



*Ain Shams University
Faculty of Science
Chemistry Department*

Chemical Studies on the Extraction of Uranium and Phosphoric Acid from the Crude Acid

A Thesis Submitted By

Romany Nabil Ammanoeil Sabet Rizk

(B.Sc. in Chemistry-Faculty of Science-Ain Shams University - 2006)

For the Partial Fulfillment of the Requirements of the Master
Degree in Science (Inorganic Chemistry)

To

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**Faculty of Science
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Approval Sheet for Submission**

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ABSTRACT

The potential use of CYANEX 923 and TBP for the extraction of concentrated phosphoric acid has been investigated. The effects of the different parameters affecting the extraction processes, namely, the shaking time, concentration of the extractant and phosphoric as well, as phase ratio and temperature were carried out. Recovery of phosphoric acid from loaded organic solutions by different stripping agents was investigated. The optimum conditions for extraction and stripping of phosphoric acid in the investigated systems were deduced.

The potential use of CYANEX 923 for the extraction of uranium from phosphoric acid solutions was also studied. The effects of the different parameters affecting the extraction process and stripping processes of U(VI) were investigated. The optimum conditions for extraction and stripping of uranium and the possible recovery of uranium from high phosphoric media were also studied.

Application studies on the extraction of phosphoric acid from crude wet process phosphoric acid and from a leached solution of apatite phosphate rock were carried out based on the obtained experimental results. A flow sheet describing the proposed method for the recovery of phosphoric acid from the crude acid and from the phosphate rock is given and discussed.

CHAPTER 1

INTRODUCTION

1.1. GENERAL

Wet process phosphoric acid (WPPA) generally contains a number of organic and inorganic impurities that affect the grade of the acid and impart undesirable color. Different grades of purified phosphoric acid can be used on a large scale. Technical grade phosphoric acid contains $P_2O_5 = 85\%$, $Cl^- = 0.0005\%$, $SO_4 = 0.005\%$, $Fe = 0.002\%$, $As = 0.008\%$ and heavy metals = 0.001% . On the other hand, food grade phosphoric acid contains $P_2O_5 = 85\%$, $Cl = 0.0005\%$, $SO_4 = 0.008\%$, $As = 0.001\%$, heavy metals = 0.001% and $F = 0.001\%$ (**Ahmed, 2008**). Pharmaceutical grade phosphoric acid contains $P_2O_5 = 85\%$, $Cl = 0.005\%$, $SO_4 = 0.01\%$, $As = 0.00015\%$, heavy metals = 0.001% and $Fe = 0.005\%$ (**European Pharmacopeia, 2013**)

Traditionally, furnace-grade phosphoric acid or chemically wet processes acid (WPA) were used on large scale in many industrial fields. The industrial phosphoric acid produced contains uranium concentration levels of 40-120 mg/L and may be considered as a non-negligible source of uranium. (**Walters, et al., 2008**).

1.2. PRODUCTION OF PHOSPHORIC ACID

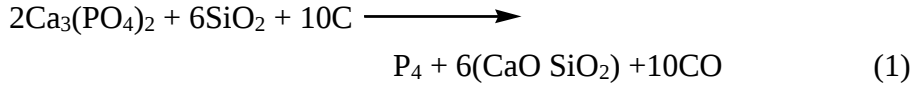
Phosphoric acid is produced by treating the fluoroapatite ore with strong mineral acids (H_2SO_4 , HNO_3 or HCl), using the furnace or wet processes.

1.2.1. Furnace Process

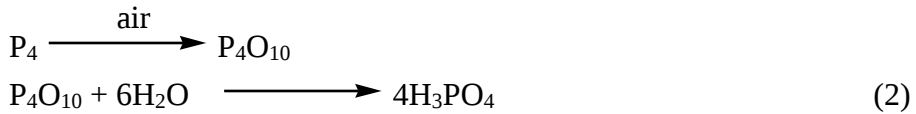
This process depends on the production of elemental phosphorus, which is then converted to phosphoric acid (**Burt, and Barber, 1952**). The elemental phosphorus is produced by the electrothermic reduction of fluoroapatite with carbon (coke). The silica added to the furnace charge behaves as strong acid at the high temperature

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(about 1500°C) and combines with the calcium constituent of the fluoroapatite to form calcium silicate. The overall reaction, when neglecting the fluoride, carbonate and other nonphosphatic constituents, may be represented as follows:



Some portion of fluorine in the apatite lattice is volatilized as silicon tetrafluoride, while the majority is removed in the molten calcium silicate slag. From Eq. (2) the condensed elemental phosphorus is burned in air to form the phosphorus oxide vapor (P_4O_{10}), which reacts with water to produce phosphoric acid:

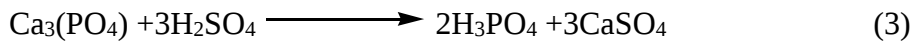


1.2.2. Wet Process

In this process, the phosphate ore is treated with strong mineral acid, H_2SO_4 , HNO_3 or HCl to produce phosphoric acid.

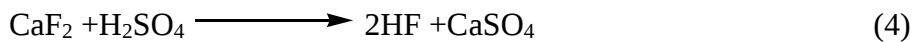
1.2.2.1. Wet process with sulfuric acid

When phosphate rock is treated with H_2SO_4 the apatite lattice is destroyed and the apatite constituents solubilize producing phosphoric acid, in a so-called wet process (**Kirk and Othmer, 1951 & Nordengren, et al., 1955**). In this process, the tricalcium phosphate is dissolved in a phosphoric acid solution and (98%) sulfuric acid is added to precipitate calcium sulfate according to the following over all reaction:



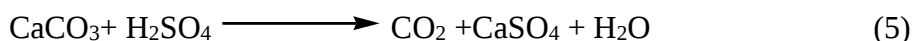
(Various side reactions may occur)

Calcium sulfate and hydrogen fluoride are produced by the reaction of calcium fluoride with H_2SO_4 :

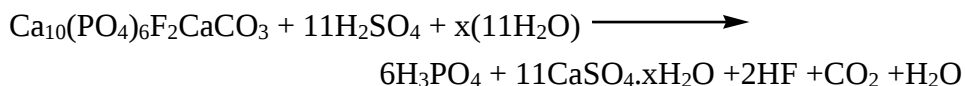


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Carbon dioxide, calcium sulfate and water are produced when calcium carbonate reacts with H_2SO_4 ,



Reactions (1), (2) and (3) may be represented by the following reaction:



Different calcium sulfate salts are formed, depending on the process conditions such as the acid concentration and the temperature; in this respect, either calcium sulfate hemihydrate ($x = 1/2$, HH), dihydrate ($x = 2$, DH) or anhydrite ($x = -0$, AH) is formed. Fig.(1) shows the effect of reaction conditions on the formation of calcium sulfate species.

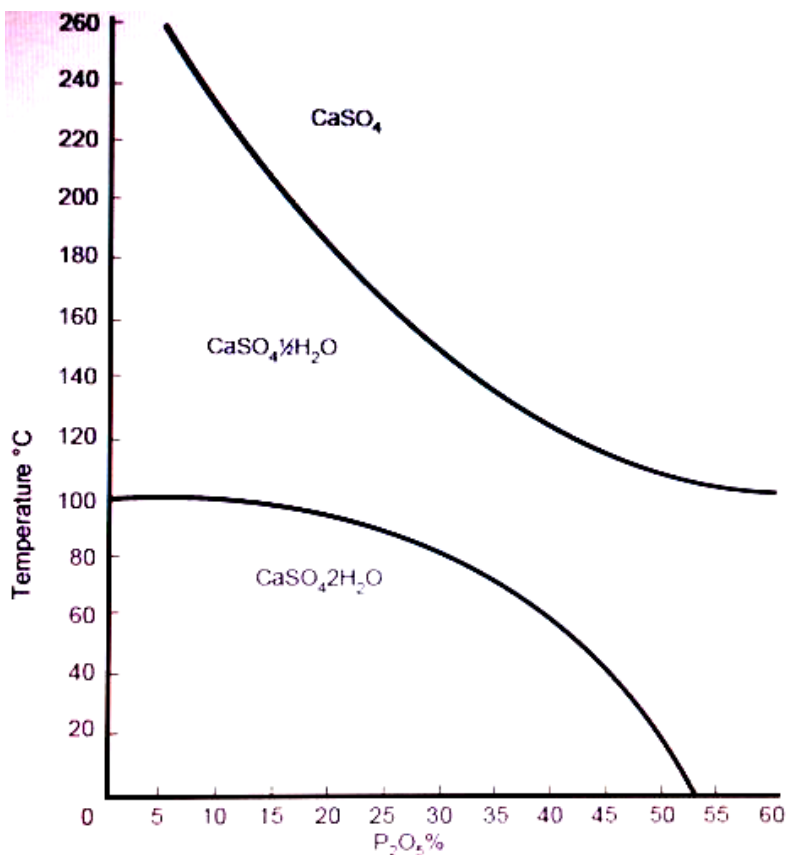
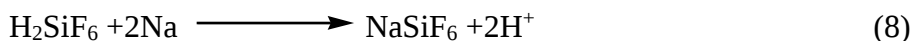
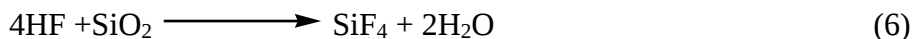


Fig.(1): Effect of temperature on calcium sulphate crystallization.

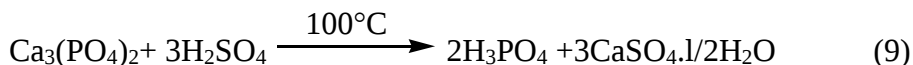
Introduction

Silica may react with hydrogen fluoride produced to form silicon tetrafluoride, which then hydrolyses to form fluorosilic acid which may react with any sodium fluorosilicate;



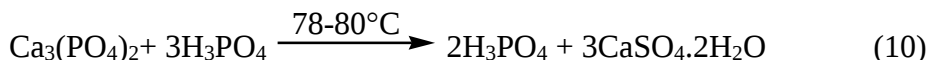
In Anhydrite process (AH), the phosphate rock was allowed to react with 98% sulfuric acid and the resulting acidified solution was heated for about 30 min. at 200 to 240°C. In some cases, the digestion was carried out under pressure at elevated temperature, about the boiling point, to give an acid containing 40 to 51 % P₂O₅.

Corrosion and filtration difficulties were the major problems of this process (**Liljenroth, 1928 & Piombino, 1964**). In producing high phosphoric acid concentration, the rock is dispersed into a premixed slurry, the filtrate from washing of CaSO₄.5H₂O filter in the subsequent stage is mixed with H₃PO₄ to prepare a circulation acid that is mixed with H₂SO₄ to produce a mixed acid containing < 60-wt % H₂SO₄. The mixed acid is used for decomposition of phosphate rock. Thus phosphate rock (668 kg/h) was decomposed with mixed acid and filtrate to produce cake (1235 kg/h) and H₃PO₄ (400kg/h) containing 52% P₂O₅ and 1.3% H₂SO₄. Phosphoric acid is produced from phosphate rock containing carbonates by treating the rock with recycled H₃PO₄ from CaSO₄ filtration (**Smalter, 1963**). The Hemihydrate process (HH) (**Nielsson and Yates, 1953**) offers the potential advantage over the dihydrate of producing acid of 38-42 % P₂O₅ which may be directly used in diammonium phosphate manufacture and would also requires only one evaporation stage for concentration to 54% merchant-grade phosphoric acid and the digestion step is carried out at 100°C;



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The Dihydrate process (DH) operates at 78-80°C and 28-30% P₂O₅ acid concentration to promote the formation of calcium sulfate in the dihydrate forms;



Sulfuric acid is mixed with phosphoric acid (18-22% P₂O₅) and recycled reaction slurry, then the dry ground phosphate rock is added in a slightly less than the stoichiometric proportion to maintain a slight excess system where temperature and acid concentration are carefully controlled to ensure good crystal formation and completeness of reaction. A high recycle ratio is maintained, i.e. 20 parts of slurry are recycled through the system for every one part pumped to the filter. The reaction slurry is separated on the filter and a 3 stages counter current wash of the calcium sulfate cake takes place. The 19% P₂O₅ acid is returned to the reactor for control purpose. The calcium sulfate cake is slurried up and pumped away. The 28- 30% P₂O₅ acid is pumped to intermediate storage. 28-30%P₂O₅ is concentrated to 52% by vacuum evaporation and pumped to final storage.

The Hemihydrate- Dihydrate process (HDH) (**Larsson, 1933 & Liljenroth, 1928 & Piombino, 1964; Organization for European Economic, 1953**) involves precipitation of calcium sulfate in the hemihydrate form followed by recrystallization to dihydrate. This process produced large, well-formed dihydrate crystals and it was claimed that phosphate substituted in the calcium sulfate lattice was released and dissolved during recrystallization.

1.2.2.2. Wet process with nitric acid

In this process, the phosphate ore is treated with (56%) nitric acid solution (**Nielsson and Yates, 1953**). The phosphate ore is decomposed to monocalcium phosphate salt according to the equation;

