

# Preconcentration of Low Grade Sedimentary Phosphate Ore Using Selective Flocculation

R. Parsaei, M.Sc.<sup>1</sup>, A. Alamdari, Ph.D.<sup>1\*</sup>, A. Jahanmiri, Ph.D.<sup>1</sup>, and M.A. Rajabzadeh, Ph.D.<sup>2</sup>

<sup>1</sup> Department of Chemical Engineering, Shiraz University, Post Code: 713485-1154, Shiraz, Iran.

<sup>2</sup> Department of Earth Sciences, College of Sciences, Shiraz University, Post Code: 71454, Shiraz, Iran

\*E-mail: [alamdari@shirazu.ac.ir](mailto:alamdari@shirazu.ac.ir)

## ABSTRACT

Selective flocculation was used as a preconcentration method of a low grade sedimentary phosphate rock. Microscopic observations on thin sections revealed that the phosphorus bearing compounds replace relicts and are interstitial to carbonate minerals. The phosphate particles are mainly less than 100 microns and ore mineral liberation requires ultrafine grinding. Flocculation experiments were carried out using sodium hexametaphosphate as dispersant and starch or carboxymethylcellulose as flocculant. The floc size distribution during flocculation periods was determined by hydrometry analysis and the settled flocs were assayed for P<sub>2</sub>O<sub>5</sub> using the atomic absorption spectrometry method. The experimental results indicate that the maximum separation efficiency is obtained at 50 and 5 (g/kg solid) concentrations of sodium hexametaphosphate and starch, respectively, when flocculation time is around 10 minutes.

(Key words: selective flocculation, mineral processing, industrial minerals, non-metallic ores, phosphate rock).

## INTRODUCTION

Phosphorus is essential in agricultural and industrial developments and it is a commodity in demand. Reduction in high grade phosphate deposits, in conjunction with the great increase in phosphorus demands, makes the beneficiation of low grade deposits attractive. A large deposit of very low grade sedimentary phosphate rock from Lar Mountain in Kohgiluyeh-va-Boierahmad, a southern province of Iran, is mainly comprised of limestone which contains around 2.4% P<sub>2</sub>O<sub>5</sub> as disseminated collophane particles generally less than 100 microns in size. The ore situation in host rock necessitates fine grinding of the rock. This produces a large

volume of fines and ultrafines which not only diminishes the efficiency of conventional ore processing methods such as flotation but also causes an increase in loss of desired materials into gangue. For instance, in the 1970's more than 30% of the mined phosphate rocks in Florida was lost and purged into gangue dams because of fineness (Somasundaran, 1986; Somasundaran and Moudgil, 1988; Wills, 1997).

Selective flocculation is a potential process for solid-solid separation in fine size ranges and involves the following steps: 1) dispersion of fine particles of the solid mixture; 2) selective adsorption of a flocculant on the particular components to form flocs; 3) floc growth, which is generally achieved by conditioning at low shear; and, 4) floc-separation either through sedimentation, elutriation, sieving, or flotation (Somasundaran, 1986; Somasundaran and Moudgil, 1988; Wills, 1997; Mathur et al., 2000).

Starch is composed of linear and branched polymers and has been greatly used in beneficiation of phosphate rocks as flocculant (Pearse, 2005 and Devenport et al., 1962). Dogu and Arol (2004) used starch to remove dark-colored minerals as impurity from feldspar using the process of selective flocculation. Cellulose derivatives, starches, and polysaccharides possessing carboxyl groups are able to adsorb on apatite particles in a suspension including apatite and silicate (Baudet, 1980). Polyacrylic acid in the alkaline pH ranges is also able to adsorb on apatite surfaces due to the formation of a strong bond of calcium carboxylate (Pradip and Moudgil, 1991). Hydrolyzed polyacrylamides adsorb on quartz and separate it from apatite in the pH ranges of 7 to 10 due to hydrogen bonding and electrostatic interaction (Pradip et al., 1991). Due to low selectivity of polyacrylamides for beneficiation of calcareous phosphate rocks, modified polyacrylamides are used preferably. Pradip et al. observed a

significant improvement in selectivity using a synthesized modified polyacrylamide (Pradip et al., 1993). Attia and Yu synthesized a polymer, adding tiron to polyacrylamide in a solution containing formaldehyde and observed an enhancement in beneficiation of calcareous phosphate rock using this polymer (Attia and Yu, 1993).

It is also pertinent to note that most researchers have used a type of synthesized phosphate rock in their selective flocculation studies (Baudet, 1980; Pradip et al., 1991; Pradip and Moudgil, 1991; Pradip et al., 1993; Attia and Yu, 1993). However, our understanding concerning the beneficiation of natural phosphate rocks by selective flocculation is extremely limited. The presence of different impurities in natural rocks complicates the study and may affect the mechanism of flocculation. Here, we present the results of the study on selective flocculation in beneficiation of a natural phosphate rock. The method may be regarded as preconcentration of low grade natural phosphate compounds.

## EXPERIMENTAL DETAILS

The nature of the phosphorus bearing compounds and the host rock was investigated using different techniques. Microscopic observation on some thin sections of the sedimentary host rock was used for determining the size and distribution of the phosphate minerals in the rock along with the associated minerals. Refractive and reflection methods were used in the observations.

A representative 100 kg sample of phosphate ore from Lar Mountain was selected and split to 1 kg samples using a Jones riffle sampler. The samples were analyzed using wet chemistry and X-Ray diffraction methods to determine the chemical and mineralogical compositions of the phosphate compounds and the host rock. The examinations suggested that the selective flocculation may be used as a preconcentration method in processing of low grade natural phosphate rock.

Determination of the ore-bearing rock was followed by flocculation experiments. The samples were ground to 85% smaller than 44 microns in a Tema® grinder and the experiments were carried out in a jar test apparatus using slurries of 2% solid concentrations under alkaline

condition (pH range of 8-10) which favors selective adsorption of flocculant on phosphate minerals (Pradip et al., 1993 and Attia and Yu, 1993). The rock particles were dispersed during a period of 10 minute agitation at the speed of 180 rpm using sodium hexametaphosphate ((NaPO<sub>3</sub>)<sub>6</sub>, NaHMP) aqueous solution as a dispersant. Then, the flocculant solution was added to the suspension dropwise in about 30 seconds while the agitation speed was reduced to 90 rpm.

Starch or carboxymethylcellulose (CMC) at different concentrations was used as flocculant (Pearse, 2005). After the required time of flocculation elapsed, the flocculated particles were allowed to settle and then the upper phase of the suspension was drained by a vacuum pump. The settled phase of the suspension was dried, weighted, and assayed for P<sub>2</sub>O<sub>5</sub> contents using the atomic absorption spectrophotometry method (Jeffery, 1981).

A sample of dried settled phase (0.5g) was dissolved in HClO<sub>4</sub> and HF under evaporation condition. The solution was diluted by ascorbic acid and was held overnight. The optical density of the solution was measured using an 827 nm wavelength spectrophotometer.

The size distributions of flocs during the period of flocculation were determined using the hydrometry method which is based on measurements of suspension density and its depletion with time due to settling of particles in a fluid (ASTM Standards, 1989).

## RESULTS AND DISCUSSION

The results of the chemical analysis of the sample carried out in the first portion of the experiments are shown in Table 1. The standard limits of the components in the concentrate suitable for the feed of the phosphoric acid plant of a local petrochemical complex are also included in Table 1.

As Table 1 shows, most of the components present in the phosphate rock of Lar Mountain are not in the allowable weight percent ranges. The minerals present in the sample distinguished by XRD method are shown in Table 2.

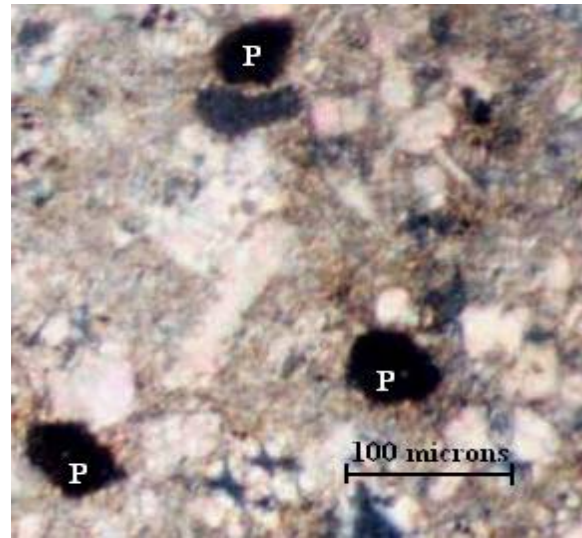
**Table 1:** Chemical Composition of the Raw Phosphate Rock from Lar Mountain.

Composition	wt%	Standard limit
P <sub>2</sub> O <sub>5</sub>	2.38	32 .0 min
CaO	42.0	49 .2 max
MgO	0.84	0 .7 max
Fe <sub>2</sub> O <sub>3</sub>	2.88	0 .2-0 .5 max
Al <sub>2</sub> O <sub>3</sub>	0.57	0 .2-0 .5 max
SiO <sub>2</sub>	17.63	6.0-8.0max
Na <sub>2</sub> O	0.52	0.4 max
K <sub>2</sub> O	0.68	0 .9 max
CO <sub>2</sub>	32.37	4.0 max

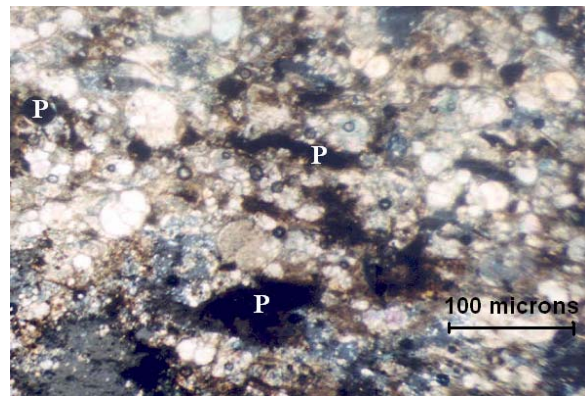
**Table 2:** Mineralogical Composition of the Raw Phosphate Rock from Lar Mountain.

Mineral	Formula	wt%
Flourapatite	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub>	11.2
Calcite	CaCO <sub>3</sub>	63.4
Quartz	SiO <sub>2</sub>	5.1
Feldspar	(K,Na)AlSi <sub>3</sub> O <sub>8</sub>	4.2
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	7.3
Limonite	FeO(OH)	8.8

Microscopic observations showed that the phosphate compounds are distributed in host limestone as collophane particles (amorphous apatite) in two major forms. At the first occurrence, which is the dominant form, the collophanes substituted the fossil relicts in the biochemical limestone. The particles vary from oval to round shapes (Figure 1). At the second occurrence the collophanes appear in the rock as irregular interstitials (Figure 2). The size of the phosphorus bearing-compounds is generally less than 100 microns, although in some cases it may reach 300 microns. The chemical and mineralogical analyses of the Lar Mountain limestone indicate that the tenor of P<sub>2</sub>O<sub>5</sub> is around 2.4 wt% and the rock is essentially composed of calcite with minor clay, quartz, and limonite. The intimate occurrence of phosphate compounds with calcite and occasionally with clay minerals makes the beneficiation of Lar Mountain phosphate rock probably impractical by common physical methods.



**Figure 1:** Phosphate Rock of Lar Mountain under Magnification (P indicates phosphate compounds).



**Figure 2:** Irregular Appearance of Cellophane in the Host Rock (P indicates phosphate compounds).

The phosphate compounds in the rock must be liberated such that their surfaces will be able to adsorb the flocculants. Figure 1 shows that the liberation size for the studied phosphate rock is around 40 microns. However, in some thin sections, the average size of collophane particles was measured in the range 100-200 microns. Nevertheless, the samples were milled below 44 microns in order to inevitably liberate the fine phosphate mineral particles.

For obtaining the optimal dispersant and flocculant concentrations and the sedimentation time at which the selective flocculation can be used as a preconcentration method in low grade natural carbonate rocks, grade, recovery, and separation efficiency were calculated for each flocculation experiment. Assuming a feed material assaying  $f$  %  $P_2O_5$ , is upgraded into a concentrate assaying  $c$  %  $P_2O_5$ , then:

$$Recovery = \frac{100Cc}{f}$$

$$Separation\ Efficiency = \frac{100Cm(c-f)}{(m-f)f}$$

where  $C$  is the fraction of feed which enters concentrate and  $m=27.9\%$  is the percentage of  $P_2O_5$  in apatite (Wills, 1997).

Table 3 shows the results of flocculation experiments for the case where the flocculant was starch and the settling time was one minute. The results show that for starch concentration of 10 g/kg solid the grade increases as the dispersant concentration increases. Consequently, the maximum grade is obtained when the concentration of dispersant is highest. This suggests that when the dispersant concentration is high, only the flocs which have enlarged through flocculation and become heavier (mostly phosphate minerals), can overcome the repulsive forces induced by the dispersant and settle down. However, other particles not influenced by flocculant (mostly non phosphate minerals) do not enlarge and remain suspended.

Table 4 shows the results when the flocculant was CMC and the settling time was one minute. The experiments with CMC also resulted that for flocculant concentrations of 1 and 5g CMC per kg solid, the grade increased as the dispersant concentrations increased. The maximum grade was attained when the concentration of flocculant was 1g CMC per kg solid and that of dispersant was 50g NaHMP per kg solid. Table 5 shows the results when the flocculant was starch and the settling time was 15 minutes. These results show an improvement in recoveries and separation efficiencies when the concentrations of flocculant were 5 and 10g starch per kg solid. The maximum recovery was achieved when the

concentration of starch was 10g per kg solid and the concentration of dispersant was 10g per kg solid. However, since grade is a limiting factor, the optimum operational conditions would be more restricted. Table 6 shows the results when the flocculant was CMC and the settling time was 15 minutes. For this case of study, the beneficiation was not satisfactory.

Based on these experiments, it seems that in beneficiation of Lar Mountain phosphate rock, the selective flocculation improved recovery and grade at the maximum separation efficiency when concentrations of 5g of starch per kg solid and 50g sodium hexametaphosphate per kg solid were used and the settling time for floc separation was 15 minutes.

The size distributions of flocs during their growth at highest separation efficiency were followed by the hydrometry analysis. Figure 3 illustrates the cumulative size distributions at different times during the course of flocculation process. At the first ten minutes, the floc growth continues due to the flocculant adsorption on the phosphate particles, the particles enlarge, and the size distribution evolves. As the process continues, the enlargement increases significantly and finally the breakage of flocs takes place at longer mixing time. It seems that flocculation time of 10 minutes would be adequate.

## CONCLUSIONS

Chemical and mineralogical compositions of Lar Mountain phosphate rock were determined using the XRF and XRD techniques, respectively. The liberation size for this rock was estimated as around 40 microns.

Flocculation experiments which were carried out using different concentrations of flocculant and dispersant, showed that higher efficiencies and grades were attainable when the concentration of dispersant NaHMP was 50 g per kg of dry solid and the concentration of starch used as flocculant was 5 g per kg dry solid and the settling time was 15 minutes. It is concluded that a higher concentration of dispersant would apparently result in a higher grade of phosphate. Hydrometry analysis revealed that flocs only grew significantly in the early minutes of the process.



**Table 3:** Effects of Concentrations of NaHMP and Starch on Grade, Recovery, and Separation Efficiency. (Sedimentation Time: 1 min)

Starch (g/kg solid)									
NaHMP (g/kg solid)	1			5			10		
	Grade	Recovery	S. E.	Grade	Recovery	S. E.	Grade	Recovery	S. E.
1	4.97	70.18	61.15	4.49	57.98	45.55	4.16	44.57	31.89
10	4.87	56.73	48.49	4.19	22.45	16.21	5.47	67.62	63.87
50	5.32	52.47	48.48	6.37	53.38	55.89	6.25	52.37	54.22

**Table 4:** Effects of Concentrations of NaHMP and CMC on Grade, Recovery, and Separation Efficiency. (Sedimentation Time: 1 min)

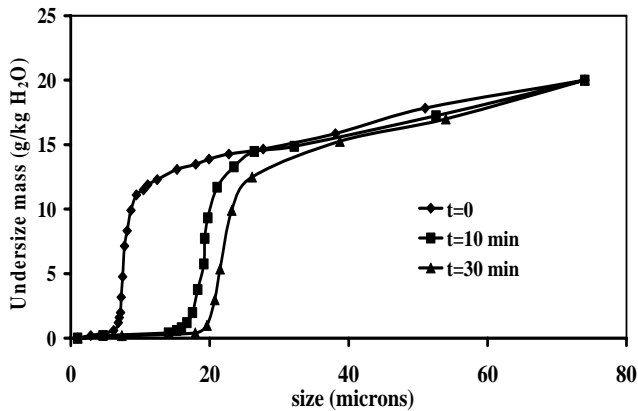
CMC (g/kg solid)									
NaHMP (g/kg solid)	1			5			10		
	Grade	Recovery	S. E.	Grade	Recovery	S. E.	Grade	Recovery	S. E.
1	4.16	62.17	44.48	4.72	57.05	47.29	3.79	47.89	29.79
10	5.06	57.55	50.96	5.43	71.6	67.24	5.75	60.03	58.82
50	6.79	60.71	66.07	6.71	58.07	62.65	5.71	52.55	51.24

**Table 5:** Effects of Concentrations of NaHMP and Starch on Grade, Recovery, and Separation Efficiency. (Sedimentation Time: 15 min)

Starch (g/kg solid)									
NaHMP (g/kg solid)	1			5			10		
	Grade	Recovery	S. E.	Grade	Recovery	S. E.	Grade	Recovery	S. E.
1	3.19	56.88	24.15	5.22	93.21	84.79	4.37	80.44	61.24
10	2.48	38.77	2.61	4.93	87.36	75.55	5.68	98.81	95.24
50	2.50	34.61	2.78	6.59	90.93	97.37	5.37	83.35	77.59

**Table 6:** Effects of Concentrations of NaHMP and CMC on grade, Recovery, and Separation Efficiency. (Sedimentation Time: 15 min)

CMC (g/kg solid)									
NaHMP (g/kg solid)	1			5			10		
	Grade	Recovery	S. E.	Grade	Recovery	S. E.	Grade	Recovery	S. E.
1	2.95	53.81	17.38	2.44	37.54	1.54	3.06	48.76	18.11
10	3.06	46.99	17.46	2.98	43.8	14.74	3.10	45.56	17.64
50	3.75	51.41	31.4	2.86	40.86	11.46	3.57	48.06	26.78



**Figure 3:** Comparison of Cumulative Size Distributions of Floccs at Various Times of Flocculation for the Experiment (at conditions: sedimentation time=15 minutes, concentration of NaHMP= 50 and that of starch= 5 g/kg solid).

The experiments carried out in this study showed that an upgrading of a natural phosphate rock from 2.4%  $P_2O_5$  to 6.6 % at a recovery of 90% and a separation efficiency of 97% was possible. Therefore, the selective flocculation may be used as a method of preconcentration of low grade natural phosphate compounds.

#### SYMBOLS USED

$c$	percentage of $P_2O_5$ in concentrate
$C$	fraction of total feed which enters concentrate
$f$	percentage of $P_2O_5$ in feed
$m$	percentage of $P_2O_5$ in apatite

#### REFERENCES

Annual Book of ASTM Standards. 1989. D422-63, Vol. 04.08, *Soil and Rock: Standard Method for Particle Size Analysis of Soils, Building Stones, Geotextiles*: Philadelphia, PA, USA. pp 86-92.

Attia, Y. A. and Yu, M. 1993. "Feasibility of Design of Selective Polymers for the Separation of Dolomite from Apatite by Selective Flocculation". In: El-Shall, H., Moudgil, B. M. and Wiegel, R., (Editors). *Beneficiation of Phosphate: Theory and Practice*.

Society for Mining, Metallurgy and Exploration, Inc.: Littleton, Colorado. pp. 209-223.

Baudet. 1980. "Selective Flocculation Process for Treating Fines of Phosphate Ores". U.S. Patent 4,235,709.

Devenport, J.E., Carroll, F., Kieffer, G.W. and Watkins, S.C. 1962. "Beneficiation of Florida Hard Rock Phosphate: Selective Flocculation". *Industrial & Engineering Chemistry Process Design and Development*. 8: 527-533.

Dogu, I., and Arol, A. I. 2004. "Separation of Dark-Colored Minerals from Feldspar by Selective Flocculation Using Starch". *Powder Technology*. 139(3): 258-263.

Jeffery, P.G. and Hutchison, D. 1981. *Chemical Methods of Rock Analysis*. 3rd Ed. Pergamon Press: Oxford, UK.

Mathur, S., Singh, P. and Moudgil, B.M. 2000. "Advances in Selective Flocculation Technology for Solid-Solid Separations". *International Journal of Mineral Processing*. 58: 201-222.

Pearse, M. J. 2005. "An Overview of the Use of Chemical Reagents in Mineral Processing". *Minerals Engineering*. 18(2): 139-149.

Pradip, Kulkarni, R. A., Gundiah, S. and Moudgil, B.M. 1991. "Selective Flocculation of Kaolinite from Mixtures with Tribasic Calcium Phosphate using Hydrolyzed Polyacrylamides". *International Journal of Mineral Processing*. 32: 259-270.

Pradip and Moudgil, B. M. 1991. "Selective Flocculation of Tribasic Calcium Phosphate from Mixtures with Quartz using Polyacrylic Acid Flocculant". *International Journal of Mineral Processing*. 32: 271-281.

Pradip, Sankar, T. A. P., Kulkarni, R. A., Gundiah, S. and Moudgil, B. M. 1993. "Selective Flocculation of Apatite from Mixtures with Dolomite, Calcite, and Quartz using Modified Polyacrylamide Flocculants". In: El-Shall, H., Moudgil, B. M. and Wiegel, R. (Editors), *Beneficiation of Phosphate: Theory and Practice*. Society for Mining, Metallurgy, and Exploration, Inc: Littleton, Colorado. pp. 183-192.

Somasundaran, P. 1986. "An Overview of the Ultrafine Problem". In: Wills, B. A. and Barley, R. W. (Editors), *Mineral Processing at a Crossroads*. Nijhoff Publishers: Leiden, The Netherlands. pp. 1-28.

Somasundaran, P. and Moudgil, B. M. 1988. *Reagents in Mineral Technology*. Marcel Dekker: New York, NY.

Wills, B.A. 1997. *Mineral Processing Technology*. 6th edition. Pergamon Press: Oxford, UK.

## ABOUT THE AUTHORS

**R. Parsaei** received her B.Sc. and M.Sc. degrees in chemical engineering from Shiraz University in 2001 and 2004, respectively. She is presently a Ph.D. student at the University of Waterloo, Canada. Her interests are in particle technology and enhanced oil recovery.

**A. Alamdari** holds a Ph.D. degree in chemical engineering from the University of NSW, Australia, 1994. He currently is a faculty member of Shiraz University and his research interests are in crystallization and particle technology.

**A. Jahanmiri** received his Ph.D. degree in chemical engineering from UMIST, England in 1989. He is presently a faculty member of Shiraz University. His interests are in process controls and simulation.

**M. A. Rajabzadeh** is a faculty member of Shiraz University at the Dept. of Earth Sciences. He received his Ph.D. degree in geology from the National Poly-technique Institute of Nancy, France in 1998. His research interests are in economic geology and industrial minerals.

## SUGGESTED CITATION

Parsaei, R., A. Alamdari, A. Jahanmiri, and M.A. Rajabzadeh. 2006. "Preconcentration of Low Grade Sedimentary Phosphate Ore Using Selective Flocculation". *Pacific Journal of Science and Technology*. 7(1):77-83.

