Decomposition of saudi phosphate rock with nitric acid

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The factors affecting the use of nitric acid for dissolution of low grade Saudi rock phosphate of As-Sanam area has been investigated. Samples of the low-grade phosphate ore have been treated with nitric acid at different concentrations (4 - 9 M) and reaction times (5 - 120 minutes) and under different temperatures (25-60 °C). The following conditions for the recovery of P_2O_5 are recommended: acid concentration, 6 M; quantity of a acid, 10% in excess over the stoichiometric requirement; duration of acidulation, 30 minutes; and temperature, 40 ± 0.1 °C. The effect of particle size on the recovery of P_2O_5 was studied. It was found that the recovery was efficient even for samples that have an average particle size of 0.5 mm.

تمت دراسة العوامل المؤثرة على ذوبانية خام فوسفا تسعودى منخفض الدرجة من منطقة السناء في حامض النتريك. ذو تلركيزات مختلفة (٤- ٩ مولار) لأزمنة مختلفة (٥-١٢٠دقيقة) وعند درجة حراره مختلفة (٢٥- ٦٠م°) وكانت الظروف المفضلة هى : تركيز الحامض : ٦ مولار، كمية الحامض : ١٠ % زيادة على الكمية النظرية . زمن المعالجة : ٣٠ دقيقة ودرجة الحرارة ٤٠ ± ١ مئوية .وقد تم أيضا دراسة تأثير حجم حبيبات الخام على ذوبا نية الخام حيث بينت النتائج ان تأثير حجم الحبيبات ضئيل وكانت درجة الاذابة عا ليه حتى لحبيبات خام متوسط الحجم (٥,٠مم) .

Keywords: Phosphaterock, Nitrophosphate, Acidulation, Stoichiometric, P_2O_5 recovered.

1. Introduction

Phosphate rock is one of the abundant and most important minerals in the Kingdom of Saudi Arabia, namely Sirhan-Turayf, coastal areas of the Red Sea, central part of the Kingdom, and close to Arabian Gulf.

Phosphate rock is considered as the basic raw material upon which phosphate fertilizers and some other industries are based. In the phosphate fertilizers industry, phosphate rock is either treated with limited quantity of about 70% H_2SO_4 to produce low grade normal superphosphate or treated with higher quantity of sulfuric acid to produce wet process phosphoric acid which is the basic intermediate used for manufacture of concentrated,mixed and compound fertilizers. The normal wet process phosphoric acid process requires phosphate rock of at least 30 % P_2O_5 concentration.Saudi phosphate ores are mostly medium to low grade quality ores requiring costly benificiation treatment to be suitable for use in the manufacture of wet process phosphoric acid and phosphate fertilizers.

It is therefore natural that Saudi fertilizer manufacturers should take a close look at processes that can produce phosphate fertilizers directly from medium or low-grade phosphate ores. The most attractive of which is known as nitrophosphate, in which rock phosphate is treat with nitric acid. The cost of this acid is likely to fall because of the availability of natural gas in Saudi Arabia and technological improvements in converting ammonia to nitric acid . Moreover, the nitrate ion supplies nutrient nitrogen and ends up in a product, either with the phosphate or in a co-product nitrogen fertilizer, whereas in sulfuric acid treatments, the sulfate ion serves no useful purpose and gypsum formed having very low nutrient value dilute the product.

Early researchers recognize that the hydrogen ion in the acid is the important factor in acidulating rock phosphate. Different processes have been developed in which phosphate rock is acidulated either with nitric acid or with a mixture of nitric acid and sulfuric or phosphoric acids, followed by ammoniation of the produced slurry, drying and granulation to produce N-P fertilizer [1 - 11]. Other processes investigated the factors affecting the acidulation of phosphate rock with nitric acid [12 - 16].

The factors affecting the dissolution of rock phosphate in nitric acid include fineness of grain, period of acidulation, acid oncentration, temperature, and acid to rock ratio.The treatment of rock phosphate with nitric acid can be approximately described in terms of a principal conversion reaction and several side reactions. Fluorapatite being the major constituent of phosphate rock, the principal reaction is [17]:

$$\underset{(s)}{Ca_{10}(PO_4)_6F_2} + \underset{(aq)}{20\,HNO_3} \rightarrow \underset{(aq)}{6\,H_3PO_4} + \underset{(aq)}{10\,Ca(NO_3)_2} + \underset{(aq)}{2HF}. \quad (1)$$

The side reactions are caused by the reaction of impurities present along with apatite with nitric acid. The important ones are:

$$\underset{(s)}{R_2O_3.\,X\,H_2O} + \underset{(aq)}{6\,HNO_3} \rightarrow \underset{(aq)}{2\,R(NO_3)_3} + (3+X)\,H_2O, \quad (2)$$

where R is iron or aluminum.

$$\underset{(aq)}{4\,HF} + \underset{(s)}{SiO_2} \rightarrow \underset{(g)}{SiF_4} + \underset{(l)}{2H_2O}. \quad (3)$$

$$\underset{(g)}{3\,SiF_4} + \underset{(l)}{2\,H_2O} \rightarrow \underset{(s)}{SiO_2.\,2\,H_2O} + \underset{(aq)}{2\,H_2SiF_6} \quad (4)$$

The estimation of nitric acid requirement for the dissolution of rock phosphate has been madebasis of a correct analysis of the sample used, so that the stoichiometrics of the main and the side reactions can be taken into account [18, 19].

This paper presents the results of a study on the factors affecting the dissolution of a low rade Saudi phosphate sample of As-Sanam area in nitric acid.

2. Experimental materials

The main materials used were low grade Saudi phosphate ore of As-Sanam area and analar reagent nitric acid assay 69%, nufactured by Surecem Products Ltd. Chemical analysis of the ground rock was carried out according to standard methods [20- 21]. The As- Sanam Phosphate sample used analyzed as follows: P_2O_5, 15.12%; CaO, 23.92; MgO, 0.05; Fe_2O_3, 0.64; Al_2O_3, 0.94; CO_2, 6.54; and SiO_2 and acid insoluble, 52.92 percent.

3. Experimental procedures

A series of experiments was conducted to find out the influence of acid concentration and temperature on the degree of dissolution of P_2O_5 in phosphate sample used.The ore was ground so that 98% passed through 350 mesh Tyler equivalent. A weighed sample was added to the stoichiometric requirement of nitric acid of specified concentration, then kept at a specified constant temperature using a thermostatic water bath. The period of contact in each case was varied from 5 to 120 minutes. The mixture of phosphate sample and acid was stirred using a mechanical stirrer at a rate of 1000 rpm. At the end of the specified time interval, the slurry was filtered, and then the filtrate was analyzed for P_2O_5. The concentration of nitric acid used was varied from 4 - 9 M and the temperature was varied from 35 - 60 °C. The influence of acid to rock ratio was investigated by varying it from the stoichiometric requirement of 20 : 1 to 30 : 1, keeping temperature at 40 ± 0.1 °C, acid concentration at 6 M and the period of contact at 30 minutes. Another series of experiments was conducted to find out the effect of particle size of phosphate sample on the recovery of P_2O_5.The following sized fractions were used: -35 +65, 65 +100, -100 +170 and -170 mesh Tyler equivalent, keeping temperature at 40 ± 0.1 °C, acid concentration at 6 M, acid to rock mole ratio of 20: 1 and the period of contact at 30 minutes.

4. Results and discussion

Figures 1-4 show the influence of acid of concentration and temperature acidulation on the recovery of P_2O_5 from phosphate sample. They indicate that the recovery decreases as acid concentration increases.

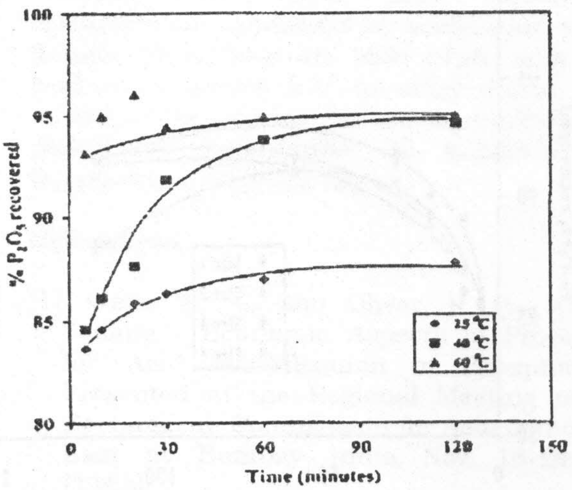

Fig 1. Influence of temperature and time on the % recovery of $P_2 O_3$ at 4 M HNO.

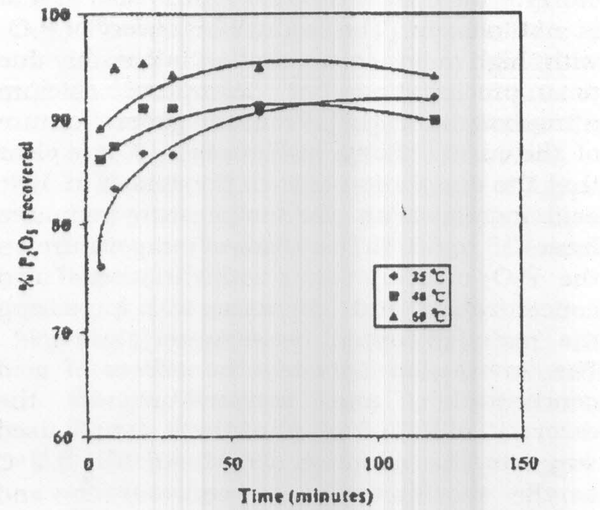

Fig 2. Influence of temperature and time on the % recovery of $P_2 O_5$ at 5 M HNO_3.

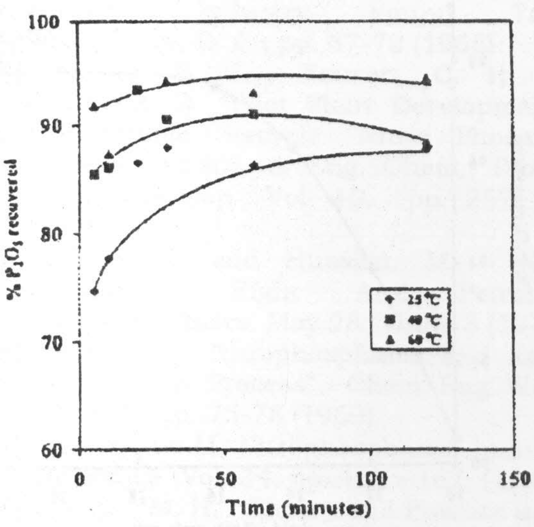

Fig 3. Influence of temperature and time on the % recovery of $P_2 O_5$ at 6 M HNO_3.

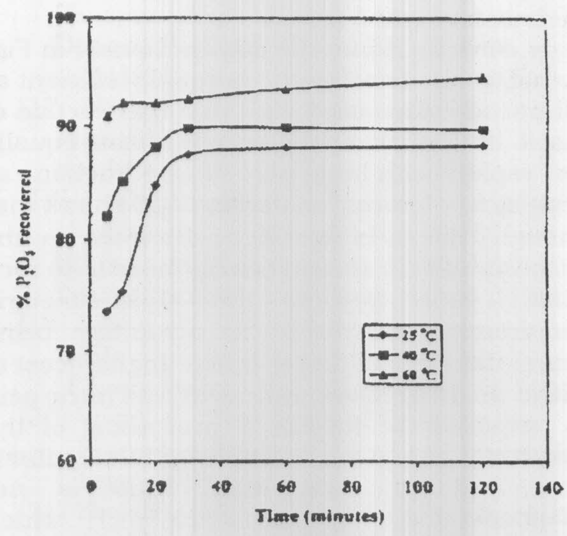

Fig 4. Influence of temperature and time on the % recovery of $P_2 O_5$ at 9 M HNO_3.

To avoid excessive dilution of the resulting slurry, the concentration of nitric acid at 4 M is not chosen. The reduced recovery of P_2O_5 with high acid concentration is possibly due to precipitation of complex calcium nitrophosphate [12]. From the general nature of the curves shown in Figures 1- 4, it is clear that the dissolution of rock phosphate in itric acid increases as the temperature increases from 25 to 60 °C.The effect of temperature on the P_2O_5 recovery varies with variation of acid concentration and decreases with increasing the period of contact between rock and acid . The interaction between the effects of acid concentration and temperature on the recovery of P_2O_5 from phosphate sample used suggests the adoption of 6 M and 40 ± 0.1 °C as the recommended acid concentration and temperature, respectively.

The data presented in Fig. 5. shows that the major part of P_2O_5 was extracted within the first 10 minutes. A reaction time ranging from 10 minutes to 1 hr is sufficient to almost completely dissolve the P_2O_5 content in phosphate sample. However, for practical considerations, 30 minutes may be taken as the recommended period.

It is obvious from the data presented in Fig. 5.that rock dissolution is equally efficient at all particle sizes tried, and that the reaction of trock with nitric acid proceeds almost equally as rapidly with large particle size fractions as with finely ground material. Fig.6.shows that though there is a slight increase in the recovery of P_2O_5 on increasing the acid to rock mole ratio beyond the stoichoimeteric requirement of 20: 1; the advantage being more than offset by a much higher cost of nitric acid.Therefore, unless excess nitric acid is required for further processing of the resulting slurry into nitrophosphate fertilizer, the acid to rock mole ratio is not recommended to exceed 22 : 1, which corresponds to 10% in excess over the stoichiometric acid requirement as indicated by reaction 1.

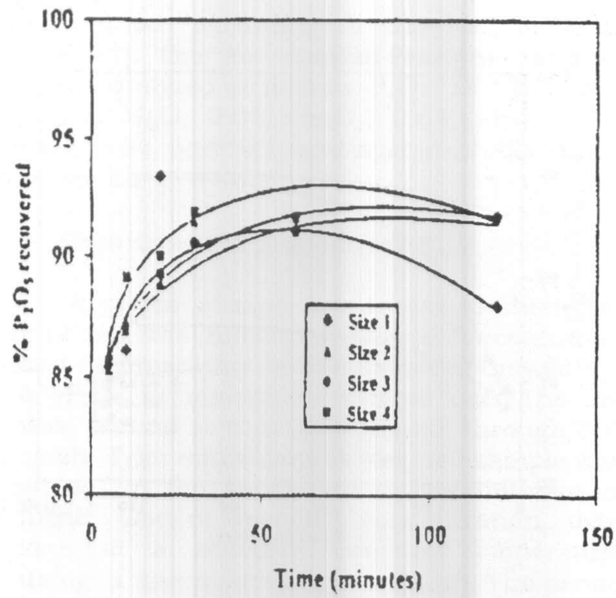

Fig 5. Influence of particle size of phosphate material or recovery of P_2O_5 at 40 °C and 6M HNO_3.

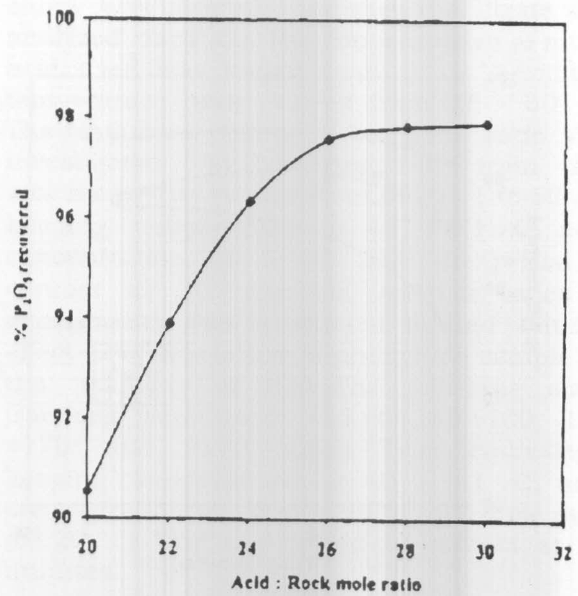

Fig. 6. Influence of acid: rock mole ratio on % recovery of P_2O_5 at 40 °C and 6M HNO_3 and 30 min.

5. Conclusions

The factors affecting the use of nitric acid for dissolution of low grade Saudi rock phosphate of As-Sanam area has been investigated.The recommended conditions of the results of the present study indicates that fine grinding of phosphate rock is not necessary for attaining satisfactory recovery of P_2O_5. A material as coarse as 0.5 mm is attacked by nitric acid rapidly.The ecommended conditions for acidulation of As-Sanam phosphate ore with nitric acid are: acid concentration, 6 M; quantity of acid, 10% in excess over the stoichiometric requirement; period of acidulation, 30 minutes; and temperature, 40 ± 0.1 °C

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Received July 20, 2000
Accepted October 14, 2000