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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Supervised By

Prof. Dr. Ebtissam A. Saad	**Prof. Dr. Jacqueline A. Daoud**
Prof. of Inorganic and Radiochemistry, Faculty of Science, Ain-Shams University	Prof. of Radio-Inorganic Chemistry, Hot Laboratories Centre, Atomic Energy Authority

Dr. Ismail M. Ahmed

Assistant Prof. of Inorganic chemistry,

Hot Laboratories Centre,

Atomic Energy Authority

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Approval Sheet for Submission

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This thesis has been approved by Supervisor Committee:

Prof. Dr. Ebtissam A. Saad

Prof. of Inorganic and Radiochemistry, Faculty of Science, Ain-Shams University

Prof. Dr. Jacqueline A. Daoud

Prof. of Radio-Inorganic Chemistry, Hot Laboratories Centre, Atomic Energy Authority

Dr. Ismail M. Ahmed

Ass. Prof. of Inorganic chemistry, Hot Laboratories Centre, Atomic Energy Authority

This thesis for M.SC. Degree has been approved by:

Prof. Dr. Hatem El Taei Adel Rahman El Batal

Prof. of Inorganic Chemistry, National Research Centre

Prof. Dr. Nagia Abdelhameed El Alaily

Prof. of Radiation chemistry, National Center for Radiation Research and Technology

Prof. Dr. Ebtissam A. Saad

Prof. of Inorganic and Radiochemistry, Faculty of Science, Ain-Shams University

Prof. Dr. Jacqueline A. Daoud

Prof. of Radio-Inorganic Chemistry, Hot Laboratories Centre, Atomic Energy Authority

Date of Examination: / / 2018

Head of Chemistry Department

Prof. Dr: Ibrahim H. Badr

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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-l20 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 fluoroaptite with carbon (coke). The silica added to the furnace charge behaves as strong acid at the high temperature (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:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 6(CaO\ SiO_2) + 10CO \qquad (1)$$

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:

$$P_4 \xrightarrow{\text{air}} P_4O_{10}$$

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4 \qquad (2)$$

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:

$$Ca_3(PO_4) + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4 \qquad (3)$$

(Various side reactions may occur)

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

$$CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4 \qquad (4)$$

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

$$CaCO_3 + H_2SO_4 \longrightarrow CO_2 + CaSO_4 + H_2O \qquad (5)$$

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

$$Ca_{10}(PO_4)_6F_2CaCO_3 + 11H_2SO_4 + x(11H_2O) \longrightarrow 6H_3PO_4 + 11CaSO_4.xH_2O + 2HF + CO_2 + H_2O$$

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.

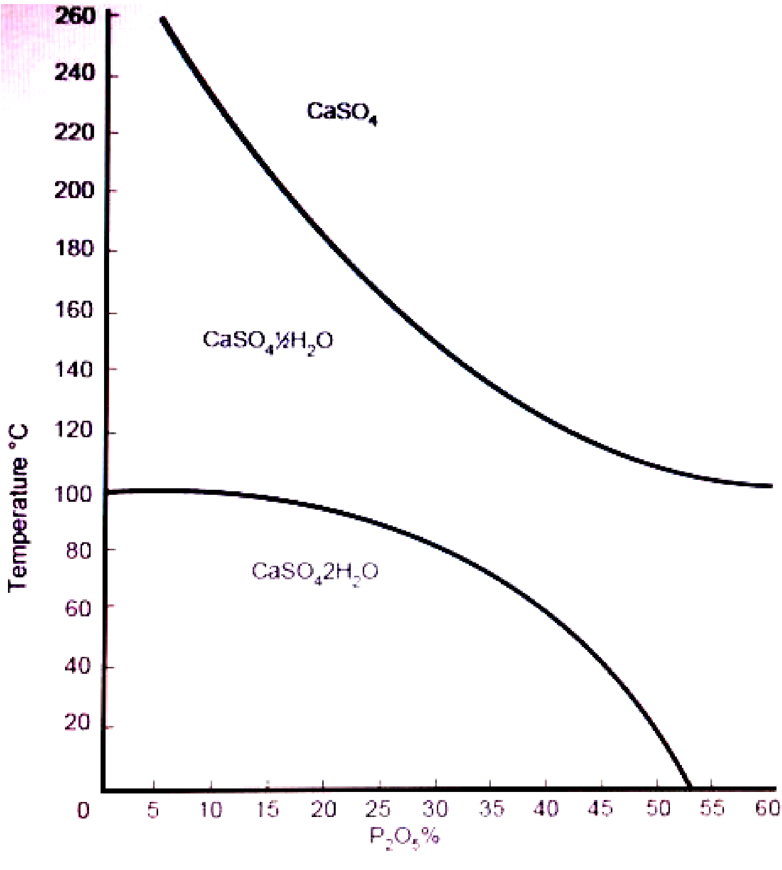

Fig.(1): Effect of temperature on calcium sulphate crystallization.

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;

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \qquad (6)$$

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2 \qquad (7)$$

$$H_2SiF_6 + 2Na \longrightarrow NaSiF_6 + 2H^+ \qquad (8)$$

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 % P_2O_5.

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 $CaSO_4.5H_2O$ filter in the subsequent stage is mixed with H_3PO_4 to prepare a circulation acid that is mixed with H_2SO_4 to produce a mixed acid containing < 60-wt % H_2SO_4. 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 H_3PO_4 (400kg/h) containing 52% P_2O_5 and 1.3% H_2SO_4. Phosphoric acid is produced from phosphate rock containing carbonates by treating the rock with recycled H_3PO_4 from $CaSO_4$ filtration ***(Smalter, 1963)***. The Hemihydrate process (HH) ***(Nielsson and Yates, 1953)*** offers the potential advantage over the dihydrate of producing acid of 38-42 % P_2O_5 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;

$$Ca_3(PO_4)_2 + 3H_2SO_4 \xrightarrow{100^\circ C} 2H_3PO_4 + 3CaSO_4.l/2H_2O \qquad (9)$$

The Dihydrate process (DH) operates at 78-80°C and 28-30% P_2O_5 acid concentration to promote the formation of calcium sulfate in the dihydrate forms;

$$Ca_3(PO_4)_2 + 3H_3PO_4 \xrightarrow{78\text{-}80°C} 2H_3PO_4 + 3CaSO_4.2H_2O \qquad (10)$$

Sulfuric acid is mixed with phosphoric acid (18-22% P_2O_5) 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% P_2O_5 acid is returned to the reactor for control purpose. The calcium sulfate cake is slurried up and pumped away. The 28- 30% P_2O_5 acid is pumped to intermediate storage. 28-30%P_2O_5 isconcentrated 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 hemihyhrate 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;

$$3CaO.\ P_2O_5 + 4HNO_3 \longrightarrow Ca\ (H_2PO_4)_2 + 2Ca(NO_3)_2 \qquad (11)$$