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Evaluation of Saudi Phosphate Rocks for Wet Process Phosphoric Acid Production

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Abstract. Laboratory analysis and test data are presented on Saudi phosphate rocks from two different deposits. A preliminary evaluation and assessment of the rocks as a raw material for manufacture of phosphoric acid is attempted, suggestion are made for the beneficiation methods.

Introduction

For the assessment of phosphate resources in northern Saudi Arabia an intensive geological survey was carried out in a nine years period (1977-1986) in the Sirhan-Turayf region. The region is proved to have about 3,000 million tons of phosphate rock. Among the several areas discovered Al-Jalamid area and Umm Wual area suggest themselves for potential exploitation [1].

On the other hand, sulphur is produced in the Kingdom as a by product of petrochemical industry in excess of one million tons per year [2], after the commencement of fertilizer complex in Al-Jubail, the Kingdom is expected to import annually 250,000 tons of P_2O_5 equivalent of phosphoric acid.

All these facts indicate that conditions are apparently suitable for the start of phosphoric acid industries in Saudi Arabia. Certainly there is a need for evaluation and assessment of the phosphate resources for the wet process phosphoric acid production. This work constitutes the first step to satisfy this need.

Although, the production of phosphoric acid from the phosphate rock by wet process has been known for more than a hundred years, the design of a phosphoric acid plant is still made by empirical methods. The quantitative effect of rock properties on the process variables cannot be exactly predicted unless pilot plant studies are performed. However, the chemical and physical analysis of the rock can indicate qualitatively how it will behave when used in the wet process and can give clues for possible beneficiation methods.

The representative rock samples for this study were collected from Al-Jalamid and Umm Wu'al areas after a thorough examination of geological data on the variation of composition in the region and by consultation of geologists who actually worked in the geological survey mentioned above.

Important Factors and their Implications on Process Technology

A) The factors directly related to the properties of the phosphate rock

P_2O_5 content

The P_2O_5 content is the first factor to be considered, to find out how much raw material is needed for a certain capacity. Pure fluorapatite ($Ca_{10}F_2(PO_4)_6$ main phosphate bearing constituent of the rock), contains 42.26 percent P_2O_5. Any value of P_2O_5 content lower than this implies extra transportation cost and excessive use of sulphuric acid in the acidulation step as seen in Table 1.

Table 1. Effect of P_2O_5 content of phosphate rock on the raw material requirement [3]*

	Grade of rock % P_2O_5	Rock requirement tons/ton of P_2O_5 in acid
Al-Jalamid	25.86	4.11
Low grade rock	29	3.67
Umm-Wual	32.46	3.28
High grade rock	38	2.80

* For 94 percent P_2O_5 recovery in dihydrate process

CaO content and CaO/P_2O_5 ratio

CaO content is important due to two reasons. The first is the fact that CaO in excess of the stoichiometric ratio corresponding to that in fluoropatite (CaO/P_2O_5 ratio in fluoropatite is 1.31) is usually found as $CaCO_3$ and this compound reacts with sulphuric acid during acidulation. Sulphuric acid requirements of some phosphate rocks are shown in Table 2. The second reason is the determination of the beneficiation method. When the $CaCO_3$ content of the rock is high, beneficiation is considered either by flotation or calcination depending on the properties of the rock and the availability of the low priced fuel for calcination.

Table 2. **H_2SO_4 Requirement of phosphate rock [4]**

	Al-Jalamid	Tunis, Gafsa	Umm-Wual	USSR, Kola
CaO/P_2O_5 ratio in the rock	2.046	1.66	1.57	1.28
H_2SO_4 requirement, tons/ton of P_2O_5	3.89	3.09	2.95	2.34

MgO content and MgO/P_2O_5 ratio

MgO is one of the most undesirable impurities in the phosphate rock. It causes difficulties both in the flotation and phosphoric acid production processes. Flotation of phosphate rocks with high MgO content is a subject of intense research [3], presence of MgO in the rock reduces the selectivity of the flotation collectors. A high MgO content of rock indicates a high expectancy of the acid produced will form precipitates [4,5] with fluorine, which may blind the filter cloth or may cause post precipitation after evaporation. In addition, the viscosity of the acid is strongly affected by the MgO content of the rock. High viscosity also means low filtration rate and a low heat transfer coefficient in the evaporator. Effect of MgO on some of the process parameters is shown in Table 3.

SiO_2 content

The corrosive action of HF formed during acidulation is reduced by reactive silica which forms SiF_4 and fluorosilicates, therefore it is desirable to have a small amount of silica in the rock. However, amounts in excess of 2 percent SiO_2 cause erosion of equipment and acceleration of corrosion. When silica is present as small particles (less than 50 micron) it usually causes blinding of the filter pores.

$R_2O_3(Al_2O_3 + Fe_2O_3)$ content and R_2O_3/P_2O_5 ratio

R_2O_3 contents above 3 percent usually decrease the plant capacity, P_2O_5 recovery, filtration rate and cause post precipitation problems. Iron and aluminum are not totally dissolved during acidulation and in some processes they are tolerable up to 5 percent. Fig. 4 is presented to assess the effect of R_2O_3 on the wet process.

CO_2 and organics contents

A high percentage of CO_2 is an indication of the presence of carbonates. This in turn indicates that beneficiation of the rock by flotation will be difficult [8]; usually rocks with appreciable amounts of organics (higher than 5-6 percent) develop a stable foam during acidulation, decrease filtration rate, and produce dark colored phosphoric acid. However, organic matter may improve crystal growth.

Table 3. Effect of MgO content of phosphate rock on the filtration rate and P_2O_5 losses [4,6,7]

Type of rock	% P_2O_5 in rock	Filtration rate	P_2O_5 lost in gypsum as % of total P_2O_5 in feed		
		ton of P_2O_5/m^2d	WS	CS	CI
USSR Kola (MgO:0.35%)	38.6	4.8	0.3	1.6	0.7
Egypt+Togo[(a)] (1:1)	33.4	4.8	0.7	2.0	2.5
Syria (MgO:0.35%)	31.8	4.0	0.3	1.6	0.2
Algeria (MgO:1.4%)	32.8	4.4	0.4	1.3	0.1
Algeria[(b)] (MgO:2%)	27.8	2.1	1.7	4.3	0.1
Egypt (MgO:4.3%)	30.2	1.9	8.5	3.1	1.1

WS: Water soluble P_2O_5

CS: Ammonium citrate soluble P_2O_5, representing co-crystallized P_2O_5 in gypsum.

CI: Ammonium citrate insoluble P_2O_5

(a): % MgO in Togo rock = 0.35

(b): The increase of Mgo from 1.4 to 2% decrease the filtration rate by more than 50%.

Table 4. Effect of R_2O_3 content on process parameters

Rock source	Composition P_2O_5 %	P_2O_3 %	Optimum H_2SO_4 conc. in reactor	Filtration rate ton of P_2O_5/m^2d	P_2O_5 yield, %
Florida	35.6	2.6	1.6	8.2	96
Western US	26.7	4.5	4.8	2.3	92
Tennessee	20.4	6.9	8.7	4.3	95

Chlorine content

Usually chlorine contents above 0.01 percent in phosphate rock cause excessive corrosion in the phosphoric acid plant. This increases the capital cost because expensive alloys must be used. The plant may shut down frequently due to the failure of some parts.

Fluorine content

Fluorine is usually present in phosphate rocks in a fairly constant F/P_2O_5 ratio of about 0.12. The main problems resulting from the presence of fluorides are corrosion, scale and sludge formation. If the Si/F (molar) ratio is greater than 4, precipitation of gelatinous compounds in the acid will occur and these will cause blocking of pipelines, pumps and the filter. If this ratio is less than 4, free fluorine will be produced during acidulation which will convert to HF, and cause severe corrosion and a possible increase in the shut down time of the plant.

Cadmium content

There is a growing concern about the influence of heavy metals on human health. Therefore, there has been extensive attention being given to the prohibition of cadmium containing fertilizers [9]. About 70 percent of the cadmium present in the phosphate rock is found in the phosphoric acid produced by conventional methods [10]. The level of cadmium allowed in the feed rock therefore should not exceed 250 ppm.

Strontium content

In hemihydrate/dihydrate (HH/DH) phosphoric acid process [11], one of the production steps is the recrystallization of $CaSO_4 . 1/2\, H_2O$ as $CaSO_4 . 2H_2O$. If SrO is present in excess of 3 percent in the phosphate rock, this recrystallization step is inhibited [10].

Rock grinding

Comminution consists one of the major items in the production cost list of the phosphate rock processing. Particle size of the rock is an important parameter in the acidulation reaction because the reaction rate is directly proportional to the total surface area exposed to the acid. In addition, in flotation, there is an optimum particle size for efficient separation and in calcination the rate of heat and mass transfer are strongly affected by the presence of apatite particles surrounding $CaCO_3$ and $MgCO_3$ particles.

X-Ray diffraction analysis

Apatite is found in nature in many different variations [*e.g.*, Fluorapatite: $Ca_{10}(PO_4)_6F_2$, francolite $Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{2+x}$, Hydroxyapatite $Ca_{10}(PO_4)_{6-x}(CO_3)_x(OH)_{2+x}$]. X-ray diffraction analysis is needed to identify the version present in a particular sample.

B) Factors related to the process conditions as well as the rock properties

These factors can be determined by processing the rock in a bench scale or a pilot plant, although they are not in the scope of this investigation they are included here for the sake of completeness.

P_2O_5 recovery

This is the amount of P_2O_5 in the phosphoric acid produced expressed as a percentage of total P_2O_5 present in the rock fed. It very highly depends on the reactivity of the rock, sulphate level in the reactor and the kind of process chosen.

Cake efficiency

It is a measure of P_2O_5 retained in the cake after the filtration of the reactor slurry. It depends on the particle size and crystalline structure of the gypsum crystals in the cake, and the presence of gel-like material in the acid. The crystal structure in turn is highly dependent on the sulphate level and temperature of the acidulating tank, and the impurities in the rock. The effect of the impurities is not exactly known except that Al_2O_3 promotes crystallization [12]. Gel-like material in the acid is formed when the R_2O_3 level in the rock is high.

Steam cost

The rate of steam used depends on the concentrations of acid at the entrance and exit of the evaporator which is used to concentrate the filtrered acid. When there is a sulphuric acid plant nearby the steam produced there can be utilized in the evaporator to reduce the steam cost.

On line factor

It is a measure of how often the process is interrupted by malfunction of equipment (*e.g.* excessive scaling on the filters and evaporators depending on the impurities in the rock, problems with sludge transportation, difficulties in crystallizer control, excessive corrosion, lack of spare parts, etc.).

Experimental Results and Discussion

The chemical analysis of the phosphate rock samples obtained from Al-Jalamid and Umm-wual areas are given in Table 5 together with the analysis of the commercially used rocks. The amount of rock taken from each deposit was 25 tons. At least 10 samples were taken from each lot and analyzed with Inductively Coupled Plasma

Table 5. **Comparison of Saudi phosphate rocks with commerically used rocks [3,5]**

	Percent by Weight			
	Commercial		Saudi (as received)	
Constituent	**Range**	**Median**	**Al-Jalamid**	**Umm-Wual**
P_2O_5	29-39	33	25.86	32.46
CaO	45-54	51	52.91	50.84
SiO_2	0.2-8.7	2	1.17	2.77
$Al_2O_3+Fe_2O_3(R_2O_3)$	0.4-3.4	1.4	0.31	0.44
MgO	0.05-0.8	0.5	0.84	0.19
Na_2O	0.1-0.9	0.5	0.21	0.86
CO_2	0.2-7.5	4.5	9.24	3.8
F	2.2-4.35	3.7	0.1	0.84
Cl	0.0-0.5	0.02	0.03	2.52
SO_3	0.0-3.0	1.0	2.22	2.27
Weight Ratios				
CaO/P_2O_5	1.28-1.65	1.45	2.046	1.57
$(P_2O_3)/P_2O_5$	0.015-0.1	0.04	0.012	0.0135
MgO/P_2O_5	0.002-0.03	0.015	0.032	0.005
$(R_2O_3+MgO)/P_2O_5$	0.027-0.12	0.06	0.044	0.019

Atomic Emission Spectrometer. Statistically these analyses had 95 percent confidence limits. Sieve analyses and P_2O_5 content in various size ranges of the phosphate rock samples are presented in Table 6 and 7.

These are the average of a number of sieve analysis conducted on 8 samples taken and has about 92 percent confidence limits for P_2O_5 analyses and 90 percent confidence limits for sieve analyses. P_2O_5 analyses were performed by employing the colorimetric phospho-vanado-molybdate method. The P_2O_5 content of Al-Jalamid

Table 6. **Sieve analysis and P_2O_5 content of Al-Jalamid rock (as received)**

Sieve opening mm	**Differential retained W/W %**	**Cumulative retained W/W %**	**P_2O_5 content W/W %**	**Portion of total P_2O_5 W/W %**
40.00	20.58	20.58	18.67	17.48
9.51	7.00	27.58	22.12	7.05
4.75	9.90	37.48	21.23	9.56
2.00	12.60	50.08	19.68	11.29
1.18	6.36	56.44	20.45	5.92
0.425	10.90	67.34	21.32	10.56
0.250	8.83	76.17	25.67	10.33
0.106	15.33	91.50	28.42	19.85
Pan	8.50	100.00	20.59	7.96

Table 7. Sieve analysis and P_2O_5 content of Umm-Wual rock (as received)

Sieve opening mm	Differential retained W/W %	Cumulative retained W/W %	P_2O_5 content W/W %	Portion of total P_2O_5 W/W %
3.36	6.10	6.10	16.8	3.19
2.00	0.96	7.06	18.60	0.55
1.18	1.22	8.28	20.78	0.78
0.595	3.60	11.88	28.20	3.16
0.297	12.91	24.79	31.37	12.61
0.250	12.31	37.10	33.20	12.73
0.150	52.00	89.10	34.51	55.90
0.106	4.35	93.45	34.26	4.64
0.075	2.35	95.80	33.70	2.47
Pan	4.20	100.00	30.31	3.97

rock is lower than those of the commercially used rocks implying an obvious necessity for beneficiation. Sieve analyses results for Al-Jalamid rock show that it is not possible to obtain any size range (by simple sieving) which contains more than 28.42 percent P_2O_5 therefore prospects for beneficiation by sieving do not look very optimistic.

High CaO/P_2O_5 and CO_2 values in Table 5 and X-ray diffraction analysis in Table 8 show that $CaCO_3$ is present in Al-Jalamid rock as the major impurity. Calcination can be considered as a beneficiation method. In Fig. 1 the thermogravimetric curve for Al-Jalamid rock exhibits a decline between 800°-900°C. This is the weight loss due to CO_2 evolution which is also confirmed by the DTA curve and high CO_2 percentage in the chemical analysis. P_2O_5 content of Al-Jalamid rock can also be increased by flotation, there is an extensive research activity [13] on the flotation of carbonate rich phosphate rocks, and recently a new promising method has been found [14]. Beneficiation methods applied to decrease CaO are expected to decrease MgO level also, because both substances are present as carbonates. SiO_2 content of both of the Saudi phosphate rocks is low, to decrease the corrosive effect of HF, it may be necessary to add some silica. However, the main corrosive action must be expected from excessively high chlorine content in Umm-Wual rock. Feasible methods must be found to reduce the level of chlorine before this rock can be considered for phosphoric acid production.

The wet grinding Bond's work index values obtained experimentally for Al-Jalamid rock ranges between 17.75 and 25.92 kwh/ton which compare with the work indices of Florida rock [5] (18.5-20.0 kwh/ton). The work indices obtained for the Umm-Wual sample are in the range of 29.0 to 30.0 kwh/ton. These compare with the work index of South African rock [5].

For a possible beneficiation operations liberation size for Al-Jalamid rock was found to be 0.425 mm by studying the various particle size ranges of rock under

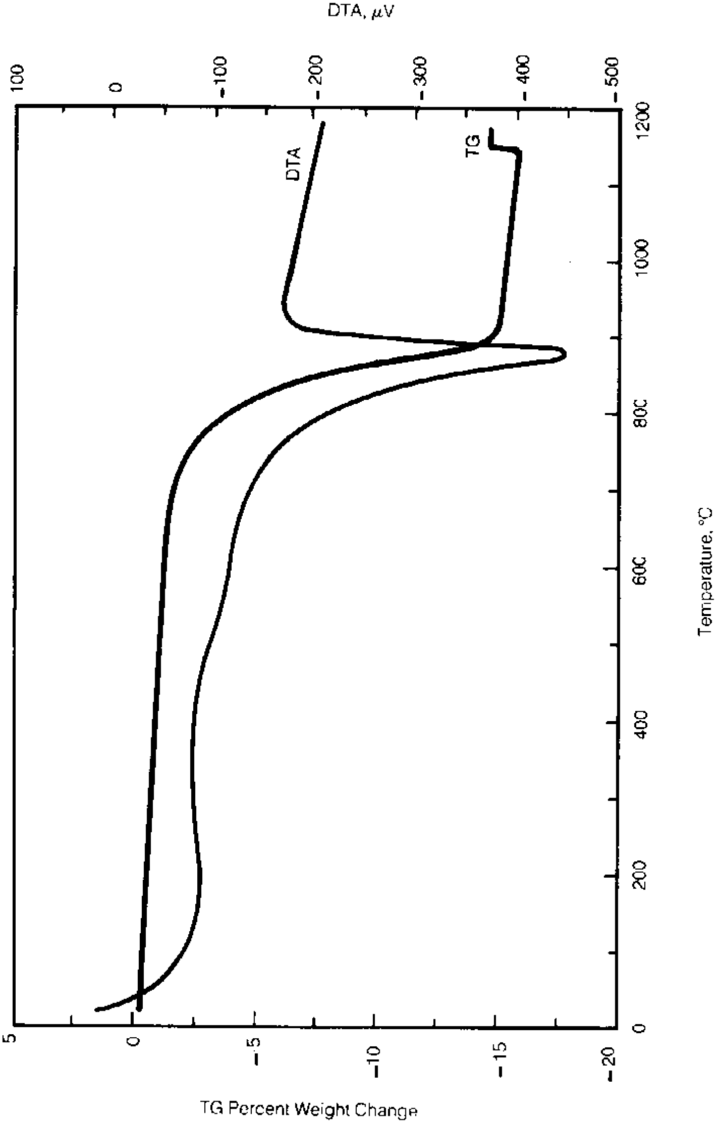

Fig. 1. DTA and TGA curves for Al-Jalamid rock

Table 8. **X-ray diffraction analysis results**

Mineral	Umm-Wual rock (weight percent)	Al-Jalamid rock (weight percent)
Fluorapatite	59.0	40.5
Quartz	4.0	2.0
Calcite	36.0	57.5
Kehoelite	1.0	0.0

microscope to see under which size the pieces of calcite and apatite are separated from each other. This value seems to be quite economical when compared with the particle size range for flotation of Florida rock (0.4-0.1 mm). Liberation size was not determined for Umm-wual rock since its P_2O_5 content is high and it will not be subjected to flotation or calcination. The surface area of Umm-Wual rock is 16.64 m^2/gr and that of Al-Jalamid rock is 7.18 m^2/gr (both measurements were performed by BET equipment). These measurements compare quite well with the values given for the commercial rocks in Table 9.

Table 9. **Specific surface area of some commercial phosphate rocks [13] (-200/+240 m)**

Phosphate rock	Surface area (B.E.T.) m^2/gr
Morocco	20.1
Togo	12.7
Florida	13.5
Nauru	11.2
Taiba	7.5
Polaborwa	0.4*
Kola	0.1*

* The last two rocks are of igneous origin

The preliminary tests performed on bench scale for the acidulation of both phosphate rocks show that it is possible to obtain at least 90 percent P_2O_5 recovery. The filtration test results indicate 95 percent cake efficiency, it is believed that P_2O_5 recovery and cake efficiency can be improved by the addition of some Al_2O_3 in the phosphate rock samples.

Conclusions

The preliminary analyses and tests performed on the Saudi phosphate rocks lead to the following conclusions:

1) P_2O_5content of the Umm-Wual rock is as high as the commercially used phosphate rocks, however, it contains intolerably high percentage of chlorine.

2) The level of impurities in the Al-Jalamid rock is high and obviously it needs to be beneficiated before being used as a raw material for phosphoric acid production.

3) Silica content of both types of ore is low, while the main impurity is in the form of carbonates of calcium and magnesium, therefore beneficiation by both flotation and calcination methods must be considered.

4) The high MgO content of Al-Jalamid rock must be reduced in order to avoid the production of acid with high viscosity and low filtration rate.

5) The levels of P_2O_3, fluorine, cadmium and strontium are all low implying low gel production during filtration and low post evaporation precipitation. Low HF production during acidulation, low toxicity of the product acid, and suitability of both rocks for HH/DH process are expected.

6) Addition of Al_2O_3 to both rocks can be considered to improve the crystallization of gypsum, and facilitate the cake efficiency.

7) Presence of organics and carbonates in both rocks suggest that foaming must be expected during acidulation.

8) It is possible to obtain portions relatively rich in P_2O_5 from Al-Jalamid rock by grinding and sieving, but P_2O_5 levels of these portionsare still low; and more efficient beneficiation methods are needed.

9) The grinding energy requirements of Saudi phosphate rocks are expected to be similar to those of the commercially used rocks.

10) The liberation size for Al-Jalamid rock is reasonably large so that excessive grinding is not necessary for beneficiation purposes.

11) X-ray diffraction analysis varifies the chemical analyses showing that the main impurity is $CaCO_3$ in both rocks.

12) DTA and TGA analyses give the range of calcination temperature of Al-Jalamid rock as 800° to 900°C.

13) Specific surface area of both rocks are comparable with the commercially used rocks and reaction rates expected must be at reasonably high levels.

14) Preliminary tests performed on the bench scale to obtain phosphoric acid from both rocks reveal that P_2O_5 recoveries of about 90 percent and cake efficiency of

95 percent are expected. Both figures can be improved by further pilot plant studies and adjustments in the rock impurities.

The final conclusions of this study can be that despite their drawbacks both rocks can be efficiently utilized as raw materials for phosphoric acid production. The conclusions listed above can be used as a guide in planning further studies on pilot scale. The results of the pilot scale studies can constitute the basis for feasibility studies and the final selection of the type of the process.

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تقويم خام الفوسفات السعودي ومدى ملاءمته لإنتاج حامض الفوسفوريك بواسطة الطريقة الرطبة

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ملخص البحث. لقد تم إجراء التجارب المختبرية والتحاليل الكيميائية والفيزيائية اللازمة على نوعين أساسيين من خام الفوسفات السعودي. وكذلك تمّ فعلاً تقويم هندسي تقني للخام بخصوص كفاءته وفعاليته للاستخدام كمصدر أساسي لإنتاج حامض الفوسفوريك بواسطة الطريقة الرطبة. كما تم أيضًا وضع المرئيات الفنية المناسبة لتركيز هذا الخام بما يتناسب مع ظروف المملكة.