

Beneficiation of Abu Tartur phosphate rock by partial acidulation with formic acid

G.F. Malash ^a and S.M. Khodair ^b

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

^b Berha Company for Electronic industries, Egypt

Phosphate rocks naturally occurring contain different types and quantities of impurities. These impurities should be removed from the phosphate rock prior to its processing. Among the most common impurities found in Abu Tartur phosphate rock, are the carbonates. In this study different attempts were made to reduce the content of calcium carbonate in the phosphate rock under study, using dilute formic acid. It was found out that dilute formic acid under controlled conditions of quantity, reaction time and concentration, can react with the calcium carbonate impurity, leaving the tricalcium phosphate in the rock almost un attacked. Hence, it was possible to raise the % P₂O₅ in the rock from 22.9% to 25.82 %, with a phosphate recovery of 96.36 %, at the following conditions acid quantity 60% of the stoichiometric amount required to react with the calcium carbonate, reaction time of 15 minutes, and an acid concentration of 1.2 M.

تم استخدام حامض ال فورميك المخفف لازالة شوائب الكربونات الموجوده في خام فوسفات أبو طرطور و ذلك بطريقة التحييض الجزئي للخام. يعتبر حامض ال فورميك 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 محسوبة كنسبه مئوية من الكمية النظرية الكافية فقط للتفاعل مع الكربونات، و زمن التفاعل. و كانت نتيجة هذه الدراسة كالآتي: تم رفع نسبته خامس أكسيد الفوسفور من ٢٢,٩ % الى ٢٥,٨ % بنسبة استرجاع قدرها ٩٦,٣ % و هذه النتائج قد تم الحصول عليها عند الظروف الآتية: تركيز الحامض ١,٢ مولار، كمية الحامض ٦٠ % من الكمية النظرية اللازمه للتفاعل مع الكربونات، و زمن تفاعل قدره ١٥ دقيقه.

Keywords: Phosphate rock, Beneficiation, Leaching, Recovery

1. Introduction

As high grade deposits of phosphate rock are depleted, future sources will be derived from low grade ores containing various impurities. These ores are not suitable for direct use, since impurities present will cause several problems during the industrial processing of the phosphate rock. Accordingly the first challenge to a successful phosphate industry is the reduction of the amount of impurities present in the phosphate rock to the least possible value. This is usually done by a concentration step [1] for the ore prior to its processing. Among the most common impurities found in Abu Tartur phosphate rock is the calcium carbonate impurity. This free carbonate,[2] considerably increases the demand on sulfuric acid required for acidulation, which may render the process uneconomical, in addition to the excessive foaming formed during acidulation, a phenom-

ena which necessitates the use of larger reaction vessels with higher initial cost.

1.1. Some methods used in the concentration of phosphate rock containing calcium carbonate impurity

Calcium carbonate can be removed from phosphate rock by one of the following methods. Conventional methods such as crushing and screening [3], or some other physical separation processes which include washing and desliming, and other beneficiation techniques include, calcination [4-6], flotation [7-12], or partial acidulation with dilute organic or inorganic acids [13-22].

1.2. Concentration of phosphate rock by partial acidulation

The idea of concentration of phosphate rock by partial acidulation is based on the fact

that the reactivity of the different minerals towards acids are not the same. Some minerals react with acids at a higher rate than others. And since calcium carbonate reacts with formic acid at a higher rate than tricalcium phosphate, a phenomena which was used to selectively dissolve the calcium carbonate impurity, leaving the phosphate bearing minerals in the rock almost unattacked in the solid residue.

2. Experimental procedure

Abu Tartur phosphate rock was finely ground until the whole sample passed through 150 μm sieve. The ground phosphate rock was thoroughly mixed, and then dried in an electric oven at 110 $^{\circ}\text{C}$ for 24 hours, then cooled and stored for further use. The phosphate rock was analyzed for P_2O_5 content, CaO , and acid insolubles.

A two gram sample of this ground phosphate rock was put in a 100 ml beaker containing dilute formic 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 was filtered on a sintered glass, washed several times with distilled water to remove any soluble materials. The washings were added to the filtrate. The washed solid residue was then dried in an electric oven at 110 $^{\circ}\text{C}$ until a constant weight was obtained. The filter cake was analyzed for the % P_2O_5 , and the combined washings and filtrate were analyzed for the lost P_2O_5 .

3. Results and discussion

3.1. Effect of formic acid concentration

3.1.1. Effect of formic acid concentration on the % P_2O_5 in the treated rock

As shown in figs. 1, and 2 the % P_2O_5 in the treated rock increases by increasing the formic acid concentration up to 0.6M in case of partial acidulation for 30 minutes and up to 1.2M in case of partial acidulation for 15 minutes. A further increase in the acid concentration up to 1.5 M leads to a decrease in the % P_2O_5 in the treated rock. This phenomena can be attributed to the fact that at lower acid concentrations, the formic acid is

capable of dissolving much of the carbonate impurity with a corresponding increase in the % P_2O_5 in the treated rock. However at higher concentrations of the formic acid, the polarity of the OH bond increase [23] with the consequence that its reaction with the calcium carbonate decrease, which means that less calcium carbonate will dissolve which will have an adverse effect on the % P_2O_5 in the treated rock.

3.1.2. Effect of formic acid concentration on the % P_2O_5 recovery

As shown in figs. 3 and 4 that as the concentration of the acid increase, the polarity of the OH bond will increase leading to a decrease in the formic acid reaction with the tricalcium phosphate with a corresponding increase in the % P_2O_5 recovery.

3.2. Effect of formic acid quantity

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

As shown in figs. 1,2,5,6, and 7 the increase in the quantity (measured as a percent of the stoichiometric amount required to react with the calcium carbonate) of the formic acid leads to increased P_2O_5 losses, consequently, the % P_2O_5 in the treated rock decreases. This can be attributed to the fact that as the quantity of formic acid increases, there is a greater chance of its reaction with the tricalcium phosphate found in phosphate rock leading to increased P_2O_5 losses

3.2.2. Effect of formic acid quantity on the % P_2O_5 recovery

As shown in figs. 3,4,8,9, and 10, an increase in the acid quantity leads to an increase in the P_2O_5 losses with a corresponding decrease in recovery.

3.3. Effect of time of reaction

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

It is clear from figs. 5,6,7,8, 9, and 10 that as the reaction time increases, the P_2O_5 grade and recovery increase, then decrease then increase again. This is due to the fact that dilute formic acid reacts with the calcium

carbonate and tricalcium phosphate in two parallel reactions, but the rate of reaction of the dilute formic 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,

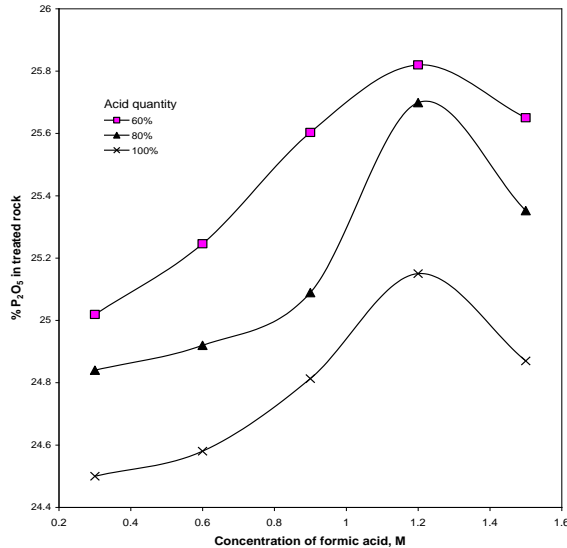


Fig. 1. Effect of acid concentration on % P₂O₅ in treated Rock using different acid quantities time = 15min.

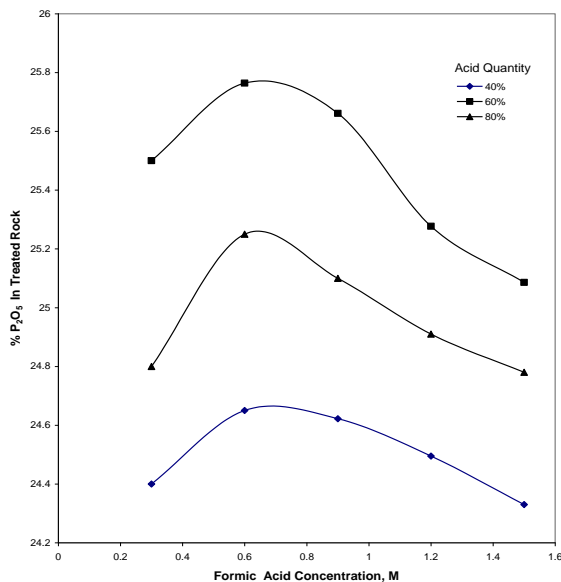


Fig. 2. Effect of acid concentration on % P₂O₅ in treated rock using different acid quantities, time=30min.

and on longer contact ie at 20 minutes, the acid will be capable of reacting with the tricalcium phosphate forming monocalcium phosphate, which is soluble and can be easily lost in the filtrate. This of course will lead to P₂O₅ losses with a corresponding decrease in the % P₂O₅ in the treated rock and also a decrease in the P₂O₅ recovery. However as the contact time increases further to 30 minutes dicalcium phosphate forms (denning phenomena)

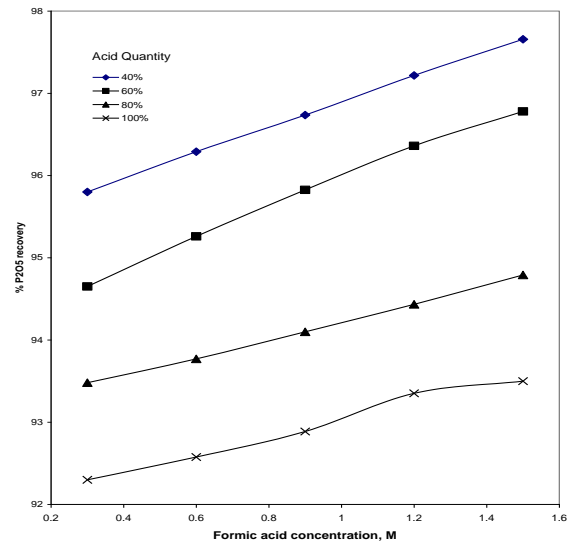


Fig. 3. Effect of acid concentration on % P₂O₅ recovery using different acid quantities time = 15min.

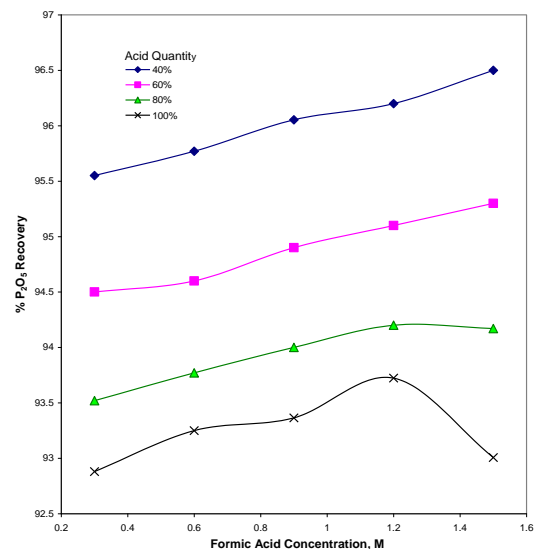


Fig. 4. Effect of acid concentration on % P₂O₅ recovery using different acid quantities, time=30min.

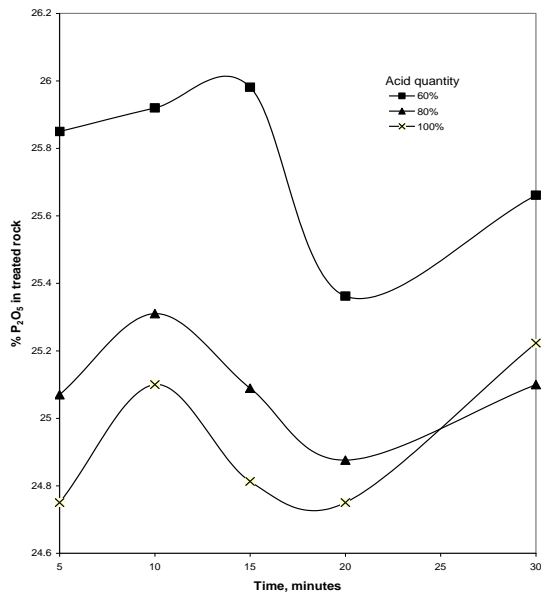


Fig. 5. Effect of time on % P₂O₅ in treated rock, acid concentration = 0.9 M.

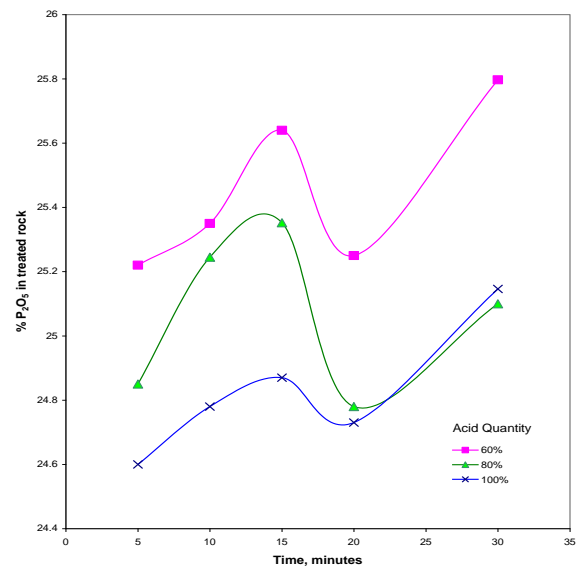


Fig. 7. Effect of time on % P₂O₅ in treated rock, acid concentration = 1.5 M.

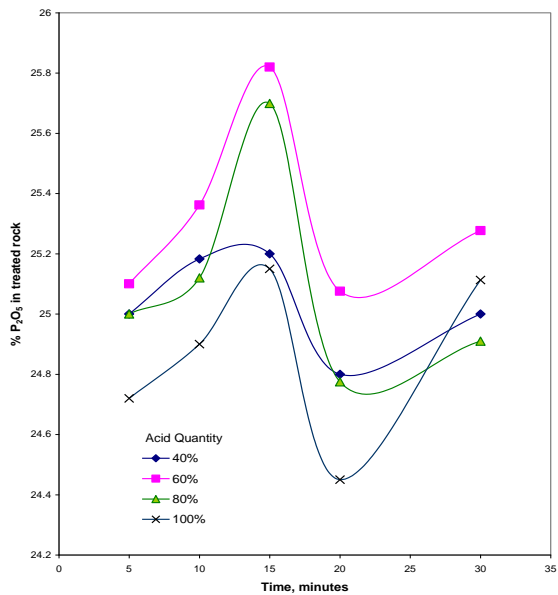


Fig. 6. Effect of time on % P₂O₅ in treated rock, acid concentration = 1.2M.

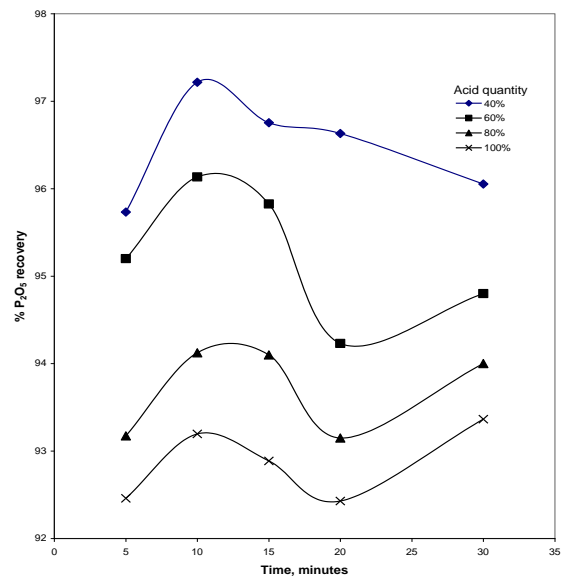


Fig. 8. Effect of time on % P₂O₅ in treated rock, acid concentration = 0.9 M.

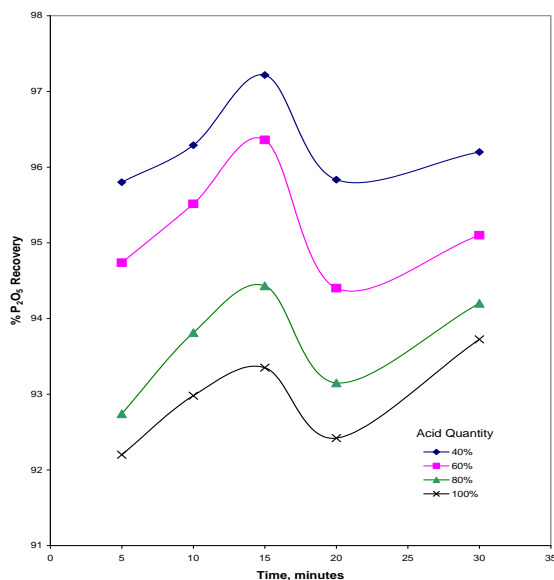


Fig. 9. Effect of time on % P₂O₅ recovery, acid concentration = 1.2M.

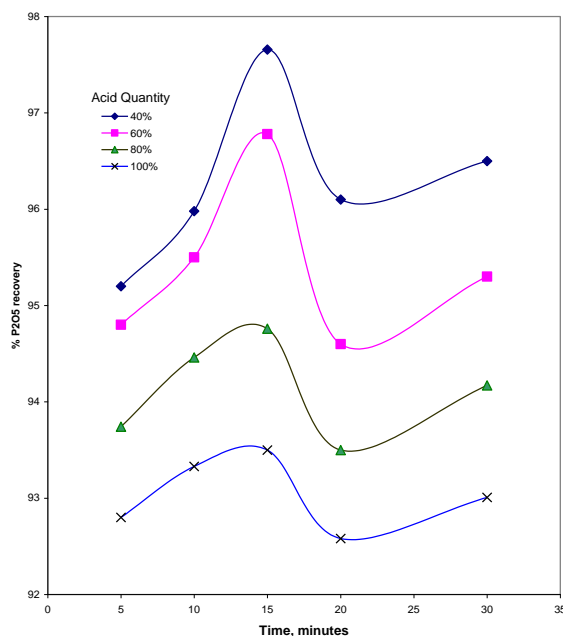


Fig. 10. Effect of time on % P₂O₅ in treated rock, acid concentration = 1.5 M.

which is not soluble as the monocalcium phosphate, and consequently it will not be lost in the filtrate with a corresponding decrease in the P₂O₅ losses which will lead to increase in the % P₂O₅ in the treated rock and also an increase in the % P₂O₅ recovery.

5. Conclusions

Abu Tartur phosphate rock can be concentrated by partial acidulating it with dilute formic acid. This is due to the fact that formic acid has the ability to selectively dissolve the calcium carbonate impurity found in the rock. The calcium formate formed is highly soluble and can be removed by filtration, leaving a solid residue enriched with the phosphate.

The factors that were studied and were found to have an effect on the partial acidulation process were:

1. Formic acid concentration
2. Quantity of the acid as a % of the stoichiometric amount required to react with the calcium carbonate
3. Reaction time

It was found out that the best results obtained were at an acid concentration of 1.2 M, acid quantity of 60 % and a reaction time of 15 minutes.

These conditions gave a concentrate containing a P₂O₅ % of 25.82% and a recovery of 96.36%.

References

- [1] Z.Z. Iqbal, "Innovations in Beneficiation of Technology for Low Grade Phosphate Rocks" pp. 135-151, 46 (2) (1996).
- [2] G.H. Mc Clellan, and L.R. Gremillion, "The role of Phosphorus in Agriculture" Chapter 3 Evaluation of Phosphate Raw materials, pp. 49-78 (1980).
- [3] T.R. Lodha, A.C. Srivastava, "Characterization of Low Phosphates and Their Beneficiation for Fertilizer Industry," Fertilizer Technology, Vol. 19, pp. 190-197 (1985).
- [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 (2001).
 - [9] Development of New Technology for Beneficiation of Florida Phosphate Resources, FIPR Publication Number 02-129-167 (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 $\text{Ca}_5(\text{PO}_4)_3\text{F}-\text{CaCO}_3-\text{H}_3\text{PO}_4$ system" *Journal of the applied chemistry of the USSR*, 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*, 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 (01) pp. 113-138 (1997).
 - [17] M.E.H. Shalabi; O.A. Mohamed, 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)*, (83), pp. 55-60 (2003).
 - [18] A. Demirbas, Y. Abali, E. Mert, "Recovery of phosphate from calcined bone by Dissolution in Hydrochloric Acid Solution" *Resources, Conservation, and recycling*, (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, TESCE* 14-23, pp. 19-21 (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).

Received January 10, 2005

Accepted March 13, 2005