Phosphate Rock Treatment with Hydrochloric Acid for Increasing P_2O_5 Content

Dr.Adel Sharif Hamadi
Chemical Engineering Department, University of Technology/Baghdad
Email:dr-adelsharif@yahoo.com
Dr.Shurooq Talib Remedhan
Chemical Engineering Department, University of Technology/Baghdad
 Haider Abd Ali
Chemical Engineering Department, University of Technology/Baghdad

ABSTRACT

   The present paper deals with the treatment of phosphate obtained from a commercial sample of Akashat phosphate ore in hydrochloric acid. The factors studied are effects of the temperature of dissolution, acid concentration, and the time required for mixing phases. The experiments were performed with 100 kg/m^3 of solid/liquid ratio, the size of the particles ranged 125-140 µm, the initial acid concentrations were 20, 30 and 40 wt% HCl, and the temperature of dissolution was kept constant at 30, 40, 50, 60 and 70 ^{o}C. The results indicated that the percentage of P_2O_5 increases as the HCl concentration increased using different time and temperatures. Also, the results showed that the best conditions for P_2O_5 recovery process according were acid concentration 40%, reaction time of 90 min, and temperature 30 ^{o}C.

Keywords: phosphate rock, dissolution, hydrochloric acid, P_2O_5.

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معالجة الصخور الفوسفاتية بحامض الهيدروكلوريك لغرض زيادة محتوى خامس اوكسيد الفسفور

الخلاصة

يتناول البحث الحالي عملية معالجة الحجر الفوسفاتي المستخرج من منطقة عكاشات العراقية بحامض الهيدروكلوريك. العوامل التي تم دراستها هي تاثير درجة الحرارة , تركيز الحامض, الوقت اللازم للخلط. لقد جرت التجارب باستخدام الظروف التالية : 100 كغم من المادة الصلبة لكل متر مكعب من المادة السائلة؛ المعدل العام لحجم الدقائق الصلبة 125 -140 مايكرومتر؛ تركيز حامض الهيدروكلوريك كنسبة وزنية 20,30 و 40% ؛ و درجة الحرارة التفاعل عند 30,40,50,60,70 درجة مئوية. لقد اثبتت النتائج بان افضل نسبة استرجاع لخامس اوكسيد الفسفور كانت عند تركيز حامض الهيدروكلوريك 40%, زمن تفاعل 90 دقيقة ودرجة حرارة 30 درجة مئوية.

الكلمات الدالة: الصخور الفوسفاتية, السماد الفوسفاتي, حامض الهيدروكلوريك, خامس اوكسيد الفسفور

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INTRODUCTION

Phosphorus is a vital resource for sustaining world agriculture. Reserves of phosphate rock are identified in many regions of the world. Iraq is one of the largest countries in the world including phosphate ores. Phosphate in Iraq comes in second place after the sulfur and where large reserves of these raw materials exist in the composition of Akashat in Western desert, one of the Marine sedimentary origins. The estimated of workable phosphate ore in excess of 1.7 billion tons most of which configurations belong to Mastrichian, Eocene and Paleocene [1].

Iraqi phosphate ores with medium quality in terms of content of phosphorus in which the proportion of phosphorus pent-oxide between 21-22% and need to focus operations in ways that simple physical for the purpose of industrial use is the main raw production of different phosphate fertilizers and phosphoric acid and can be the raw material for many chemical industries in the future.

Phosphate ore is insoluble in humid earth and therefore required treatment processing to reduce the content of gangue materials such as carbonate, silicate, feldspar, mica, calcite, dolomite and clays to meet the requirements of phosphate fertilizers [2, 3, 4]. These processes include conventional methods such as crushing and screening [5], or washing and desliming, and other beneficiation techniques include, calcination [6-8], flotation [9-14], or partial acidulation with dilute organic or inorganic acids [15-24].

The oldest route is via the addition of high concentrations of sulfuric acid to finely ground phosphate rock. This acidulation step releases phosphoric acid from the calcium phosphate salts present and produces insoluble gypsum (calcium sulfate dihydrate) according to following reaction:

$$Ca_3(PO_4)_{2(s)} + 3\ H_2SO_{4(l)} + 6\ H_2O(l) \rightarrow 2H_3PO_{4(l)} + 3\ CaSO_4\ 2H_2O_{(s)}$$
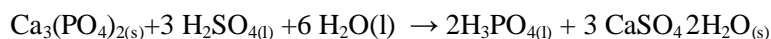
The production units include large reaction vessels where finely ground phosphate rock is first treated with weak phosphate acid and then reacted with approximately 55% sulfuric acid. In wet process with hydrochloric acid, HCl (34%) and phosphate rock react to form phosphoric acid and calcium chloride.

This process makes it possible to avoid the formation of phosphogypsum, a phenomena which necessitates the use of larger reaction vessels with higher initial cost. Since calcium chloride is soluble, it remains in solution with the acid [25].

The high concentration of the calcium cation promotes precipitation of the fluorine present in the rock. Following the separation of solid impurities, the solution is contacted with water immiscible organic solvents to minimize losses and that selectively extracts the phosphoric and hydrochloric acids and leaves the free coproduct calcium chloride in the aqueous layer as follows [26]:

$$CaF_2\ 3Ca_3(PO_4)_2 + 20\ HCl \rightarrow 6\ H_3PO4 + 10\ CaCl_2 + 2\ HF$$
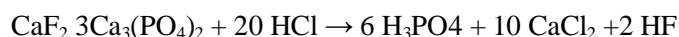
However, under specific conditions some of the phosphate is dissolved to form soluble monocalcium phosphate as follows:

$$3Ca_3(PO_4)_2 + 2\ HCl \rightarrow CaH_4(PO_4)_2 + 2CaCl_2$$
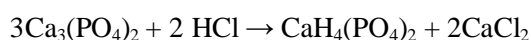
The main factors affecting the reaction rate of acid attack of phosphate are acid concentration, time of the reaction, solid/liquid ratio, particular size and temperature [27, 28, 29, 30].

The acidulation reaction is more rapid with hydrochloric acid than with sulfuric acid, and yields soluble products from both the calcium and phosphate. Thus, there is neither a need to heat the mixture to speed up the reaction, nor are there any crystal form problems requiring temperature stabilization.

The product acid from this process is often purer than that obtained from sulfuric acid acidulation, and in addition this process is claimed to recover 98–99% of the available P_2O_5 in the rock, as opposed to the 94–95%. The flowsheet of hydrochloric acid acidulation route to phosphoric acid is shown in figure (1).

EXPERIMENTAL PROCEDURE
Sample Description

The phosphate rock sample was crushed and screened to collect a fraction of general range size of 125-140 µm, using the mesh sieves of U. S. Tyler. The test sample was done for various constituents of the rock in Department of standardization and quality control /Ministry of planning and the results are given in table (1).
Total percentage of the determined constituents was found to be less than 100%. The remaining may be SiO_2, Al_2O_3, moisture, organic matter etc.

Procedure

The samples of the ground phosphate rock were dried in an electric oven at about 105 ^{o}C, cooled to room temperature and stored in closed desiccators for analysis before and after treatment with hydrochloric acid. A 50 g of the sample was added to a conical flask reactor (500 ml) a measured volume of diluted hydrochloric acid solution of a specified concentration. The reaction mixture was been agitated using a magnetic stirrer at moderate speed for a fixed time and temperature. After the reaction, the product was filtered using a Buchner funnel and filter paper. The solid matter after leaching process was washed with fixed amount of distilled water to remove any soluble matter.

Analytical analysis techniques were used to study P_2O_5 content. The concentration of P_2O_5 was calculated from material balance, and determined by titration with (0.5N) sodium hydroxide solution and phenolphthalein indicator solution until a pink color appears. The P_2O_5 content was calculated from the equation:

% total P_2O_5 = (3.55 x Vs)/W

Where Vs=Volume of 0.5N sodium hydroxide solution used.(ml), and W=Weight of sample in the liquor. (g).

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RESULTS AND DISCUSSION
Effect of Acid Concentration on $\%P_2O_5$ Recovery:

Weighted sample of the particle size of 125-140 µm were treated at constant temperatures at 30, 40, 50, 60, and 70 ^{o}C with HCl acid of 20, 30, and 40 wt% concentrations for different periods. After each period the percentage P_2O_5 dissolution was determined as shown plotted in figures 2-6, which observed that at various reaction temperature, the lower HCl concentration is a greater chance for the reaction between the phosphate and the HCl acid leading to lower values of P_2O_5 recoveries, but as concentration of acid increases, the polarity acid will increase leading in a decrease in the acid reaction with phosphate with a corresponding increase in the % P_2O_5 recovery.

Effect of Acidulation Time on $\%P_2O_5$ Recovery

It can be deduced from the figures 7-9, that an increase in acidulation time, lead to P_2O_5 content in the concentrate increase. This is due to the fact that HCl reaction can react as linearly with phosphate in the stages of the reaction forming $CaCl_2$ which is soluble and can easily lost in the filtrate, which leads to an increase in % P_2O_5 recovery.

Effect of Temperature on % P_2O_5 Recovery:

Temperature can affect the diffusion coefficient, specific reaction rate, and viscosity, but the gross effects on the process can be obtained only from experimental results. In this investigation a particle size of 125-140 µm was used at constant temperatures of 30, 40, 50, 60, 70 ^{o}C for different periods of acidulation. At the end of each period the percentage P_2O_5 was determined. Figures 10-12 show the results and observed that the P_2O_5 percentage increases with increase in temperature. This is attributed to diffusion coefficient   as the conversion is proved later to be controlled by the rate of diffusion of HCl to the reacting phosphate.

CONCLUSIONS

Akashat phosphate rock can be treatment with hydrochloric acid due to the reaction with calcium carbonate impurity formed a soluble $CaCl_2$ removed by filtration leaving a solid residue enriched in the phosphate.

The factors that were studied**:** acid concentration, acidulation time, and the temperature.

It was found that the best conditions for P_2O_5 recovery process according to this study were acid concentration 40%, reaction time of 90 min, and temperature 30 ^{o}C.

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Table (1): Analysis of Low Grade Phosphate Rock before Treatment with Hydrochloric Acid

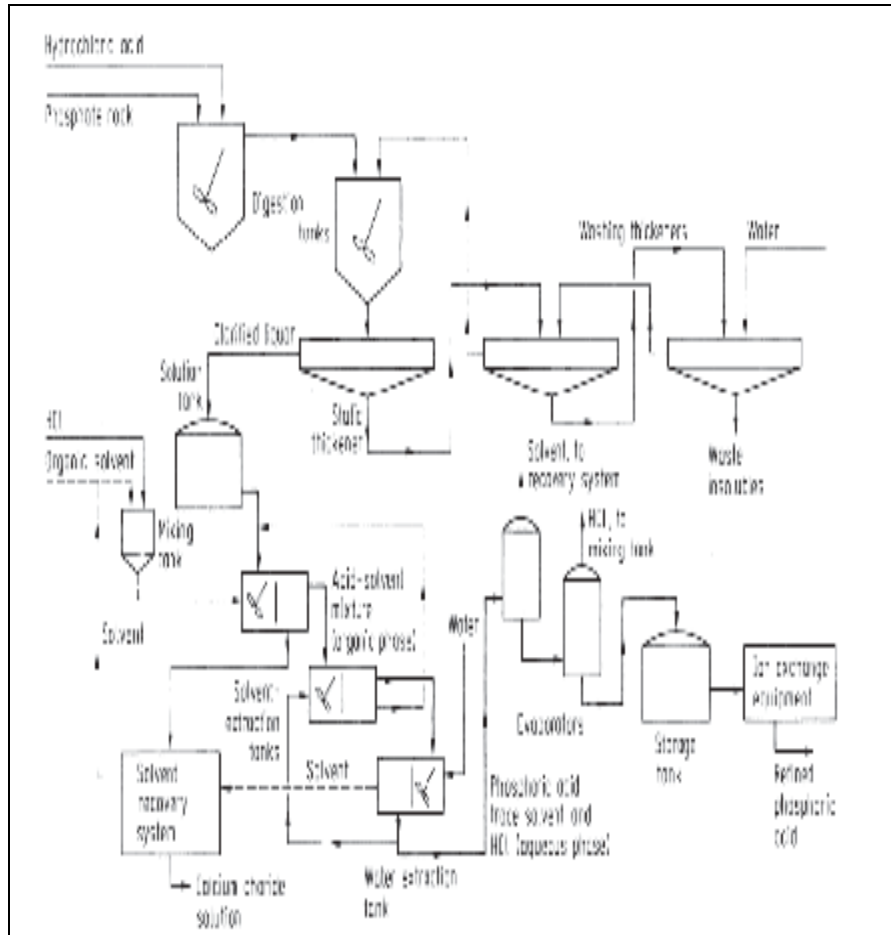| P$_2$O$_5$ (%)	CaO (%)	Na$_2$O (%)	K$_2$O (%)	MgO (%)	FeO (%)
17	18.8	0.8	0.084	1.4	0.1

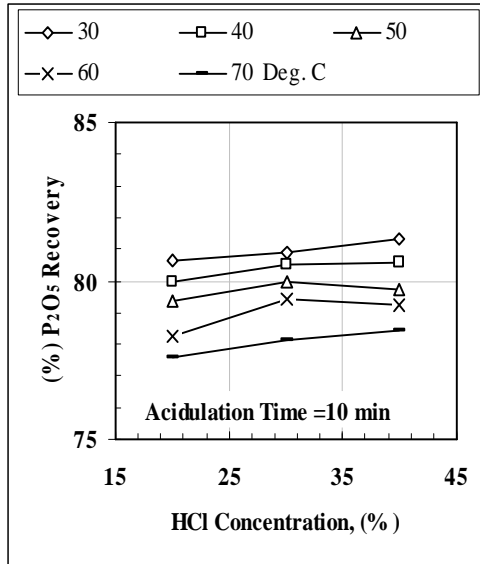**Figure (1): Flow sheet for Hydrochloric Acid Acidulation Rote to Phosphoric Acid [31]**

Figure (2): Effect of HCl Concentration on Increasing P_2O_5 of Phosphate for Different Temperature and Acidulation Time of 10 min.
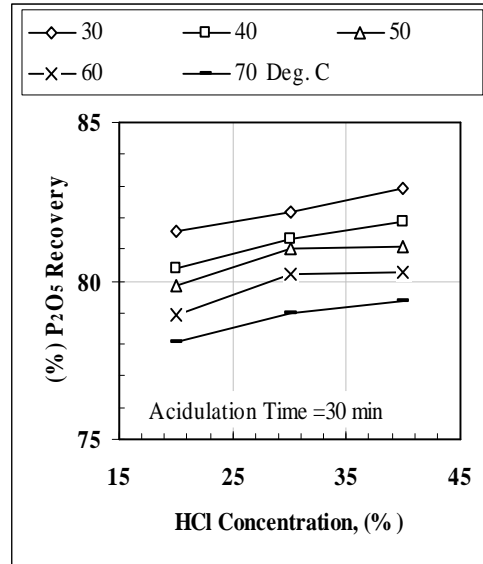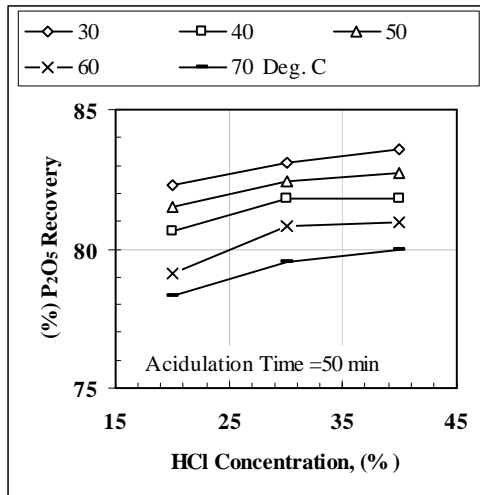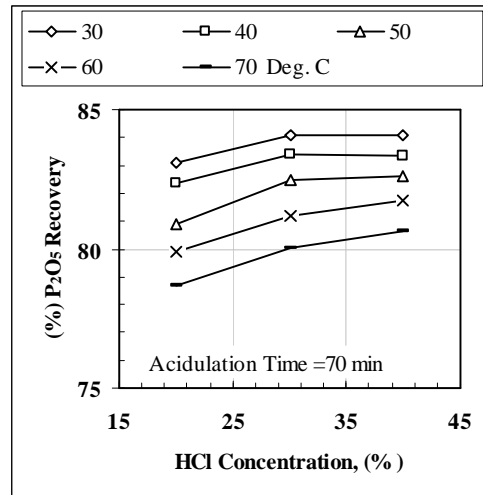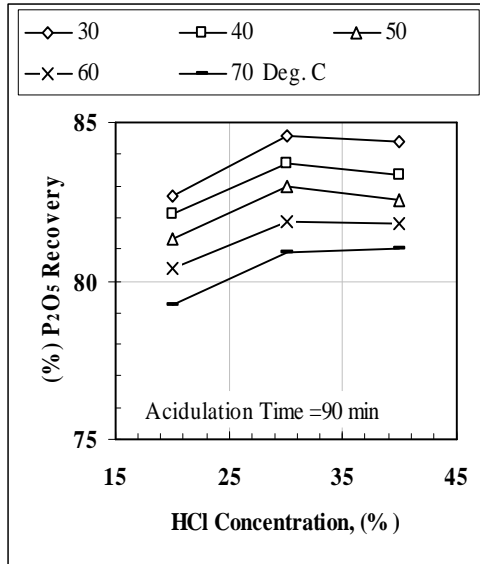

Figure (3): Effect of HCl Concentration on Increasing P_2O_5 of Phosphate for Different Temperature and Acidulation Time of 30 min.
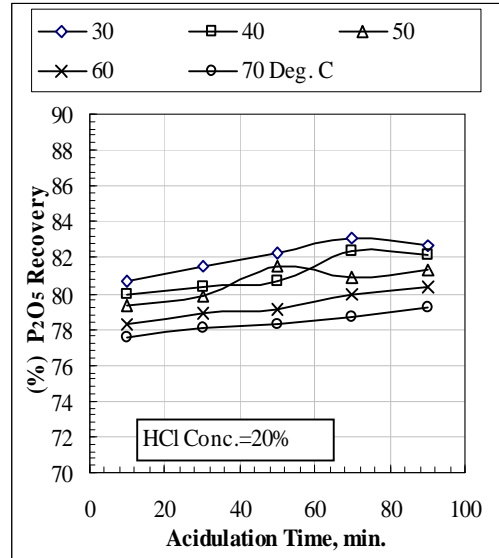

Figure(4): Effect of HCl Concentration on Increasing P_2O_5 of Phosphate for Different Temperature and Acidulation Time of 50 min.

Figure(5): Effect of HCl Concentration on Increasing P_2O_5 of Phosphate for Different Temperature and Acidulation Time of 70 min.

Figure(6): Effect of HCl Concentration on Increasing P$_2$O$_5$ of Phosphate for Different Temperature and Acidulation Time of 90 min

Figure (7): Effect of Acidulation Time on Increasing P$_2$O$_5$ of Phosphate for Different Temperature and HCl Concentration of 20%.
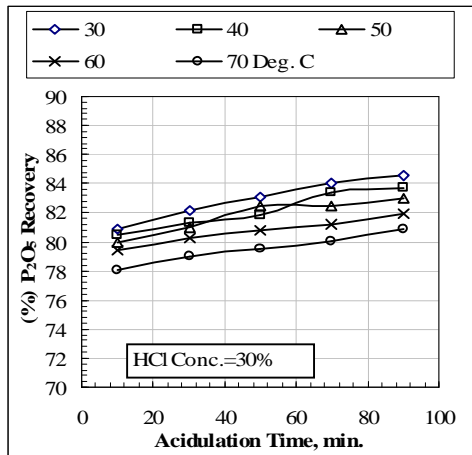

Figure (8): Effect of Acidulation Time on Increasing P$_2$O$_5$ of Phosphate for Different Temperature and HCl Concentration 30%.
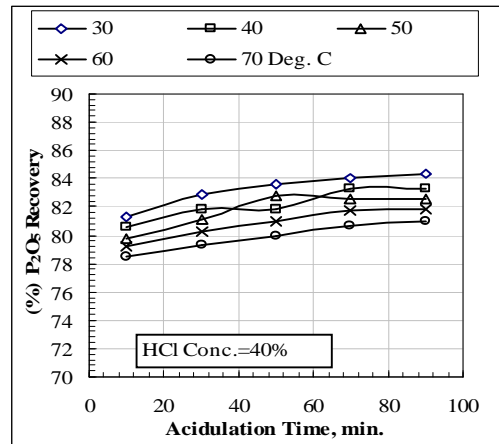

Figure (9): Effect of Acidulation Time on Increasing P$_2$O$_5$ of Phosphate for Different Temperature and HCl Concentration 40%.
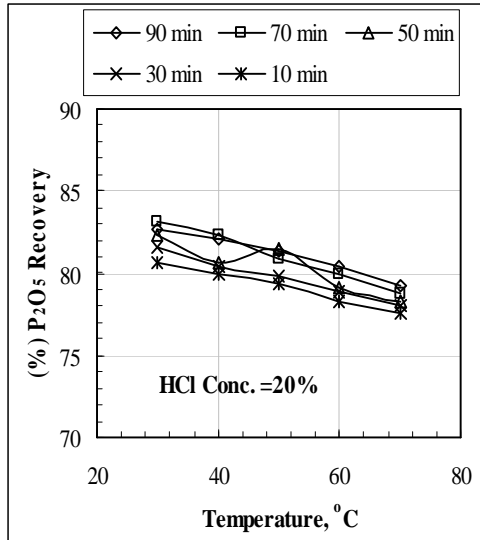
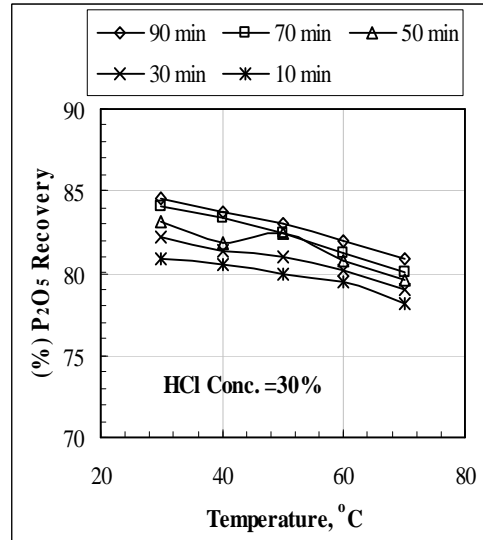**Figure (10): Effect of Acidulation Time on Increasing P$_2$O$_5$ of Phosphate for Different Temperature and HCl Concentration of 20%.**

Figure (11): Effect of Acidulation Time on Increasing P$_2$O$_5$ of Phosphate for Different Temperature and HCl Concentration of 30%.
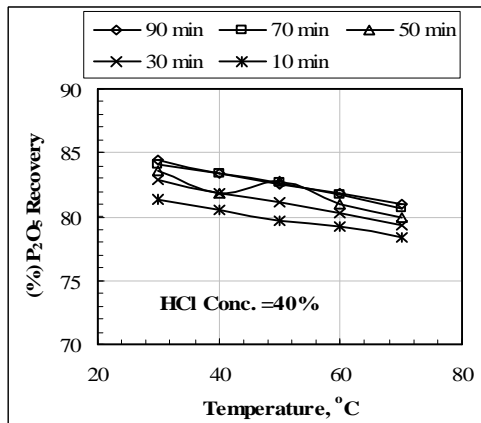

Figure (12): Effect of Acidulation Time on Increasing P$_2$O$_5$ of Phosphate for Different Temperature and HCl Concentration of 40%.