

## Comparative Study of the Dissolution of Phosphate Rock of Djebel Onk (Algérie) by the Nitric Acid and the Sulphuric Acid

Abbes Mizane and Achour Louhi

Laboratoire de Traitement des Eaux et de la, Département de Chimie

Valorisation des Déchets Industriels, University Badji Mokhtar, BP 12, Annaba 23000, Algeria

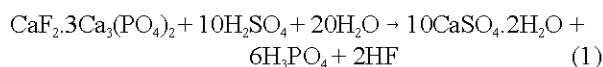
**Abstract:** The experiments which we carried out will inform us about the conditions of a better decomposition of phosphate of Djebel Onk (Algeria). The purpose of this study is to compare the conversion rates of the  $P_2O_5$  of rock phosphate obtained by nitric attack and sulphuric attack. The reactions are carried out by varying the reaction time from 3-90 min, the temperature from 20-90°C and the granulometry of phosphate of 500-40  $\mu m$ . A series of rock phosphate samples was attacked by the 2 acids and the  $P_2O_5$  was dosed by gravimetry. We noted that the reaction is very fast since at the end of 3 min only, we obtained a conversion rate of  $P_2O_5$  higher than 60%. A maximum conversion rate of 96.54% was obtained by the sulphuric attack in the following conditions: Temperature = 50°C, Reaction time = 60 min, Granulometry of phosphate = 50  $\mu m$ . The conversion rate starts to decrease at a temperature higher than 60°C for the nitric attack and at a temperature higher than 50°C for the sulphuric attack. We also deduced that a phosphate granulometry ranging between 80 and 40  $\mu m$  gives a better dissolution.

**Key words:** Phosphate rock, dissolution, sulfuric acid, nitric acid, conversion rate, nitrophosphate

### INTRODUCTION

It is well known that the phosphate rock cannot be used directly as fertilizers because of their insolubility in humid earth. In order to make them assimilated by plants especially, the phosphates are solubilized using different acids. Several authors studied the solubility of many phosphates in various acids. Thus Mizane *et al.* (1996) studied the kinetics of the dissolution of phosphate of Djebel Onk (Algeria) in nitric acid and determined the conditions for the best conversion rate into  $P_2O_5$ . This process, which makes it possible to avoid the formation of phosphogypsum, does not give the possibility of manufacturing phosphoric acid (Bouykin *et al.*, 1988). In another study (Ben Brahim *et al.*, 1999) the decomposition of phosphate rock is investigated in order to determine the partial speed of dissolution of a phosphate rock diluted in phosphoric acid.

The decomposition of phosphate rock by sulfuric acid remains the widely used industrial process. Indeed, more than 90% of the phosphoric acid produced in the world is manufactured through the digestion of phosphate rock by sulfuric acid (Calmanovici *et al.*, 1997). The apatite rocks are decomposed by sulfuric acid in the manufacturing units of phosphate-enriched fertilizers (Becker, 1989) according to the reaction:



The concentration of the phosphoric acid obtained by this reaction depends on the granules size of phosphate, stirring velocity in the reactor, residence time of the phosphate-acid mixture, as well as the filtration mode. The initial composition of phosphate rock remains the determining factor of the quality of the yielded phosphoric acid. In consequence, various studies (Calmanovici and Giulietti, 1990; Posine, 1988; Magrilova *et al.*, 1984; Goldinov *et al.*, 1978) have concluded that the phosphate chemical composition considerably influences the process of digestion.

Except the extended solubility tests carried out by Chien (1998) on the Algerian phosphate extracted from Djebel Onk mine (Algeria) for direct application as manure, few studies were devoted to the solubilization of this phosphate by acids. Consequently, the objective of this study is devoted to the determination of the best conditions of dissolution of this phosphate by the sulfuric acid and the nitric acid that remains an approach to be explored and optimized for better and convincing results.

There is another way which makes it possible to obtain directly, either of ternary manures NPK, or of the

binary compounds NP. It is the nitric way or the nitrophosphates. The process more used currently is process ODDA (Hignett, 1975) of the manufacture of the nitrophosphates which is based on the reaction (2). The calcium nitrate under product of this reaction is crystallized and the liquor east is filtered in order to manufacture manure NP. The quality of this manure depends on the chemical composition of rock phosphate.



## MATERIALS AND METHODS

This study is divided into 2 parts. The natural phosphate is attacked by the nitric acid then by the sulphuric acid in various conditions of the reaction: temperature of the reaction, residence time of the reagents and granulometry of phosphate. The product of the reaction is filtered and an aliquot part is taken filtrate in order to determine the quantity of  $\text{P}_2\text{O}_5$ . The results of these experiments are expected to make it possible to compare the conversion rates into  $\text{P}_2\text{O}_5$  in the nitric attack and the sulfuric attack of phosphate.

The phosphate ore used in this study comes from the mine of Djebel Onk (Algeria). The chemical composition, determined by x-rays and traditional elementary analysis, is presented in Table 1.

**Dosing out of  $\text{P}_2\text{O}_5$ :** In order to measure out the produced amounts of  $\text{P}_2\text{O}_5$ , the gravimetric method with the quinoline phosphomolybdate is employed. This method, also called Perrin-Wilson-Dahlgren Method with the quinoline phosphomolybdate (ISO-3357/1975), has the advantage of being applicable for phosphoric acid as well as for phosphates and manures. It is also specially recommended for being faster than the gravimetric method with the ammonium phosphomolybdate (Jeffery *et al.*, 1989). In general, both precision and reproducibility are a reference method. For these reasons, the Perrin-Wilson-

very well ensured with this method. Finally, it is appropriate for the isolated analyses and can be used as Dahlgren Method is recommended by the French Standards AFNOR (NF U42 HOM, 1987) to dose out phosphates and phosphate-enriched fertilizers.

**Principle of the method:** The method is based on the hydrolysis of the phosphate test specimen using prolonged boiling in the presence of hydrochloric acid. The phosphoric ion is precipitated as quinoline phosphomolybdate in the presence of acetone. After filtration and washing, the precipitate is placed in a crucible out of sintered glass of porosity 3-15  $\mu\text{m}$  and dried during 30 min in a regulated drying oven at 250°C. After cooling in a desiccator until the ambient temperature is reached, the crucible is weighed in an analytical balance of an accuracy of 0.1 mg. Previously, the empty crucible is dried during 15 min in a regulated drying oven at 250°C and cooled in a desiccator and weighed in similar conditions.

## Reagents:

- Distilled water, (produced in the laboratory)
  - Nitric acid at 60% (d = 1.37) NORMAPUR® for analysis
  - Hydrochloric acid at 36% (d = 1.18) NORMAPUR® for analysis,
  - Sulfuric acid at 95% (d = 1.84) NORMAPUR® for analysis
  - Citro-molybdic reagent (prepared as stipulated in ISO-3357/1975).
- All the reagents are ProLabo products

## Equipment:

- Current laboratory equipment,
- Crucible out of sintered glass of porosity 3-15  $\mu\text{m}$ ,
- Analytical balance of precision 0.1 mg, KERN 770, Germany,
- Electric furnace, Type Nabertherm, Germany,
- Laboratory crusher, Janke and Kunkel, IKA Labotechnic, Germany,
- Set of sieves with meshes of 40, 50, 80, 160 and 250  $\mu\text{m}$ .

## RESULTS AND DISCUSSION

The phosphoric anhydride content, expressed in weight percent, is calculated using the following formula

Table 1 : Composition of Djebel Onk (Algeria) phosphate ore

Substance	Concentration (%)	Substance	Concentration (ppm)
Moisture	0.02		
P2O <sub>5</sub>	28.98	Cd	11
SO <sub>3</sub>	3.22	As	< 5
CO <sub>2</sub>	7.52	Hg	< 5
SiO <sub>2</sub>	2.35	MnO	14
Fe2O <sub>3</sub>	0.39	Ni	20
Al2O <sub>3</sub>	0.48	Cu	20
CaO	49.96	Zn	85
MgO	1.66		
Na2O	0.33		
K2O	0.15		
Cl -	0.04		
F -	3.34		
TiO <sub>2</sub>	0.3		
Organic Matters	0.27		

$$P_2O_5 \text{ (wt\%)} = \frac{fM_1}{M_2} 100 \quad (3)$$

Where

$M_1$ : Yielded precipitate mass (g),

$M_2$ : Test specimen mass (g).

The parameter  $f$  is the conversion factor of quinoline phosphomolybdate into phosphoric anhydride. It is obtained from the relation:

$$f = \frac{0.5M(P_2O_5)}{M_{PMQ}} \quad (4)$$

Where:

$M_{P_2O_5}$ : Molar mass of  $P_2O_5$

$M_{PMQ}$ : Molar mass of quinoline phosphomolybdate,  $(C_9H_7N)_3H_3(PO_4 \cdot 12MoO_3)$ .

#### Variation of conversion rate ( $\alpha$ ) as a function of the time:

A phosphate ore sample of composition as indicated in Table 1 is attacked by the nitric acid then by the sulphuric acid at various the time of the reaction. A series of samples, 100 g each, is prepared from the phosphate. The quantity of acids used is 20% in excess compared to Stechiometry. The reaction is stopped at prescribed times raging within the interval 3-90 min. Heat removal from the reactor is ensured by indirect contact using a flat-bottomed container with a recently prepared solution. The cooling solution is made from ammonium nitrate ( $450 \text{ g L}^{-1}$ ) with 34.8% nitrogen. The obtained product is vacuum-filtered and  $P_2O_5$  content is determined from a 50 mL aliquot part using gravimetry. It was not necessary to carry out the reaction beyond 90 min as the and reaction is exothermic total evaporation of the acids takes place. We worked with phosphate having a granulometry of  $80 \mu\text{m}$  and the temperature of the reactor is maintained at  $50^\circ\text{C}$ . The conversion rate  $\alpha$  is calculated on the basis of total mass of  $P_2O_5$  contained initially in 100 g of phosphate rock (Table 1).

The reaction conversion rate ( $\alpha$ ), expressed in % of  $P_2O_5$ , is calculated using the following relation:

$$a = \frac{M_t(P_2O_5)}{M(P_2O_5)_{\text{initial}}} 100\% \quad (5)$$

Where:

$M_{t(P_2O_5)}$ : Total mass of  $P_2O_5$  produced during the reaction,

$M_{(P_2O_5)_{\text{initial}}}$ : Total mass of  $P_2O_5$  in 100g of phosphate rock

The results of these experiments are summarized in Table 2. Table 2 shows the evolution of the

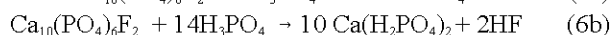
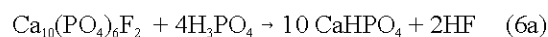
Table 2: Variation of conversion rate ( $\alpha$ ) as a function of the time

Time (min)	$\alpha$ (%) (*)	$\alpha$ (%) (**)
3	60.48	65.42
5	63.96	65.83
10	72.05	66.18
20	82.26	75.09
30	87.62	83.06
40	91.59	87.89
50	95.16	91.99
60	96.43	93.99
70	96.35	95.48
90	96.37	95.86

(\*) nitric attack; (\*\*) sulphuric attack

conversion rate ( $\alpha$ ) at the specified conditions as a function of time of reaction

Under our experimental conditions, we studied the variation of the conversion rate according to time. in the case of the nitric attack, we noted that as from 50 min the reaction is slow. On the other hand, for the sulphuric attack, we observed a clear evolution. This increase is most probably due to the formation of monocalcic phosphate (Sluis *et al.*, 1987). Indeed, when sulfuric acid is totally consumed, reactions (6a and b) of phosphate with phosphoric issued from reaction (1) may take place as shown: We observed that the 2 reactions of attack are fast because at the end of 3 min of the rates of 60.48 and 65.42% were realized respectively for  $HNO_3$  and  $H_2SO_4$ . at the end of 60 min a rate maximum of 96.43% was carried out by the nitric attack :



These two reactions favor the yielding of  $P_2O_5$  in the soluble form. It is well established that the reaction of phosphate with phosphoric acid is used industrially to manufacture the richest fertilizer with  $P_2O_5$ .

#### Variation of conversion rate ( $\alpha$ ) as a function of the temperature:

The same experiment is carried out at various temperatures. The reaction time is fixed at 60 min and the granulometry of phosphate is selected to  $80 \mu\text{m}$ . The results of these experiments are summarized in Table 3.

The variation of the conversion rate according to the temperature is represented by Table 3. We noted that at a temperature of  $20^\circ\text{C}$ , the conversion rate obtained by the sulphuric attack is higher approximately 10% compared to that of the nitric acid. The rate maximum (96.44%) was carried out by the sulphuric attack at a temperature of  $50^\circ\text{C}$ . Beyond this temperature, we observed in both cases a light reduction in the conversion rate.

**Table 3: Variation of conversion rate ( $\alpha$ ) as a function of the temperature**

Temperature (°C)	$\alpha$ (%) (*)	$\alpha$ (%) (**)
20	78.01	89.32
30	90.13	90.38
40	94.27	93.89
50	96.38	96.44
60	96.4	93.12
70	94.24	93.02
80	92.78	93.01
90	91.21	92.46

(\*) nitric attack; (\*\*) sulphuric attack

**Table 4: Variation of conversion rate ( $\alpha$ ) as a function of the granulometry of phosphate**

Granulometry ( $\mu$ m)	$\alpha$ (%) (*)	$\alpha$ (%) (**)
500	95.24	92.21
400	95.37	92.88
250	96.01	94.67
160	96.34	95.06
80	96.5	96.38
50	96.52	96.54
40	96.5	96.48

(\*) nitric attack; (\*\*) sulphuric attack

**Variation of conversion rate ( $\alpha$ ) as a function of the granulometry of phosphate:** In this experiment, the phosphate of various granulometry (Table 4) is attacked by the nitric acid. The same phosphate is then attacked by the sulphuric acid and the conditions of the reactions remain always the same ones (temperature = 50°C, time of reaction = 60 min. The results of these experiments are summarized in Table 4.

We noted that granulometry influences considerably the conversion rate. For a granulometry of rock phosphate ranging between 80 with 40  $\mu$ m, of best the conversion rates were obtained for both reaction of attack. However, a rate maximum of 96.52% was carried out by the nitric attack for a granulometry of 50  $\mu$ m.

## CONCLUSION

The comparative study of the attack of rock phosphate by the nitric and sulphuric acid realized under the same conditions showed us as:

- The two reactions of attack are fast,
- At the end of 50 min, from better conversion rate were obtained by the nitric attack. The maximum rate (96.54%) was obtained by the sulphuric attack at a temperature of 50°C, a 60 min time and for a granulometry of 50  $\mu$ m
- In both cases of acid attack, best the dissolution of the phosphate is carried out with a granulometry ranging between 80 and 40  $\mu$ m.

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