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ORIGINAL ARTICLE

Influence of the calcination time on the dissolution of merchant phosphates from Tahoua (Niger)

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ABSTRACT
In this work, we studied the calcination time and the dissolution of the merchant and calcined Tahoua phosphates in sulfuric acid solution (0.02 M). The objective is to determine the optimal calcination time of Tahoua merchant phosphate in order to limit the energy consumption of the process and to obtain an agronomic quality product as a substitute for manufactured phosphorus fertilizers. Tahoua merchant phosphate was calcined at different times corresponding to 30 minutes; 1 hour and 2 hours. X-ray diffraction allowed the chemical characterization of the merchant and calcined phosphates. Their specific surface areas and micropore volumes were determined by the Brunauer, Emmett and Teller (BET) method. A comparative test of the dissolution of merchant and calcined phosphates in sulfuric acid solution was performed to evaluate the effect of calcination on solubility. The content of phosphoric anhydride increased from 20.26% for the uncalcined merchant phosphate to 30.6% after 1 hour of calcination. The specific surfaces, microporous volumes and the content of phosphorus dissolved as P_2O_5 in the sulphuric acid solution are respectively 390.980 m^2/g; 354 cc/g; 22.5% for merchant phosphate and 403.946 m^2/g; 364 cc/g; 26% for the product calcined in 1 hour. These results show that the optimal calcination time for Tahoua merchant phosphate for a quality product is 1 hour.
***Keywords**: sulfuric acid, calcination, Tahoua merchant phosphate, calcined phosphate.*

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INTRODUCTION

Phosphorus is one of the three essential elements for plant nutrition. The main source of phosphorus is rock phosphate. Tahoua merchant phosphate is a product obtained by physical treatment of Tahoua rock phosphate and was sold to Nigerian farmers as a soil amendment. Phosphates are also the raw material for the industrial manufacture of phosphorus fertilizers and phosphoric acid. But phosphates must answer quality requirements depending on the use. Thus, for direct application to the soil the phosphate must be water soluble so that the phosphorus element is released and available to the plant. In the field of fertilizer production, the product must have at least 30% P_2O_5 content. For the manufacture of phosphoric acid the requirements are such that: the merchant product must be at least 30%; the CaO/P_2O_5 ratio must be less than or equal to 1.65; the admitted MgO contents vary between 0.1 and 0.6%; the feral mass (Al2O3+ Fe_2O_3) must be less than or equal to 3%; the SiO_2 content must not be less than 5%; the quantity of organic matter must be reduced finally, the admitted contents of Na_2O and K_2O are of the order of : Na_2O < 0.5 % and (Na_2O + K_2O) < 1 % [1,2,3]. Tahoua merchant phosphate is a powder obtained from the crushing, grinding and pulverization of Tahoua rock phosphate nodules [4]. Tahoua rock phosphate is a sedimentary phosphate of the fluorapatite type. Studies have shown that its chemical composition varies according to the origin of the nodules and its average grade is 23% P_2O_5. It contains many impurities such as organic matter. Its low reactivity does not favour its direct application in agriculture. Moreover, it does not answer the quality requirements for fertilizer and phosphoric acid production [2,5,6]. Hence the need to subject it to additional treatments to improve its quality. With this in mind, we proceeded with its calcination in order to improve its qualities. However, this operation consumes large amounts of energy [7,9,10]. The objective of this study is to optimize the calcination time of the Tahoua merchant in order to limit energy consumption without impacting the quality of the calcined product.

MATERIAL AND METHODS

Materials

The Tahoua Merchant Phosphate : This is the powder obtained after the crushing, grinding and pulverizing operations of the nodules of Tahoua rock phosphate. The use of this product as a soil conditioner by Nigerian farmers has not yielded the expected results. Its specific surface area is 390.980 m^2/g, its P_2O_5, its content of $P_2O_5$is 20.6% and itsCaO/P_2O_5 ratio is 2.58 [7].

Apparatus : The apparatus used are :

- a Heraeus adjustable furnace used for the calcination of Tahoua merchant phosphate ;
- a Mettler analytical balance model PM3000 for mass measurement ;
- a DR 3800 molecular absorption spectrophotometer of HACH CAMPANY origin.

Chemical solutions : The chemical solutions used in this work are of commercial origin :

- sulfuric acid 1N with a molar mass of 98 $g.mol^{-1}$,density 1.84 and of Normapur origin ;
- phosver® 3 reagent for phosphates : It is a solution previously prepared for 10 mL of sample original HACH CAMPANY.

Methods

Calcination : 100g of Tahoua merchant phosphate with particle size between 100 and 150 µm are placed in an adjustable oven at a temperature of 850°C. We varied the calcination times for 30 min, 1 hour and 2 hours. The cooling time of the products at the exit of the kilnis 24 hours.

Determination of specific surfaces and volumes of micropores : The specific surfaces and volumes of the micropores were determined by adsorption of nitrogen N_2 at 77 K.

Preparation of the 0.02M solution of H_2SO_4 : In a 50mL beaker containing the commercial 1Nsulfuricacid solution, we took 40mL using a graduated pipette. This quantity was introduced into a 1L volumetric flask previously washed, rinsed and containing half distilled water. The volume was made up to the mark with distilled water. Finally the solution is homogenized and labeled.

Attack of merchant and calcined phosphate by the 0.02M sulphuric acid solution : Attack of merchant and calcined phosphate by the 0.02M sulphuric acid solution In a 500 mL beaker previously rinsed with demineralized water, 0.1g of merchant or calcined phosphate is introduced and 100 mL of the acid solution is added. After 1 hour stirring at 500 rpm on a magnetic stirrer, the mixture is filtered and the level of phosphoric anhydride (P_2O_5) dissolved in the filtrate is determined by dosing.

Determination of the dissolved phosphorus content : We used the phosphorus determination method with PhosVer® 3. This method is based on the formation of a phospho-molybdate complex whose reduction by ascorbic acid and is accompanied by the development of blue coloration. The intensity of the coloration is proportional to the amount of phosphorus present in the solution. 10 mL of the previously diluted filtrate is added to a tank. The PhosVer® 3 powder is then added. After 2 minutes rest, the dissolved phosphoric anhydride is determined using a DR 3800 molecular absorption spectrophotometer from HACH CAMPANY at a wavelength of 400 nm. The amount of P_2O_5 contained in the sample is calculated using the formula below [9] :

$$R = \frac{\text{Read} * \text{Vext} * \text{F}}{Pe}$$

With R: P_2O_5 in mg/Kg; Read: value read on the spectrophotometer; Vext: extraction volume in mL; F: Dilution factor;Pe: test sample in g.

$$\%P_2O_5 = \frac{R}{10000}$$

RESULTS AND DISCUSSION

Change in rate of decrease in sample mass as a function of calcination time : The results presented in Fig.1 illustrate the variation in the rate of decrease in sample mass following the calcination at 850°C of 100g of Tahoua merchant phosphate as a function of time. It can be seen on the one hand that the amount of phosphate introduced decreased at the end of the calcination, and on the other hand that the rate of decrease in sample mass increases as the residence time in the kilnis prolonged. These rates are 2.5%, 4.29% and 8.56% respectively after a residence time of 30 minutes, 1 hour and 2 hours. According to several authors, sedimentary phosphates contain impurities such as organic matter and accessory minerals such as quartz, clays and carbonates (dolomite and calcite). Heat treatment is one of the easy means used to improve the quality of natural phosphates [11,12]. Moreover, the values we obtained show that the Tahoua market product contains many impurities.

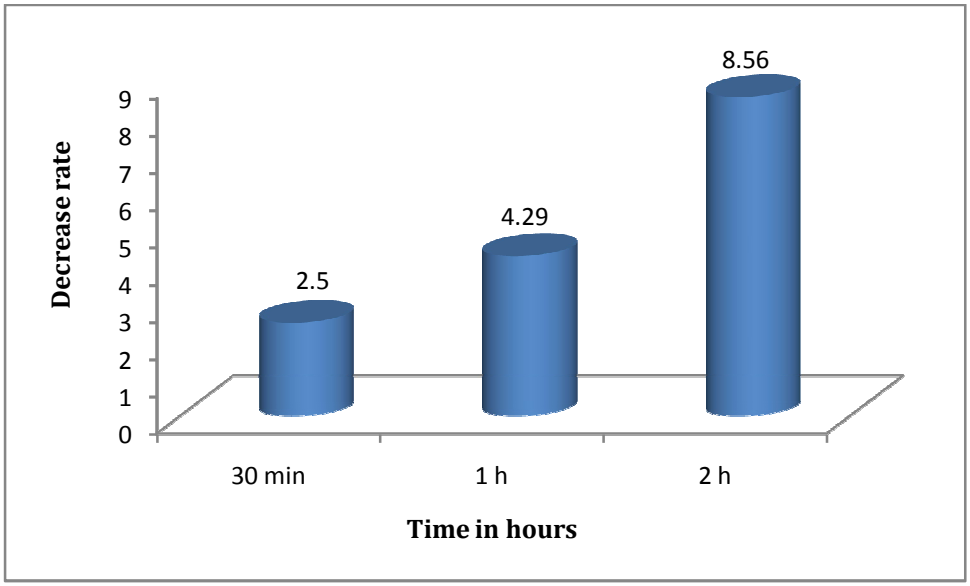

Fig.1 Rate of Sample Mass Decline by Calcining Time

Chemical composition of Tahoua merchant phosphate before and after calcination : The chemical composition of both samples was determined by energy dispersive X-ray fluorescence. The results are shown in table 1 below. This chemical composition of the different products shows that calcination not only enriched the merchant phosphate in P_2O_5, but also reduced most undesirable compounds except Fe_2O_3, regardless of the residence time considered in this study.

Table 1. Chemical composition of merchant and calcined phosphates

Oxides composition (%)	PMT	$PME_{1/2}$	PME_1	PME_2
SiO_2	3,35	0,059	0,05	0,05
TiO_2	0,34	0,22	0,18	0,19
Al_2O_3	4,64	0,64	0,59	0,6
Fe_2O_3	9,89	13,46	15,07	14,47
P_2O_5	20,26	29,9	30,6	30,8
CaO	53,18	51,28	51,23	50,71
MgO	0,76	0,02	ND	0,01
Na_2O	0,92	< 0,001	ND	< 0,001
K_2O	0,049	< 0,001	ND	< 0,001
MnO	0,92	0,792	0,773	0,723
LOI	5,2	3	0,83	1,2

LAW: Loss of Ignition
PMT: merchant phosphate from Tahoua
PME1/2: phosphate calcined for 30 minutes
PME1: phosphate calcined for 1 hour
PME2: phosphate calcined for 2 hours

Percentage variation in P_2O_5 as a function of calcination time : Fig.2 shows the evolution of the percentage of P_2O_5 as a function of the calcination time. The curve shows two parts. The first part in which the P_2O_5 rate increases from 20 to 30% after half an hour. A second part in the form of a horizontal step during which the P_2O_5 rate remains practically constant. Similar results have been obtained during the heat treatment of other sedimentary phosphates by other authors [9].

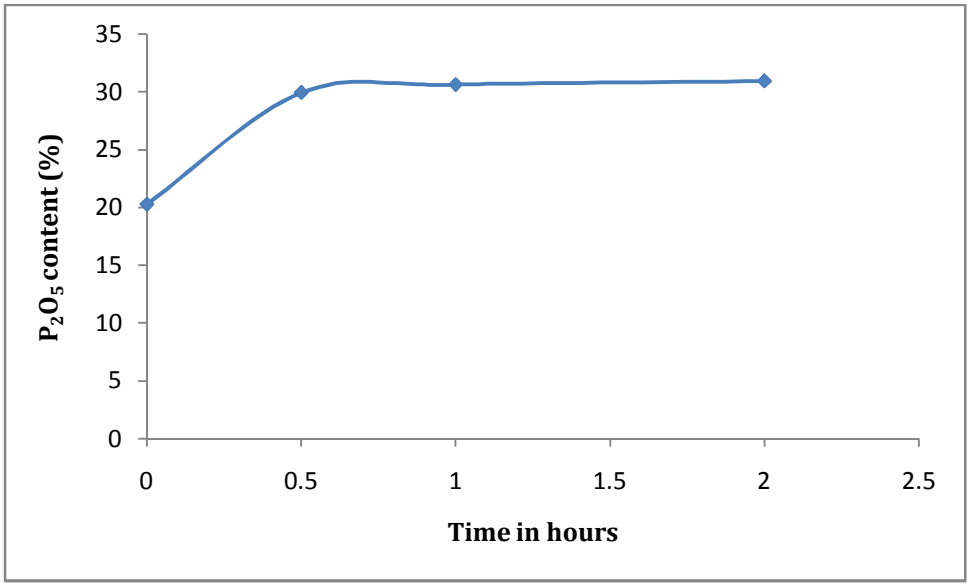

Fig.2 Variation of the percentage of P_2O_5 as a function of the calcination time

Evolution of the CaO/P_2O_5 ratio as a function of calcination time : The evolution of the CaO/P_2O_5 ratio as a function of calcination time is shown in fig.3. This ratio gives information on the amount of sulfuricacid to be used in the attack of a rock phosphate during the production of phosphoric acid. According to some authors a report ≤ 1.65 is recommended. In the case of merchant Tahoua phosphate, this ratio is 2.58 before treatment. In 30 minutes of calcination it decreases to 1.71. After 1 hour of calcination it decreases slightly and becomes equal to 1.67. After 2 hours of calcination it remains at the same value. Our results show that the optimal calcination time to have a ratio very close to the recommended one is 1 hour.

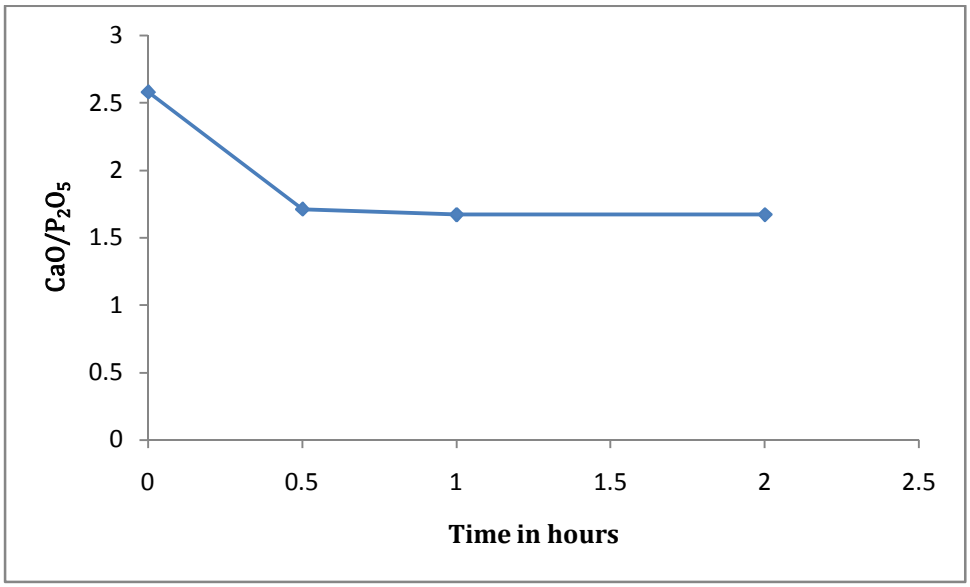

Fig.3 Evolution of the CaO/P_2O_5 ratio as a function of calcination time

Values of specific surface areas and micropore volumes as a function of calcination time : The specific surface areas and micropore volumes determined for the different calcination times are shown in table 2. We have noticed that the specific surface area decreases when the product is calcined for 30 minutes. The specific surface area decreases from 390.98 m^2/g to 377.332 m^2/g before and after treatment respectively. These results are in agreement with those found in the literature by other authors who report that calcination favors the expansion of the particles, which will cause the pore volumes to decrease, thus reducing the specific surface area [10].However, we have noted an increase in specific surface area when the calcination time is prolonged. Indeed, it is 403.946 m^2/g for 1 hour of calcination

and 407.246 m^2/g for 2 hours of calcination. This could be attributed to the increase in micropore volumes. Theseincreasefrom0,354 cc/g before calcination to 0.364 cc/g and 0.363 cc/g after 1 and 2 hours of calcination respectively.

Table 2. Values of Specific Surface Areas and Micropore Volumes

Sample	Specific surface area (BET)	Micropore volume
PMT	390,980 m^2/g	0,354 cc/g
$PME_{1/2}$	377,332m^2/g	0,342cc/g
PME_1	403,946 m^2/g	0,364cc/g
PME_2	407,246 m^2/g	0,363 cc/g

Study of the dissolution of merchant and calcined phosphate in 0.02M sulphuric acid solution : The reactivity of a phosphate is measured in the laboratory by dissolving the product in acid extraction solutions [1]. The contents of dissolved P_2O_5 of merchant and calcined Tahoua phosphate in the 0.02 M sulfuric acid solution are shown in Fig.4 below. Phosphate calcined in 1 hour dissolves better (26% P_2O_5) than merchant phosphate (22.5%) and phosphate calcined in 30 minutes (22%). This difference could be explained by variations in specific surfaces. Indeed, some authors have reported that the increase in specific surface area increases the solubility and reactivity of the product [13,14].

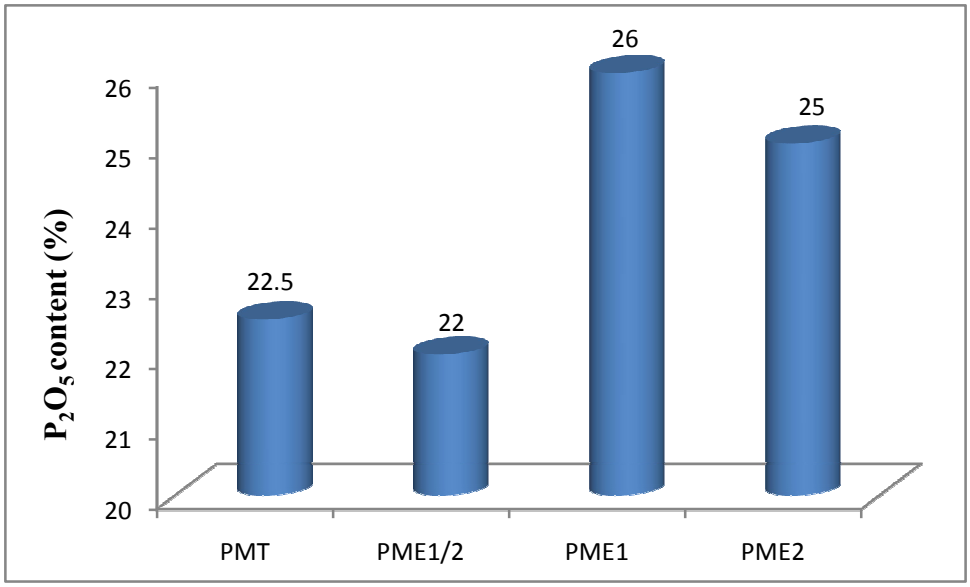

Fig.4.Dissolved P_2O_5 content of merchant phosphate and calcined in sulfuric acid solutions 0.02 M

CONCLUSION

At the end of this study; the results show that the optimal calcination time for Tahoua merchant phosphate is 1 hour. The product obtained can open perspectives both in direct application in agriculture and in the industrial field for the manufacture of fertilizers and phosphoric acid.

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