution", Resources, Conservation, and Recycling, Vol. 26, pp. 251-258 (1999).

[19] S.I. Abu Eishah, "A New Technique for the Beneficiation of Low Grade Carbonate Rich Phosphate Rock by Digestion with Dilute Acetic Acid and Solutions: Pilot Plant Testing Studies", Minerals Engineering, Vol. 4 (5/6), pp. 573-586 (1991).

[20] S.I. Abu Eisha and W. Saddedin., "An Experimental Investigation for the Minimization of the Carbonates in Hard Phosphate Rocks", third congress of Chemical Engineers Cairo- Egypt, pp. 19-21 TESCE 14 23 (1998).

[21] W. Sadeddin, "Minimization of Free Calcium Carbonates in Hard and Medium Hard Phosphate Rocks Using Dilute Acetic acid Solutions. Int. Journal of Mineral Processing", Vol. 30, pp. 113-125 (1990).

[22] J.E. Lawver, W.O McClintock and R.E. Snow, "Beneficiation of Phosphate Rocks," A State of the Art Review. Miner Sci. Eng., Vol. 10 (4), pp. 278-94 (1978).

[23] R.T. Marrison and R.N. Boyd, Organic Chemistry, Fourth Edition, Allyn and Bacon Inc., Boston (1983).

[24] Z. Iqbal, "Beneficiation of Low Grade Carbonate Rich Phosohate Rocks Using Dilute acetic Acid", Fert. Res, Vol. 34 (2) (1993).