Obtaining the partially acidulated phosphate rocks by means of intermediate-grade phosphate and diluted phosphoric acid: Influence of some parameters

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In this work, some parameters during the partial acidulation by phosphoric acid of phosphate 53.75% BPL (bone phosphate of lime) having different particle sizes are determined. P_2O_5 recovery is obtained by performing a series of reactions using phosphoric acid diluted from 10 to 40 wt.% and with reaction times ranging from 10 to 50 minutes. The best conversion rates are obtained with the following reaction parameters: phosphates size: 88–177 μm , reaction time: 50 minutes and phosphoric acid concentration: 40 wt.%. In the second part, the water-soluble P_2O_5 of PAPRs (Partially Acidulated Phosphate Rocks) obtained with phosphoric acid 30% and 40 wt.% is measured. The results of experiments showed that the water-soluble P_2O_5 has reached 15.2% for PAPRs obtained by reacting phosphate 88 μm with phosphoric acid 40 wt.%.

Keywords: PAPRs, phosphate rocks, phosphoric acid, water-soluble P_2O_5 .

INTRODUCTION

Phosphate rocks (PRs) from different sources are expected to behave differently in acidulation process because the composition of these rocks varies from one deposit to another¹. Therefore, PRs contain one or more phosphate minerals suitable for commercial use, such as fluorapatite $3Ca_3(PO_4)_2 \cdot CaF_2$. Chemistry of acidulation of apatite crystal structure is complicated. It is highly dependent on competing or synergistic factors specific to the type of phosphate rock mineral, such as porosity, surface area and impurities content, especially in the form of metal oxides of the general formula R_2O_3 ². According IAEA³ (International Atomic Energy Agency), the mineralogy of phosphorus rich rocks is complex and there are more than 200 known phosphate minerals. The grade of raw phosphate depends on the total phosphorus content, type of impurities and amount of impurities. Total phosphorus is expressed as⁴:

Phosphorus pentoxide P_2O_5 ;

Calcium phosphate $Ca_3(PO_4)_2$ (BPL), where:

$$\% P_2O_5 \times 2.1853 = \% BPL \quad (BPL \times 0.4576 = \% P_2O_5)$$

Phosphate ores are divided into three groups according to their P_2O_5 content: low-grade ores (12–16% P_2O_5), intermediate-grade ores (17–25% P_2O_5), and high-grade ores (26–35% P_2O_5). Deposits that could be mined and processed economically to give about 28–38% P_2O_5 are considered commercial phosphate deposits⁵. Manufacturers of phosphoric acid and phosphorus fertilizers normally require a minimum content of 28% P_2O_5 , and most marketed grades of phosphate rocks contain more than 30% of P_2O_5 (65% BPL). To meet this requirement, most phosphate ores undergo beneficiation by washing and screening, de-liming, magnetic separation and flotation⁶.

Acidulation of phosphate rocks with either sulphuric or phosphoric acids produces the phosphate components monocalcium phosphate (MCP), small amounts of dicalcium phosphate (DCP) and (omitting iron and aluminium species) quantities of residual apatite depending on the degrees of acidulation⁷. The reactions

between PRs and these acids can be expressed using the following equations⁸:

PAPRs are generally prepared by reacting PRs with a less than the stoichiometric quantity of H_2SO_4 or H_3PO_4 required for preparing fully acidulated phosphate fertilizers such as single superphosphate (SSP) (Reaction 1) or triple superphosphate (TSP) (Reaction 2). The PAPRs contains part of its phosphorus in a water-soluble form $Ca(H_2PO_4)_2$ and the rest mainly as unreacted apatite (residual PRs). Processes of PRs dissolution can be summarized as follows⁹:

According to the equation (3):

- SSP is obtained when $y = 1$ and $x = 0$;
- TSP is obtained when $y = 1$ and $x = 6$;
- PAPRs is obtained when $0 < y \leq 0.75$.

In practice, the degree of PRs acidulation ranges from 20% to 50%. Compared to the SSP and TSP, several studies^{10–13} have shown that the PAPRs may be a mean to improve agricultural efficiency at lower cost. In addition, PAPRs have the advantage of being often more concentrated than SSP. Despite little information is available in literature on Cd uptake by crops from either phosphate rock or partially acidulated, PAPRs may limit the absorption of this hazardous metal¹⁴. The solubility characteristics of the directly acidulated PAPRs are affected by the type, composition and concentration of the acid used for acidulation, degree of acidulation, nature and fineness of PRs, without forgetting the method of manufacture^{15, 16}. According to IFDC¹⁷, PAPRs are less expensive and cheaper than fully acidulated

fertilizers because less acid and energy is required per unit of phosphorus in the product.

From the process point of view, it is possible to produce PAPRs commercially in several ways along the same lines as SSP and TSP. The preferred process should be one that gives the highest possible return on investment. Indeed, in the phosphate fertilizer NPK complex, it is possible to extract the diluted phosphoric acid to the phosphoric acid plant to produce PAPRs. With this aim in mind, the following factors should be taken into account: the quality of the PRs, process simplicity and his integration with existing facilities and the availability of other raw materials and services. But in all cases, the quality of the PRs remains the principal factor in deciding which process to use^{18–20}.

The phosphates of the area of Djebel Onk, located in the Southeast of Algeria, are part of a succession of sedimentary strata formed at the end of the Cretaceous–Eocene era²¹. phosphate rock, used in the experiments, is a fluorapatite and is characterized by a granular appearance; it has a high substitution of CO₃ (CaO/ P₂O₅ = 1.75 to 1.90) and generally is low in silica and in iron²². From the literature and research we carried out on Djebel Onk phosphates, it can be concluded that only few investigations and studies were conducted on these phosphates despite their high quality (24–28% P₂O₅) and important reserves (about 2 billions of tons)²³.

The main reason for choosing this subject is to valorize Djebel Onk phosphate ore (53.75% BPL) which is not considered a merchant phosphate. The other reason is that PAPRs appear to be more an attractive alternative fertilizer of TSP. Indeed, the amount of phosphoric acid required to manufacture this fertilizer is considerably low.

MATERIAL AND METHODS

Phosphate samples mentioned in Table 1 was provided by the Algerian phosphate company (FERPHOS). All samples was analyzed by appropriate analytical methods such as spectrophotometry for SiO₂, Fe₂O₃, Cl[–] and F[–], complexometric titration with a standard solution of EDTA for CaO, MgO and Al₂O₃ and finally the flame spectrophotometry for sodium and potassium. The apparatus TECHNICON AUTO ANALYZER standardized NS²⁴. NF U42-201 was used for spectrophotometric analysis of P₂O₅ (molybdovanadate method)²⁵.

The following sieves were used to collect phosphate samples: 170 mesh, 80 mesh, 70 mesh and 35 mesh. The particles passed through these respective sieves are:

Table 1. Chemical composition of Djebel Onk phosphate 53.75% BPL

Chemical compound	Content [% mass]
P ₂ O ₅	24.60
CO ₂	11.15
CaO	45.18
MgO	4.20
Na ₂ O	1.20
K ₂ O	0.10
Fe ₂ O ₃	0.38
Al ₂ O ₃	0.20
SO ₃	2.50
SiO ₂	3.00
F [–]	3.20
Cl [–]	350 [ppm]
Organic matters (Organic C)	3.80

88 μm, 177 μm, 210 μm and 500 μm. Note that the μm values designate the average diameter of phosphate grains expressed in micrometer. The test samples are dried in an electric oven at 110°C, cooled to room temperature and stored in desiccators.

All reactions were carried out in a 500 ml cylinder glass reactor (inner diameter of 7 cm) at atmospheric pressure. For each test, 100 g of phosphate sample was mixed, in an agitated reactor, with phosphoric acid. Stirring is performed by means of a mechanical agitator, at 200 rpm, in order to accelerate the transfer of matter between the different phases. At the end of each experiment, the reactor is placed rapidly in a bath of ice, to stop the reaction, and all the reactor contents were then filtered off using a Buchner filter. The filtration is performed by a vacuum pump.

Determination of the P₂O₅ recovery

A 5 ml aliquot part of the filtrate is transferred to a 50 ml volumetric flask. After filling up to the mark with water, the P₂O₅ amount in solution is determined spectrometric ally by UV/Vis spectrophotometer PerkinElmer using molybdovanadate spectrophotometric method. The P₂O₅ recovery, expressed in % of weight was calculated by applying the formula:

$$\% \text{ P}_2\text{O}_5 \text{ recovery} = \frac{(m_0 - m) \cdot 100}{m_0} \quad (4)$$

where:

- m_0 is the initially introduced mass of P₂O₅ equals 24.60 g (the equivalent of 100 g of phosphate sample),
- m is the total analyzed P₂O₅ in the filtrate after a time t of reaction.

Determination of water-soluble P₂O₅

The partially acidulated phosphate obtained previously at different concentrations of H₃PO₄ is brought into contact with distilled water for periods of 2 to 30 days to measure the water-soluble P₂O₅. This experience is described as follows:

The sample of 1 g of the partially acidulated phosphate is contacted with 400 ml of distilled water in a closed bottle. After a defined period, the bottle is agitated for 15 minutes. To the resulting suspension, we add distilled water to volume 1000 ml. We stir it again to mix and we filter on the filter paper. Then, we take 5 ml of the filtrate and we determine the amount of P₂O₅ by the spectrophotometric method.

RESULTS AND DISCUSSION

A number of experiments were carried out in order to follow, in terms of P₂O₅ recovery, the effect of some parameters on the dissolution of the phosphate rocks by phosphoric acid. These parameters are : reaction time, concentration of phosphoric acid and particle size of phosphate rocks.

Effect of reaction time effect

The results presented in Tables 2, 3, 4 and 5 indicate that the reaction is faster during first ten minutes but in the interval 10–30 minutes, the P₂O₅ recovery increase almost proportionally as a function of time. However, regardless the acid concentration and the phosphate

particle size, the recovery P_2O_5 increases very slowly during the interval 30 to 40 minutes. This phenomenon is probably due to the diffusion of Ca^{2+} from the solid surface through the solution boundary layer a result of which, the acid concentration at the liquid-solid interface decreases the rate of dissolution of calcareous material from the apatite. Almost the same observation was made by Ashraf et al.²⁶

Effect of the concentration of H_3PO_4

The effect of phosphoric acid concentration ranging from 10 to 40 wt.% on the dissolution of phosphate rock was studied at room temperature and at 88–500 μm particle size fraction. The results presented in Tables 2, 3, 4 and 5 indicate that the P_2O_5 recovery is proportional to the phosphoric acid concentration. Indeed, more the concentration of the acid as P_2O_5 is low, more the P_2O_5 recovery is slower and more the maximum of dissolution is quickly reaches. When the phosphoric acid concentration increases from 10 to 40 wt.% the P_2O_5 recovery increased from about 14.51 to 11.84%. However, the top P_2O_5 recovery (34.80%) is obtained at higher acidulation levels (40 wt.%).

Effect of particle size of phosphate

The effect of phosphate rock particles size on the P_2O_5 recovery was studied for the different fractions: 88 μm , 177 μm , 210 μm , 250 μm and 500 μm . Experiments

are conducted under conditions giving the best P_2O_5 recovery, namely :

- Stirring speed: 200 rpm;
- Concentration of H_3PO_4 : 40 wt.%;
- Reaction time: 50 minutes.

Figure 1 shows that the P_2O_5 recovery decreases when using the phosphates with larger particles. This decrease is less significant with phosphates having 210 μm and more but phosphates having particle size lower than 210 μm give the best P_2O_5 recovery. Indeed, the maximum P_2O_5 recovery (34.8%) is obtained with phosphate passed

Figure 1. Effect of phosphate particle size on P_2O_5 recovery

Table 2. Effect of reaction time and phosphoric acid concentration on P_2O_5 recovery from phosphate particle size 88 μm

Time [min]	P_2O_5 recovery [%]			
	Concentration of H_3PO_4 = 10 wt. %	Concentration of H_3PO_4 = 20 wt. %	Concentration of H_3PO_4 = 30 wt. %	Concentration of H_3PO_4 = 40 wt. %
10	18.10	25.18	30.27	32.61
20	21.24	26.13	32.34	34.02
30	22.62	29.42	33.45	34.51
40	22.90	29.64	34.10	34.80
50	22.94	29.66	34.08	34.78

Table 3. Effect of reaction time and phosphoric acid concentration on P_2O_5 recovery from phosphate particle size 177 μm

Time [min]	P_2O_5 recovery [%]			
	Concentration of H_3PO_4 = 10 wt. %	Concentration of H_3PO_4 = 20 wt. %	Concentration of H_3PO_4 = 30 wt. %	Concentration of H_3PO_4 = 40 wt. %
10	18.03	25.12	30.11	32.54
20	21.18	26.04	32.22	33.97
30	22.44	29.14	33.61	34.18
40	22.87	29.52	34.00	34.76
50	22.90	29.60	34.02	34.80

Table 4. Effect of reaction time and phosphoric acid concentration on P_2O_5 recovery from phosphate particle size 210 μm

Time [min]	P_2O_5 recovery [%]			
	Concentration of H_3PO_4 = 10 wt. %	Concentration of H_3PO_4 = 20 wt. %	Concentration of H_3PO_4 = 30 wt. %	Concentration of H_3PO_4 = 40 wt. %
10	17.56	24.92	29.10	30.01
20	20.02	25.33	31.78	33.11
30	21.65	28.04	32.89	33.65
40	21.93	28.52	32.94	33.98
50	21.92	28.63	32.97	33.98

Table 5. Effect of reaction time and phosphoric acid concentration on P_2O_5 recovery from phosphate particle size 500 μm

Time [min]	P_2O_5 recovery [%]			
	Concentration of H_3PO_4 = 10 wt. %	Concentration of H_3PO_4 = 20 wt. %	Concentration of H_3PO_4 = 30 wt. %	Concentration of H_3PO_4 = 40 wt. %
10	15.23	21.44	26.98	28.57
20	16.58	22.67	29.32	29.82
30	18.94	22.77	30.19	32.15
40	20.02	23.54	31.92	32.71
50	20.12	23.70	32.16	32.90

through the sieve 170 mesh ($88\ \mu\text{m}$) and the sieve 80 mesh ($177\ \mu\text{m}$). This is consistent with the work of Lassus et al.²². Generally the P_2O_5 recovery is inversely proportional to the phosphate particle size which may be due to the increase of the specific surface area. These results corroborate with the work of Lefires et al.²⁷ which have concluded that the specific surface area and the isotherm adsorption/desorption of the solids are affected by the acid leaching time.

Water-soluble P_2O_5

The curves in Figures 2, 3 and 4 were obtained by acidulation of phosphates of varying sizes with phosphoric acid concentration of 30 wt.% and 40 wt.% because these acids gives better P_2O_5 recovery (see Tables 2, 3, 4 and 5). We note that for all the phosphates PAPRs obtained with acid 40% has approximately 0.8% water soluble P_2O_5 more than PAPRs obtained with an acid of 30%. When the PAPRs is left in contact with distilled water for the following periods: 2; 4; 8; 16; 20 and 30 days, we observed that the water-soluble P_2O_5 increased progressively during the first 16 days. After the 20th day, the dependence of the residence time and water-soluble P_2O_5 is almost constant. Comparing Figures 2, 3 and 4 we observe that the phosphate with a $88\ \mu\text{m}$ particle size used for the preparation of PAPRs gives the best percentage of water soluble P_2O_5 (15.2%).

Figure 2. Water-soluble P_2O_5 as function of residence time for the phosphate $88\ \mu\text{m}$

Figure 3. Water-soluble P_2O_5 as function of residence time for the phosphate $210\ \mu\text{m}$

Figure 4. Water-soluble P_2O_5 as function of residence time for the phosphate $500\ \mu\text{m}$

This value is better than that obtained by the decomposition by sulfuric acid of a high-grade phosphate (65.55% BPL)²⁰.

CONCLUSIONS

This work showed that the production of PAPRs may be feasible with intermediate-grade phosphate of Djebel Onk and modest levels of acidulation of phosphoric acid. Since this study showed that concentrated H_3PO_4 to 30 or 40 wt% gives PAPRs with good water solubility, it is therefore possible to extract the phosphoric acid before the step of concentration (Dihydrate Process)²⁸ from the phosphoric acid plant to produce this fertilizer. On these conditions, the PAPRs obtained can substitute the SSP fertilizers because they are economically profitable and probably less harmful to the environment. (to be confirmed by other studies); this is especially true because some heavy metals contained in phosphates rock will dissolve at high concentrations of acid.

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