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Calcination Effects on Sulfuric Dissolution of Phosphate Extracted from Djebel Onk Mine (Algeria)

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The main object of this study is to investigate the calcination effects on the dissolution of phosphate rock from the mine of Djebel Onk (Algeria) in the sulfuric acid. Using conventional methods, the yielded conversion rates of P_2O_5 obtained during the dissolution of both rock and calcined phosphates are compared. Initially, the phosphate rock is burned to ash at temperatures ranging from 800 to 1200 °C. Then, the quantity of P_2O_5 is dosed out at each calcination temperature. A maximum rate of 32.35 % by weight of P_2O_5 is obtained at 1000 °C. By varying the retaining time of the reagents, it is noted that the reaction of calcined phosphate with the sulfuric acid is very fast as it took only a period of 10 min to reach a conversion rate of 78.39 % into P_2O_5. In the case of phosphate rock, it is observed that the reaction is slower compared to the earlier one and a rate of 95.86 % by weight is attained by 1.5 h.

Key Words: Phosphate rock, Calcination, Dissolution, Sulfuric acid, Phosphorus pentoxide Conversion rate.

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. Mizane *et al.*[1] studied the kinetics of the dissolution of phosphate of Djebel Onk (Algeria) in nitric acid and also 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[2]. In another study[3], 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 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[4]. The apatite rocks have been decomposed by sulfuric acid in the manufacturing units of phosphate-enriched fertilizers[5], according to the reaction (1):

$$CaF_2{\cdot}3Ca_3(PO_4)_2 + 10H_2SO_4 + 20H_2O \longrightarrow 10CaSO_4{\cdot}2H_2O + 6H_3PO_4 + 2HF \qquad (1)$$

The concentration of the phosphoric acid obtained by this reaction depends on the granules size of phosphate, stirring velocity in the reactor, retaining 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[6-9] have concluded that the phosphate chemical composition considerably influences the process of digestion.

Except the extended solubility tests carried out by Chien[10] 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 work is to the determine the best conditions of dissolution of this phosphate by sulfuric acid which remains an approach to be explored and optimized for better and convincing results.

EXPERIMENTAL

Distilled water is used throughout the experiment. Nitric acid 60 % (density = 1.37); hydrochloric acid 36 % (density = 1.18) and sulfuric acid 95 % (density = 1.84) were purchased from NORMAPUR®. Citromolybdic reagent was prepared as mentioned in ISO-3357/1975. The other reagents were purchased from ProLabo.

This work is divided into 3 parts. Initially, the phosphate rock is calcined at temperatures going from 800 to 1200 °C while dosing out the quantity of P_2O_5 at each calcination temperature. The calcined phosphate, which contains the maximum of P_2O_5, was useful for the following experiments. The latter are dealing with the attack of calcined phosphate by concentrated sulfuric acid for various reaction times. Finally, the phosphate rock that was not calcined is attacked by sulfuric acid under the same conditions of reaction. The results of these experiments are expected to make it possible to compare the conversion rates into P_2O_5 in the cases of natural and calcined phosphates.

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 P_2O_5: In order to measure out the produced amounts of P_2O_5, the gravimetric method with the quinoline phosphomolybdate is employed. This method, also called Perrin-Wilson-Dahlgren method with the quinoline phosphomolybdate[11], 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[12]. In general, both precision and reproducibility are very well ensured with this method. Finally, it is appropriate for the isolated analyses and can be used as a reference method. For these reasons, the Perrin-Wilson-Dahlgren Method is recommended by the French Standards AFNOR[13] 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 to 15 μm and dried during 0.5 h 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.

RESULTS AND DISCUSSION

The phosphoric anhydride content, expressed in weight per cent is calculated using the following formula:

$$P_2O_5(\text{wt }\%) = \frac{f\,M_1}{M_2}100 \tag{2}$$

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:

$$f = \frac{0.5M_{(P_2O_5)}}{M_{PMQ}} \tag{3}$$

where, $M_{P_2O_5}$: molar mass of P_2O_5, M_{PMQ}: molar mass of quinoline phosphomolybdate, $(C_9H_7N)_3(H_3PO_4\cdot 12MoO_3)$.

Determination of P_2O_5 maximum content in calcined phosphate: A phosphate ore sample (Table-1) is calcined in an electric furnace at a series of temperatures (800, 900, 1000, 1100 and 1200 °C). The calcined phosphate is then cooled in a desiccator to ambient temperature. A test specimen of calcined phosphate obtained for each temperature undergoes hydrolysis by prolonged boiling in the presence of hydrochloric acid (d = 1.18). The filtrate is then analyzed by gravimetric method in order to determine the yielded quantity of P_2O_5. The results in weight % of P_2O_5 are presented in Table-2. Each measurement is the average of 3 separate and consecutive trials.

TABLE-1
COMPOSITION OF DJEBEL ONK (ALGERIA) PHOSPHATE ORE

Substance	Concentration (%)	Substance	Concentration (ppm)
Moisture	0.02	Cd	11
P_2O_5	28.98	As	< 5
SO_3	3.22	Hg	< 5
CO_2	7.52	MnO	14
SiO_2	2.35	Ni	20
Fe_2O_3	0.39	Cu	20
Al_2O_3	0.48	Zn	85
CaO	49.96		
MgO	1.66		
Na_2O	0.33		
K_2O	0.15		
Cl^-	0.04		
F^-	3.34		
TiO_2	0.30		
Organic Matters	0.27		

TABLE-2
CALCINATION TEMPERATURE EFFECT ON P_2O_5 CONTENT IN PHOSPHATE

Calcination temperature (°C)	P_2O_5 (wt %)
800	31.10
900	31.95
1000	32.35
1100	32.34
1200	32.34

It is concluded that the maximum content of P_2O_5 is 32.35 % at the 1000 °C calcination temperature. A sufficient quantity of this phosphate is preserved for the following experiments.

Calcined phosphate attack using sulfuric acid: A series of samples, 100 g each, is prepared from the calcined phosphate. Then, the phosphate is attacked by concentrated sulfuric acid (d = 1.84) with continuous stirring. The quantity of acid used is 20 % in excess compared to stoichiometric ratio. The reaction is stopped at prescribed times raging within the interval 3 to 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 g/L) 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 reaction is exothermic and total evaporation of the sulfuric acid takes place.

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

$$\alpha = \frac{M_{t(P_2O_5)}}{M_{(P_2O_5)_{initial}}} 100\ \% \quad (4)$$

where, $M_{t(P_2O_5)}$: total mass of P_2O_5 produced during the reaction, $M_{t(P_2O_5)initial}$: total mass of P_2O_5 in 100 g of phosphate obtained at 1000 °C (Table-2).

Table-3 shows the evolution of the conversion rate (α) at the specified conditions as a function of reaction time.

Attack phosphate rock by the sulfuric acid: The phosphate rock is crushed and then filtered in order to obtain a product with granule size close to that of calcined phosphate, *i.e.*, between 80 and 120 μm. 100 g samples of crushed phosphate are attacked by concentrated sulfuric acid (d = 1.84). The reaction attack is carried out in the same manner as in the case of calcined phosphate. The conversion rate (α) is calculated on the basis of total mass of P_2O_5 contained initially in 100 g of phosphate rock (Table-1). The results of these experiments are summarized in Table-3.

TABLE-3
VARIATION OF (α) AS A FUNCTION OF REACTION TIME FOR CALCINED PHOSPHATE AND PHOSPHATE ROCK

Time (min)	Calcined phosphate		Phosphate rock	
	P_2O_5 (wt %)	α (%)	P_2O_5 (wt %)	α (%)
3	21.40	66.15	18.96	65.42
5	21.85	67.54	19.08	65.83
10	25.36	78.39	19.18	66.18
20	25.44	78.63	21.76	75.09
30	27.21	84.11	24.07	83.06
40	28.43	87.88	25.47	87.89
50	29.13	90.05	26.66	91.99
60	29.82	92.18	27.24	93.99
70	29.79	92.08	27.67	95.48
90	29.72	91.87	27.78	95.86

Since the main goal of this study is to investigate the effect of calcination in order to ameliorate the yield in P_2O_5, it is appropriate to examine the evolution of the conversion rate as a function of reaction time. This result in illustrated in Fig. 1. It is noted that the reaction of calcined phosphate with sulfuric acid is very fast at the beginning since 78.39 % of conversion is obtained after only 10 min (Table-3). After 20 min of reaction, the reaction is progressed only with 0.24 % indicating that most of the transformation is accomplished in the early stages of the reaction. A maximum rate of conversion of 92.18 % is yielded after 1 h. Beyond this optimum, the conversion rate tends to stabilize around approximately 92 %. This rate remains almost invariable even by prolonging the reaction up to 1.5 h.

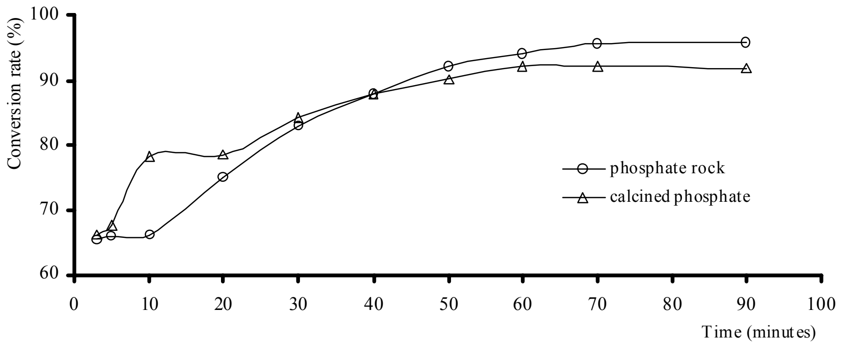

Fig. 1. Evalution of conversion rate as a function of reaction time for both rock and calcined phosphate

For phosphate rock, the reaction with sulfuric acid is also fast since a conversion rate of 66.18 % is reached by 10 min whereas it remains slower compared to the calcined case. Beyond 10 min, a increases gradually until a maximum of 95.86 % after 1.5 h of reaction. This increase is most probably due to the formation of monocalcic phosphate[14]. When sulfuric acid is totally consumed, reactions (5a and 5b) of phosphate with phosphoric issued from reaction (1) may take place as shown below:

$$Ca_{10}(PO_4)_6F_2 + 4H_3PO_4 \longrightarrow 10CaHPO_4 + 2HF \quad (5a)$$

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 \longrightarrow 10Ca(H_2PO_4)_2 + 2HF \quad (5b)$$

These two reactions favour 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.

Conclusion

Comparison of P_2O_5 conversion rates using sulfuric acid attack for both rock and calcined phosphates may lead to the following observations:

Calcined phosphate reaction is faster compared to natural phosphate and the conversion rate is high within the first 10 min. The yielded rate of P_2O_5 reached 78.39 %.

Phosphate rock exhibited the highest conversion rate after 1.5 h of reaction (95.86 %).

The continuity of phosphoric acid production processes using sulfuric attack of phosphates, it would be interesting to use calcined phosphates by transferring the obtained pulp in less than 10 min towards the filter. In this manner, it is possible to obtain a good quality phosphoric acid.

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