

## High Grade Phosphate from Syrian Phosphate at Eastern Mines

Madian Safi<sup>1</sup>, M. Bhagawanth Rao<sup>1</sup> and K. Surya Prakash Rao<sup>2</sup>

<sup>1</sup> Chemical Engineering, College of Technology, Osmania University, Hyderabad

<sup>2</sup> Applied Geochemistry (R&T), Osmania University, Hyderabad - 500 007

### Abstract

Syria is one of the major sedimentary rock phosphate producing countries in the Middle East from the Khneifiss, Eastern "A" and Eastern "B" mines. The phosphate rock of Syrian mines is being upgraded by increasing P<sub>2</sub>O<sub>5</sub> content to higher values (>28%) suitable for fertilizers and other industries. But it is not always possible to do so due to interlocking of other contents such as the higher CaO/P<sub>2</sub>O<sub>5</sub> ratio, and the high chlorine and R<sub>2</sub>O<sub>3</sub> (≈Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub>) contents.

The investigations carried out have helped us to develop upgradation of phosphate rock has three-stage carbonate flotation techniques to get high P<sub>2</sub>O<sub>5</sub> content (35 %), low chlorine content (0.02%), and CaO/P<sub>2</sub>O<sub>5</sub> ratio (1.4). Single and two-stage phosphate flotation technique were developed for getting upgraded phosphate with high P<sub>2</sub>O<sub>5</sub> content (>34%), low chlorine content (<0.07%), low R<sub>2</sub>O<sub>3</sub> (Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub>) content (<0.85%), and low CaO/P<sub>2</sub>O<sub>5</sub> ratio (<1.50).

The upgraded phosphate has a good agreement with the global market requirements of high-grade phosphate.

**Keywords:** Beneficiation, Carbonate flotation, Phosphate flotation, Impurities, High-grade phosphate.

### INTRODUCTION

A suitable phosphate for phosphoric acid production should have CaO/P<sub>2</sub>O<sub>5</sub> ratio <1.5 to reduce sulphuric acid consumption, MgO < 1% to avoid the increase of viscosity of the acid, which in turn decreases its filtration rate as well as increase in the loss of P<sub>2</sub>O<sub>5</sub>. High chlorine content increases the corrosion in the filtration plant and reduces the rate of slurry filtration (Safi et al 2005).

A report by OAML shows that the phosphate ore used for the production of phosphoric acid has P<sub>2</sub>O<sub>5</sub> (>32%), CaO (<48%), MgO (0.2-0.5%), R<sub>2</sub>O<sub>3</sub> (= Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>) (<3%), Cl (<0.03%), F (<3%), SiO<sub>2</sub> (5-12%) and organic matter (<2%) contents. On the other hand the ratios CaO/P<sub>2</sub>O<sub>5</sub> < 1.5 and Miner Element Ratio (MER) = [(Fe<sub>2</sub>O<sub>3</sub>% + Al<sub>2</sub>O<sub>3</sub>% + MgO)/P<sub>2</sub>O<sub>5</sub>%] < 0.1% have to be controlled (OAML 1998).

A report by General Fertilizer Company (GFC) in Homs-Syrian Arab Republic shows that the phosphate ore used for the production of phosphoric acid has P<sub>2</sub>O<sub>5</sub> (28-29%), CaO (48-50%), MgO (0.4-1.2%), R<sub>2</sub>O<sub>3</sub> (= Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>) (0.40-0.85%), CO<sub>2</sub> (5-8%), Cl (0.07-0.15%), F (2-4%), Na<sub>2</sub>O (0.20-0.35%), SiO<sub>2</sub> (5-9%) and H<sub>2</sub>O (1-5%) contents.

Previous studies show the increase of chlorine increases corrosion in the filtration plant while increase in F assists in forming SiF<sub>4</sub>, which changes to H<sub>2</sub>SiF<sub>6</sub>. CaO/P<sub>2</sub>O<sub>5</sub> should be < 1.5 and the excess will reduce the sulphuric acid consumption. The excess of MgO content increases the viscosity of phosphoric acid thereby decreasing the filtration rates, increasing the loss of P<sub>2</sub>O<sub>5</sub>, increasing the sulphuric acid consumption, and reduces the ability of CaSO<sub>4</sub> to form the required crystals. The

efficiency of phosphoric acid is dependent on the quality of gypsum crystals formed during the reaction of sulphuric acid with rock phosphate. The crystals should not be small or needle shape, but should be well formed to the permit filtration and washing so as to recover the maximum amount of  $P_2O_5$  from the gypsum cake. Quality of rock phosphate affects the gypsum crystal formation. The screen analysis must has +2.5 mm, +1 mm, +0.5 mm, +0.25mm, +0.125 mm, +0.053 mm, and - 0.053 mm in the ranges of 4-6 %, 5-7 %, 14-16 %, 24-28 %, 28-32%, 9-11 %, and 6-8%, respectively (GFC 2003).

In general, the phosphate ore available in Syrian mines has high amounts of chlorine and  $CaO/P_2O_5$  ratio. The low grades of Syrian phosphate were beneficiated utilizing physical methods such as crushing, grinding, wet screening, desliming, and flotation. The beneficiation processes upgraded the phosphate by increasing  $P_2O_5$  content upto >28.00 %. However, in some cases it was found that chlorine and  $R_2O_3$  contents still high and  $CaO/P_2O_5$  ratio is also high in the upgraded phosphate. This beneficiated phosphate is still having impurities effect in the phosphate industry and those impurities have to be removed.

This work aims to remove the impurities from upgraded phosphate, thereby increasing the quantity of  $P_2O_5$  content. The phosphate obtained thus will be used in the industries, which require high  $P_2O_5$  content.

## **PREVIOUS STUDY**

(Safi et al. 2005) developed three fine particle flotation techniques and optimized them for getting the best recovery. The utilized techniques for upgrading the tailings in Khneifiss mines at Syria gave 95%  $P_2O_5$  recovery. However, the upgraded phosphate has high  $CaO/P_2O_5$  ratio.

(Hanna and Anazia 1990) upgraded the phosphate rock to get a concentration of 29.5 – 30.6 %  $P_2O_5$ , 0.7 – 1.0 %  $MgO$ , and 2.8 – 8 % Insol. The recoveries from the concentration ranged from 65 to 88 %. The optimum conditions for carbonate flotation using a feed of -35 + 150 mesh size (16 %), were found 0.4 g  $H_2SO_4$ /Kg of feed as pH modifier, and three step addition of 0.3 g oleic acid / Kg of feed with 0.1 g pine oil / Kg of feed mixture for each step.

(Gaudin 1971) suggested the optimum reagents for phosphate flotation as 0.7, 0.05, 1.36, and 0.23 g/Kg for oleic acid (phosphate collector), pine-tar oil (phosphate frother), fuel oil (hydrocarbon oil), and lye (pH modifier), respectively.

## **EXPERIMENTAL WORK**

### **Materials**

The samples were collected from the Eastern mines at Syria by conning and quartering [the sample procedure was described by (Safi et al 2005)] with - 6 mm particle size mesh. Four samples were collected from different mines and the samples (-6 mm) were ground to (-1.190 mm) particle size for experimental work.

Sample collected from the hard tailings located at Eastern mines related to A-Factory was identified as  $S_1$ .

Two samples collected from the soft concentrated phosphate located at the Eastern mines "B" were identified as  $S_2$ , and  $S_3$ .

The sample collected from the soft concentrated phosphate located at the Eastern mines "A" was identified as  $S_4$ .

### **Procedures**

Jaw crusher was used for minimizing the particle size of the samples upto -6.000 mm followed by grinding using M20108 (7" x 14" Denver Model laboratory Rod Mill).

XRF Spectrometry experiments were carried in Philips MagiX PRO sequential XRF. Dedicated computer was used to do the regression analysis to prepare calibration curves using the standard sample 120c (Florida Phosphate Rock) given by NIST with the reference samples given by GECOPHAM.

The elements analyzed by XRF were F, P<sub>2</sub>O<sub>5</sub>, CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, while the total chlorine content was determined using the analytical method given by (GECOPHAM 2002) and (AFPC 1980).

Wet screening was carried using Ro-Tap (Testing Shaker-Serial No-22666), Ohio-T-674.

Flotation equipment used in the work is Versatile Flotation Cell- (VFC). (Model MEO.44114 SR.NC.VFC-14-3; Denver DR Flotation Machine).

## RESULTS AND DISCUSSION

After making 2.600 Kg sample from the sample S<sub>1</sub> for wet screening, using two sieves of 65 and 400 meshes (Tyler mesh) by dividing the ground sample to seven batches, each batch < 400 g. The total time for the process was 70 minutes. Chemical analysis of the obtained fractions and the entire sample is shown in Table 1 from which it can be observed that the original sample is poor in P<sub>2</sub>O<sub>5</sub> content with high chlorine content and high CaO/P<sub>2</sub>O<sub>5</sub> ratio. The fraction +0.210 mm was rejected and subjected to desliming of -0.037 mm. The fraction of -0.210+0.037 mm with 51.33 % (-200 mesh) was subjected to attrition for 10 minutes. Then it was treated to three-stage carbonate flotation as given by (Hanna and Anazia 1990) using 0.4 g H<sub>2</sub>SO<sub>4</sub>/Kg of feed as pH modifier and three step addition of mixture of 0.3 g oleic acid / Kg of feed and 0.1 g pine oil / Kg of feed for each step. The impeller speed during the process was maintained at 1100 rpm, solid/water ratio at 0.25 and pH at 5.5. The enriched phosphate has 35 % P<sub>2</sub>O<sub>5</sub> content with 32 % and 43 % as total weight and P<sub>2</sub>O<sub>5</sub> recoveries. CaO/P<sub>2</sub>O<sub>5</sub> ratio was reduced upto 1.4 and the chlorine content was reduced to 0.02. The process showed that for getting high grade P<sub>2</sub>O<sub>5</sub> content the recovery would be small comparatively and that phosphate can be used for the industries that require higher-grade P<sub>2</sub>O<sub>5</sub> content.

Table 1: Phosphate Composition of the Studied Fractions, Analytical Head and Calculated Head of Sample S<sub>1</sub>

Openings (mm)	Elements (Weight %)							
	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Cl	F
-1.190+ 0.210	22.52	8.54	52.03	0.28	0.35	1.11	0.25	3.49
- 0.210+0.037	26.26	4.10	55.40	0.30	0.28	0.55	0.17	3.52
-0.037	15.42	7.34	52.02	0.92	0.70	1.25	0.22	2.97
Head	23.09	6.20	53.65	0.40	0.38	0.87	0.21	3.41

Similarly 1900 Kg sample was collected from the sample S<sub>2</sub> and was subjected to similar treatment as S<sub>1</sub>. The total time for the process here was 50 minutes. Chemical analysis of the fractions and the entire sample is shown in Table 2 from which it can be observed that the original sample is rich in P<sub>2</sub>O<sub>5</sub> content (29.17%) with high CaO/P<sub>2</sub>O<sub>5</sub> ratio (1.99) and high chlorine content (0.17%). The fraction +0.210 mm was rejected and treated similarly to desliming the fraction -0.037mm by wet screening upgraded the phosphate upto 31.15 % P<sub>2</sub>O<sub>5</sub> content. The process decreased CaO/P<sub>2</sub>O<sub>5</sub> ratio upto 1.78 and chlorine content was reduced upto 0.11%. The upgraded fraction (-.0210+0.037 mm) was subjected to attrition for 10 minutes followed by phosphate flotation with the optimum reagents given by (Gaudin 1971); with 0.25 (solid/water ratio). The impeller speed during the process was 1100 rpm and pH was found to be 8.5. The flotation time was 15 minutes and the upgraded phosphate has 36.60 % P<sub>2</sub>O<sub>5</sub> content with P<sub>2</sub>O<sub>5</sub> recovery 93 %. By this beneficiation technique CaO/P<sub>2</sub>O<sub>5</sub> content was reduced upto 1.45 and chlorine content was reduced upto 0.03 %. The obtained phosphate is very rich and can be used as feed to the fertilizer plant and other chemical industries according to (GFC,

2003) and (OSML, 1998). It maybe blended with low-grade phosphate rock available in the mines. According to its P<sub>2</sub>O<sub>5</sub> content it has higher price in the global market comparatively.

**Table 2: Phosphate Composition of the Studied Fractions, Analytical Head and Calculated Head of Sample S<sub>2</sub>**

Openings (mm)	Elements (Weight %)							
	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Cl	F
-1.190+0.210	28.58	9.31	50.97	0.28	0.28	0.51	0.21	3.70
-0.210+0.037	31.15	3.83	55.33	0.30	0.32	0.50	0.11	3.84
-0.037	26.41	8.67	50.06	0.89	0.67	1.18	0.23	3.76
Head	29.20	6.87	52.61	0.42	0.38	0.65	0.17	3.77

Grinding 1.500 Kg of the sample S<sub>3</sub> upto -65 mesh (-0.210 mm) and the obtained sample was subjected to the wet screening process over the screen -400 mesh (-0.037 mm). Chemical analysis of the fractions and the entire sample is shown in Table 3. From which it can be observed that the original sample is rich in P<sub>2</sub>O<sub>5</sub> content (33.47%) with slightly high CaO/P<sub>2</sub>O<sub>5</sub> ratio (1.53) and slightly high in chlorine content (i.e. 0.09%). The sample also has high R<sub>2</sub>O<sub>3</sub> (Al<sub>2</sub>O<sub>3</sub>+Fe<sub>2</sub>O<sub>3</sub>) > 0.85%. Desliming the fine particles (-0.037 mm) by wet screening upgraded the phosphate upto 35.79 % P<sub>2</sub>O<sub>5</sub> content and decreased CaO/P<sub>2</sub>O<sub>5</sub> ratio upto 1.46. Chlorine and R<sub>2</sub>O<sub>3</sub> contents were reduced upto 0.05% and 0.80%, respectively. The high-grade phosphate (35.79% P<sub>2</sub>O<sub>5</sub>) has acceptable amounts of chlorine content, R<sub>2</sub>O<sub>3</sub> content and CaO/P<sub>2</sub>O<sub>5</sub> ratios as given by (GFC 2003) and (OSML 1998).

**Table 3: Phosphate Composition of Obtained Fractions, Analytical and Calculated Head of Sample S<sub>3</sub>**

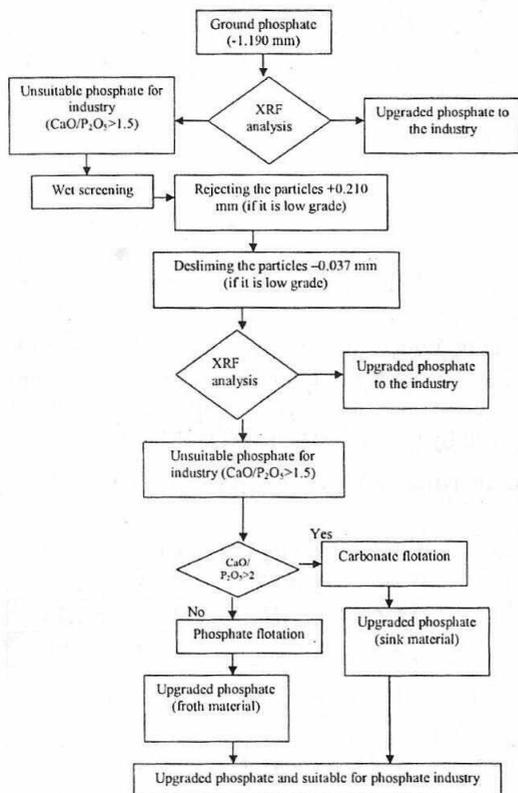
Openings (mm)	Elements (Weight %)							
	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Cl	F
-0.210+0.037	35.79	5.28	52.20	0.34	0.36	0.37	0.05	4.07
-0.037	27.21	7.88	48.62	0.83	0.69	1.16	0.20	3.78
Head	33.47	5.98	51.23	0.47	0.45	0.58	0.09	3.99

**Table 4: Phosphate Composition of Obtained Fractions, Analytical and Calculated Head of Sample S<sub>4</sub>**

Openings (mm)	Elements (Weight %)							
	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Cl	F
-0.210+0.037	31.05	8.33	51.29	0.44	0.46	0.61	0.07	3.85
-0.037	19.15	11.77	49.83	0.90	1.04	1.56	0.18	3.26
Head	26.53	9.63	50.74	0.61	0.68	0.97	0.11	3.63

Grinding 2.000 Kg of sample S<sub>4</sub> upto -0.210 mm and the sample was subjected to the wet screening process over the screen 400 mesh (0.037 mm). Chemical analysis of the fractions and the entire sample is shown in Table 44 from which it can be observed that the original sample has P<sub>2</sub>O<sub>5</sub> content (26.52%) with high CaO/P<sub>2</sub>O<sub>5</sub> ratio (1.91) and high in chlorine and R<sub>2</sub>O<sub>3</sub> contents (i.e. 0.11% and 1.29%, respectively). Desliming the fine particles (-0.037 mm) by wet screening upgraded the phosphate upto 31.05 % P<sub>2</sub>O<sub>5</sub> content and decreased CaO/P<sub>2</sub>O<sub>5</sub> ratio upto 1.65. Chlorine and R<sub>2</sub>O<sub>3</sub> contents were reduced upto 0.07% and 0.90%, respectively. The high-grade phosphate (31.05% P<sub>2</sub>O<sub>5</sub>) was separated and subjected to attrition for 10 minutes followed by two-stage phosphate flotation with the optimum reagents given by (Gaudin 1971), solid/water ratios was 0.25 and 0.60 in the first and second stages, respectively. The pH was found in the range of 8.5-9.0. The flotation time was 20 minutes (15+5) for the first and second stages, respectively. The upgraded phosphate has 33.17 % and 37.19 % P<sub>2</sub>O<sub>5</sub> content for the first and second stages, respectively. The upgraded phosphates from both stages were blended and the obtained concentrated phosphate has 34.78 % P<sub>2</sub>O<sub>5</sub> content with P<sub>2</sub>O<sub>5</sub> and total weight recoveries for the entire process as 76 % and 98 %. The chemical analysis of the enriched phosphate in the both stages and the blended concentrate is shown in Table 5. By this

beneficiation technique CaO/P<sub>2</sub>O<sub>5</sub> content was reduced upto 1.51 and chlorine content was reduced upto 0.06 %. The obtained phosphate is very rich and can be subjected as a feed to the fertilizer plant and other chemical industries according to (GFC 2003) and (OSML 1998). It maybe blended with low-grade phosphate rock available in the mines. According to its P<sub>2</sub>O<sub>5</sub> content it has higher price in the global market comparatively.



**Fig. 1: The General Algorithm for Beneficiation Different Grades of Syrian Phosphate to Get High-Grade Phosphate with Acceptable Impurities Contents**

In the beneficiation processes (wet screening and flotation) local tap water from NMDC Lab.-Hyderabad-INDIA was used and it has the composition Nil mg/l CO<sub>3</sub><sup>2-</sup>, 341 mg/l HCO<sub>3</sub><sup>-</sup>, 136 mg/l Ca<sup>2+</sup>, 74 mg/l Mg<sup>2+</sup>, 920 mg/l soluble salt and pH 7.45 (IPM-Department of Water Analysis).

Figure 1 shows the general algorithm for beneficiation different grades of Syrian phosphate to get high-grade phosphate with acceptable impurities contents.

**CONCLUSION**

The beneficiation of phosphate increases P<sub>2</sub>O<sub>5</sub> content but it should also consider the other impurities in the phosphate ore such as CaO, Cl, and R<sub>2</sub>O<sub>3</sub>. The general algorithm shows the treatment of different grades of phosphate (even with high P<sub>2</sub>O<sub>5</sub> content). For the phosphate having CaO/P<sub>2</sub>O<sub>5</sub> > 2 it was suggested wet screening, desliming of fine fractions (-0.037 mm), rejection of coarse fractions (+0.210mm), and three-stage carbonate flotation. High grade of phosphate was obtained having 35 % (P<sub>2</sub>O<sub>5</sub> content) with 1.4 CaO/P<sub>2</sub>O<sub>5</sub> ratio. For the phosphate having 1.5 < CaO/P<sub>2</sub>O<sub>5</sub> < 2 single or multi-

**Table 5: Upgraded Phosphate Composition by Two Stages Phosphate Flotation and the Blended Concentrate**

Elements (Weight %)	Concentrated phosphate (1 <sup>st</sup> stage)	Concentrated phosphate (2 <sup>nd</sup> stage)	The blended concentrate
P <sub>2</sub> O <sub>5</sub>	33.17	37.19	34.78
SiO <sub>2</sub>	5.25	5.38	5.30
CaO	52.78	51.89	52.42
Fe <sub>2</sub> O <sub>3</sub>	0.43	0.29	0.37
Al <sub>2</sub> O <sub>3</sub>	0.36	0.26	0.32
MgO	0.72	0.33	0.56
Cl	0.06	0.05	0.06
F	3.77	4.03	3.78

stage phosphate flotation and the phosphate was obtained having  $>34\%$   $P_2O_5$  content. By this beneficiation technique  $CaO/P_2O_5$  content was reduced to  $<1.50$ . Chlorine and  $R_2O_3$  contents were reduced to  $<0.07\%$  and  $<0.85\%$ , respectively. For the sample  $S_3$  it was found that only desliming of fine particles (0.037 mm) is required to decrease the impurities in the phosphate and getting it upgraded and acceptable for phosphate industry.

The high quality phosphate obtained from the mentioned processes gives a good agreement and an acceptable composition in the global market. It can be used for the industries require high quality phosphate composition. It maybe blended with low grades of phosphate for getting suitable grade of phosphate to be provided to wet process phosphoric acid.

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