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The Separation of Uranium During the Preparation of Analar Grade Phosphoric Acid by Organic Solvents

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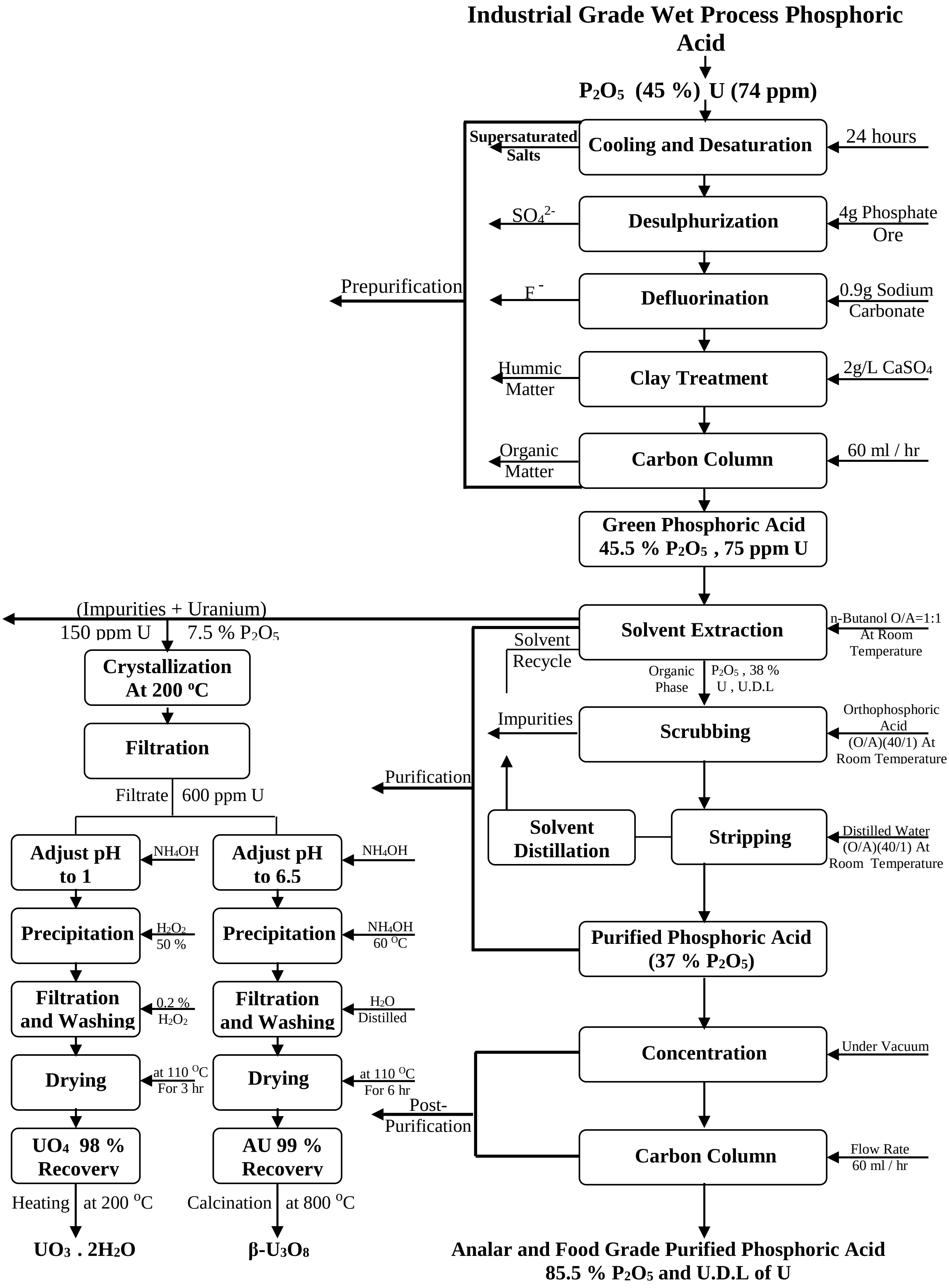

Figure (20): Proposed Technical Flow Sheet for Purification of Industrial Grade Wet Process Phosphoric Acid to Analar and Food Grade Quality besides, the Separation of Uranium

CHAPTER I

INTRODUCTION

1.1General Outline

Wet process phosphoric acid contains a variety of impurities as well as the required phosphate content because it is manufactured from phosphate ores. It is for this reason that wet-process phosphoric acid has historically been precluded from use in certain non-fertilizer applications, such as its use in the food and detergent industries and on other industries where a high purity is necessary.

Acid produced by thermal route, on the other hand, has a much higher purity, essentially containing only the phosphate values, since the phosphorus is separated from phosphate rock before acid manufacture, and has generally been used in these applications. However, because of the large quantities of energy that are required to manufacture thermal phosphoric acid, its cost has risen considerably in the last ten years or so. Consequently a number of companies have developed techniques to purify wet process acid such that it can be used to replace the purer thermal acid in certain situations.

As indicated, wet process phosphoric acid when it is freshly manufactured contains a variety of impurities. Many of these impurities particularly are removed from the acid whatever its use, by techniques such as clarification. While other purification techniques are employed depend on the use for which the acid is intended. For food and technical grade acid, the levels of the following materials in the acid must at some stage be considered, calcium, magnesium, sulphate, iron and other trace materials fluorine, heavy metals such as arsenic and lead and organic matter.

Many different techniques have been considered for purification of wet process acid to food and technical grades, which will be reviewed later on. However solvent extraction has been most widely employed, forms the basis of the majority of commercially operated purification units moreover it is easier to recover any of the valuable elements from the raffinate, such as uranium as an added value to solvent extraction process.

In Egypt, the first commercial plant of wet process phosphoric acid by the dihydrate process (Norske – Hydro Fissions process) using Sebaiya wet phosphorites, has come into stream in late 1984 by Abu Zaabal Fertilizer and Chemical Company recently gives the name Poly Serve For Fertilizers.

The nominal production of this plant is 600,000 ton P_2O_5. In the Norseke – Hydro fission dihydrate process, the input ore should be ground so that 65% of it passes – 100 mesh size, the temperatures of the reaction of sulfuric acid with the ore should be between 80 – 82 ^{0}C while the filtrate acid temperature should be between 56 – 70 ^{0}C. The free amount of the sulfuric acid should be between 3 and 5 %. The produced dilute acid 30% P_2O_5 could be concentrated to 45% by an evaporator whereby more impurities, namely fluoride are precipitated.**(1)**

1.2 Literature Survey

There are many methods used to purify phosphoric acid from impurities such as solvent extraction, solvent precipitation, indirect purification, clarification, ion exchange**(2)**, …….etc.

1.2.1 Purification of wet process phosphoric acid by organic solvents

The use of organic solvents has probably received most attention for the purification of wet process phosphoric acid, they may be used in either of two ways for extraction or precipitation.

In the former technique wet process phosphoric acid is brought into initial contact with a practically or substantially water immiscible organic solvent, into which a majority of the phosphoric acid is extracted. After the two phases have been separated, the aqueous phase or raffinate, which contains some phosphoric acid and most of impurities, can be used for the manufacture of fertilizer such as single super phosphate. The organic phase, however, contains very few of the impurities and the phosphoric acid that is subsequently re-extracted from the solvent has a much higher purity than the original acid.**(3)**

Obviously the process is not that simple, though it is necessary for example to ensure that all the solvent is recovered from both the raffinate and the purified acid. But there are two aspects that are of major importance: choice of solvent and the impurities present in the acid. In the latter technique a water miscible solvent, usually with an alkali metal or ammonium ions, is mixed with the acid and tends to through many of soluble impurities out of solution.

A considerable amount of solvent has been studied as extractant of wet process phosphoric acid, including alcohols,**(4)** esters, **(5)** ethers, **(6)** ketones, **(7)** amines **(8)**.

1.2.1.1 Purification of wet–process phosphoric acid by tributyl phosphate (TBP)

Extraction with tributylphosphate (TBP) is one way of purifying phosphoric acid. The distribution of phosphoric acid between the organic and aqueous phases in the system H_3PO_4-Fe_2O_3-H_2O-TBP and H_3PO_4-

Al_2O_3-TBP was investigated at 22^0C. An equation was developed for the phosphoric acid distribution coefficient. The empirical phosphoric acid distribution coefficient depends on the concentration of Mg(II), Fe(III) and Al(III), impurities in the solution.**(9)**

Extraction of phosphoric acid with concentrated TBP is studied at 25^0C. In the extraction process the hydrate, di- and monosolvates of the acid are formed. The extraction constant and degree of solvate hydration are calculated. It is established that disolvate is the main compound of the organic solvent at low concentration of acid, monosolvate content increases with the increase of acid concentration.**(10)**

1.2.1.2 Purification of wet-process phosphoric acid by methyl- isobutyl ketone (MIBK)

MIBK was used for purification of phosphoric acid from major impurities of (Ca, Al, Fe, SO_4^{2-}, F^-). Distribution of phosphoric acid (PA) and impurities as well as selectivity of MIBK for PA, has been studied as a function of the phosphoric acid concentration in the organic phase. The results are compared to other solvents (iso-amyl alcohol, dibutyl ether and dipropyl ether). MIBK seems to have the best selectivity for phosphoric acid against SO_4^{2-}, and it shows an intermediate behavior between those of iso-amyl alcohol and ethers with regard to metallic impurities.**(11)**

Solubility and liquid-liquid phase equilibrium data are presented for the ternary system, phosphoric acid methyl isobutyl ketone at 25^0C and 40^0C. Binodal curves tie line and distribution curves have been determined. Hand's method has been used to correlate tie lines and to calculate the coordinates of plait points. The heterogeneous region at 40^0C appeared to be slightly broader than that at 25^0C, and slopes of the tie line are somewhat higher. The solubility of these systems increased with decreasing temperature. The distribution curves indicated that MIBK was an effective extractant for concentrated phosphoric acid solutions only.**(12)**

MIBK is used to purify phosphoric acid at temperatures between 25 ^{0}C to 50 ^{0}C. The weight ratio of MIBK to aqueous impure phosphoric acid is from 1:1 to 1.5:1. Separating organic phase from aqueous raffinate phase, scrubbing phase by contacting with an aqueous phosphoric acid 30-50%, releasing the phosphoric acid from scrubbed organic phase by contacting with water by A/O ratio from 0.1:1 to 0.2:1 in two current stages to form an aqueous phase containing purified phosphoric acid, aqueous phase containing a total metallic content less than 100ppm relative to phosphoric acid and recycling MIBK to first step.**(13)**

Solvent extraction wet process phosphoric acid was obtained by contacting a 2-stage counter-current extraction at a temperature in the range 35^0C–40^0C, using MIBK at organic aqueous ratio 2.5:1. The organic phase was scrubbed in four counter stages with 6.3% of purified phosphoric acid to reduce the Fe and Mg content. This extract was then contacted with water at 20^0C. This produce an aqueous phase at a rate of 13.7 gal/h with specific gravity 1.4 and having a P_2O_5 content of 40.5%, 0.63% SO_3, Fe (25ppm), Mg (5ppm).**(14)**

Methyl isobutyl ketone (MIBK) was used for the purification of wet process phosphoric acid, by liquid-liquid extraction, by adjustment operating parameters; concentration of the feed acid, mass ratio of solvent and feed acid, temperature and number of extraction stages. A defined quality of stripped solution was used to strip the purified acid from organic phase.**(15)**

Methyl isobutyl ketone (MIBK), was used for the purification of wet process phosphoric acid (WPA) at 40^0C. In the first step, the distribution of the main components (H_3PO_4, H_2O, MIBK) and the major impurities of (WPA) between the conjugated phases was systematically studied. The expression of phase composition in terms of H_3PO_4, H_2O and MIBK on an impurity – free basis enabled to compute the characteristics of the H_3PO_4 counter current multistage extraction using the Mc-Cabe Thiele method. From graphical results, optimum conditions to conduct the extraction of H_3PO_4 from concentrated WPA (53.5-58% P_2O) were determined.**(16)**

1.2.1.3 Purification of wet process phosphoric acid by ethers

The results obtained when studying the purification of wet process phosphoric acid with dibutyl ether are reported**(17)**. Percent PA and impurities; Fe, Al, Mg, SO_4^{2-} and F^- extracted into the organic phases are given. The variation of the percent extracted into the organic phase for the different component has been studied as function of the phosphoric acid weight percent in the organic phase. Results have been compared with those corresponding to other solvents previously studied. Dibutyl ether shows good purification behavior for metallic impurities and SO_4^{2-}, but seems to be not very suitable for F^- purification due to its high F^- extraction capacity.

Solubility and liquid-liquid phase equilibrium data have been determined for the ternary system water-phosphoric acid isobutyl ether at 25^0C. Data for the binodal curve have been obtained by analyzing the phosphoric acid percentage in both organic and aqueous phases. The phosphoric acid extraction of dibutyl ether has been compared to that of several solvents previously studied showing that dibutyl ether has a phosphoric acid extraction capacity similar to propyl ether and lower than iso-amyl alcohol.**(18)**

At low temperature the isopropyl ether extracts substantially more P_2O_5 than at higher temperature. The impurities distributing ratio between the extracted organic phase and the residual acid phase in this solvent is very advantageous since very few impurities go over to the organic phase together with the P_2O_5 and this is substantially less than for an alcohol-type solvent having 5-6 carbon atoms. P_2O_5 extracted from acid by mixed solvents formed by 95% to 50% isopropyl ether and 5% to 50% tributyl phosphate by volume at temperature of 10^oC and one volume of phosphoric acid extracted with four volumes of used solvent. The P_2O_5 is re-extracted from the organic phase by water.**(19)**

1.2.1.4 Purification of wet process phosphoric acid by amines

In an investigation of Cd removal of wet process phosphoric acid (WPA) by extraction with trialkyl amines in kerosene, it was found desirable to get a better understanding of the extraction behavior of all acid present in WPA. Since at least some of these (HF and H_2SiF_6) are undesirable contaminants. Much work has been done in order to find methods for their separation from phosphoric acid. Solvent extraction belongs to the methods explored and also utilized in full scale for that purpose. Results from the studies of Cd extraction from WPA with Alamine 336 in aromatic kerosene indicated possibilities to combine the removal of Cd with a flow sheet for production of purified phosphoric acid. For this purpose, but also in order to explain and optimize Cd extraction, the equilibrium for extraction of the major acid components would have to be incorporated into a multicomponent extraction model.**(20)**

Purification of phosphoric acid by solvent extraction with chain aliphatic amine is investigated. Extraction of Cd is extensively examined regarding the importance of the aqueous phase, the diluent and the amine. The solubility of tri-octylamine is determined in water and phosphoric acid solution. Properties of valuable constituent such as uranium and yttrium are seen. Modeling of the system is performed by adapting Bromly’s model for electrolytes to the different dissociation/ association equilibrium aqueous phase. In the organic phase simple expressions are used for the non-ideal behavior. Amine-acid equilibrium are investigated for all acids present in industrial phosphoric acid.**(21)**

When amines are used as solvent extractant, those preferred are the alkyl substituted amines, in which the alkyl substituents have a six or more carbon atoms in chain including branched chain alkyl radical. Tri-carbide amine is used for the purification of phosphoric acid after dissolved in inert water immiscible diluents such as kerosene. The preferred stripping agent is water and sulfur dioxide, this combination forms sulphurous acid. This gas in the presence of water will strip the phosphoric acid from solvents, including unreactive with the acid and the solvent. It can be separated from the acid by direct heat or vacuum distillation. Sulfur dioxide is a volatile acid anhydride gas which is compatible and unreactive with strong acids and solvents used for solvent extraction of acid (22)**.** This procedure can be used for other extractants well known in the art. These are lower alkyl phosphate esters, such as butyl, octyl, tributyl, trioctyl phosphate and other solvents. (23)

Phosphorites of sedimentary origin utilized in manufacturing fertilizers, contain uranium and thorium compounds of their radioactive decay, as well as cadmium, arsenic and fluoride. Some part of them may transit into phosphoric acid. The main purpose of cleaning phosphoric acid is its removal of uranium and thorium as well as the removal of toxic Cd. The above task can be achieved by solvent extraction technique using polyalkyl amine phosphate and tri-octylamine, respectively. The equilibrium distribution of uranium and Cd within the phases, the effect of extractant concentration and the temperature of the process were studied(24).

1.2.1.5 Purification of wet process phosphoric acid by alcohols

A process for extracting phosphoric acid from aqueous solution is performed by contacting the acid with a mixture of a minor proportion of a water insoluble amine and a major portion of an aliphatic alcohol. The latter contains from 4 to 12 carbon atoms per molecule, and the water insoluble amine is a secondary or tertiary amine having a total from 10 to 36 carbon atoms per molecule or primary amine having at least 14 carbon atoms per molecule. The purified phosphoric acid is recovered from the alcohol-amine phase by back extraction with water; the precipitation of metallic impurities is prevented by the addition of sequestering agent to the aqueous phosphoric acid. (25)

A mixture of hydrophobic and hydrophilic extractant is used to separate phosphate values from impurities found in wet phosphoric acid. In one approach, impurities are removed from phosphoric acid and the phosphate values are recovered by introducing polyphosphate and ammonium ions into the mixture of low and high molecular weight alcohol having 1-3 and 4-12carbon atoms, respectively in a single stage. One of the alcohols is hydrophilic and the other is hydrophobic. The phosphate values and the impurities are separated from their respective extractant solutions, and the alcohol is recirculated.(26)

Separation of impurities from wet process phosphoric acid by four solvents; 1-butanol, 1-heptanol, methylethyl ketone and acetone were increased by partial ammoniation of the acid but the ammoniation decreases the extraction of P_2O_5 with the four solvents tested intensively. Acetone was the most effective extractant of P_2O_5 and 1-heptanol was the least effective, butanol extracted P_2O_5 more than 1-heptanol but the latter required less water than 1-butanol to strip the acid from the organic layer. So that the concentration of H_3PO_4 in the purified acid was about the same for both alcohols.**(27)**

1.2.1.6 Purification of wet process phosphoric acid by ketones

Diethylketone (DEK), 3-pentanon, was used for the purification of wet process phosphoric acid by solvent extraction. The impurities (Fe^{3+}, Al^{3+}, Mg^{2+}, SO_4^{2-} and F^-) distribution between conjugated phases generated show that DEK is very similar to iso-amyl alcohol regarding its purification behavior. A relation between the total impurities extracted and the amount of water plus phosphoric acid present in the organic phase was found. This would allow prediction of the purification behavior of any solvent from only the data for the pure components. **(28)**

Liquid-liquid equilibrium; solubility and tie line data, for the quaternary system water phosphoric acid, 1-pentanol and 3-pentanone, were obtained at 25^0C and atmospheric pressure, using an analytical method. 1-pentanol appears to be more effective than 3-pentanone as extractant solvent of phosphoric acid. Advantages are not observed with the use of mixed solvents in the purification of phosphoric acid by means of solvent extraction.**(29)**

1.2.1.7 Purification of wet process phosphoric acid by hydrocarbons

Crude phosphoric acid contains P_2O_5 173g/L, F^- 11.1g/L, Fe_2O_3 4.5 g/L, MgO 24 g/L and Al_2O_3 0.8 g/L. Fluoride is the most determinable impurities and must be removed. A new process to extract F^- efficiently is to use a mixed solvent consisting of amine, chloro-hydrocarbon and kerosene. It was found that the effect of diluent is more pronounced for this system than any other. The purified acid contains less than equivalent to 0.6 g/l F^-.**(30)**

The wet phosphoric acid can be purified from impurities by using a scrubbing agent consisting essentially of a metal extractant and from about 50%-90% of hydrocarbon, where the scrubbing agent interacts with impurities in the acidic solution to form a sludge phase which is removed from purified acid solution.**(31)**

The wet process phosphoric acid having concentration of P_2O_5 60% is mixed with a liquid hydrocarbon which is insoluble and immiscible in phosphoric acid, the hydrocarbons can be aromatic or aliphatic, saturated or unsaturated, the suitable hydrocarbon are kerosene and chlorohexane. If the hydrocarbons aliphatic preferably has a chain of carbon about 5 to 18 carbon atoms, the process may be carried out at temperature between 23.5°C to 45°C, the liquid hydrocarbon collected the crud-forming agents from the phosphoric acid and then separated from phosphoric acid.**(32)**

1.2.1.8 Purification of wet process phosphoric acid by using other solvents

Aluminum ions can be separated from phosphoric acid by using dodecyl naphthalene sulfonic acid (HDDNSA). The experimental results were analyzed numerically by non-linear regression. It was found that aluminum is extracted in the form of the complex ion $Al(DDNSA)_3$. The value of the equilibrium constant of the reaction was also calculated.**(33)**

Mono-octylphenyl phosphoric acid (MOPPA) has been used as an extractant for the recovery of plutonium from analytical waste solution containing phosphoric acid. The waste was generated from the analyses of mixed-Pu carbide or oxide.**(34)**

Equal volumes of 0.5M lead in 0.36-5.83M phosphoric acid and 608-225mM Cyanex-302 (mainly bis-(2,4,4-trimethylpentyl) monothio phosphoric acid) were shaken for 30 minutes. The lead content in the organic phase was stripped into 5M HNO_3 and both the extract and the aqueous were analyzed by AAS. Partition coefficients were calculated, and > 85% of Pb was extracted. This method was suitable for the purification of industrial grade phosphoric acid.**(35)**

Most of the phosphate rocks used commercially contain small quantities of metals such as uranium, lanthanides and yttrium. During the phosphate processing, by reacting the phosphate rock with sulfuric acid, 30% of lanthanides and yttrium and more than 80% of uranium, present initially in the rocks, ends up in phosphoric acid. The lanthanides, yttrium and uranium are extracted from phosphoric acid by DOPPA and TOPO. The concentration of solvent and the influence of Fe^{3+} and SO_4^{2-} were studied**(36)**.

The concentration of pre-concentration up-to 80% phosphoric acid (PA) obtained from kola apatite in one of the Polish plants by the wet processing route was carried out by sulphate precipitation, desorption of volatile component (SiF_4, HF) and liquid-liquid extraction method using 4-methyl-2-pentanone. The effect of the reagent grade $Ca(H_2PO_4)_2\ H_2O$. $CaHPO_4.2H_2O.Ca_3(PO_4)_2$ and technical grade calcium oxide, the molar ratio of $Ca^{2+}$to $SO^{2-}{}_4$ (0.8-1.5), the temperature (70°C-90°C), and the duration of precipitation time (1800-7200 S) on the extent of purification from SO_4^{2-}, were determined. The most efficient precipitation was $CaHPO_4$. $2H_2O$. The precipitation of $CaHPO_4.2H_2O$ purified phosphoric acid from $SO_4{}^{2-}$ (1.5-1.8%) to a level of (0.1-0.2%) was studied. The use of 100% SiO_2 while air bubbling and very intensive stirring of phosphoric acid at 130°C was carried to allowed the F^- concentration to decrease to 0.005%. Purification of metals was carried out at room temperature using 1:1.2 mass ratio of PA to 4-methyl-2-pentanone. The stripped phosphoric with a concentration of about 50% H_3PO_4 and 1.5% 4-methyl-2-pentanone, contained Fe, Al (0.01-0.005%) each Pb, Th < 1ppm, Cr, Co, Ni < 0.1ppm, As and Cd are not detected.**(37)**

The distribution of titanium, chromium, and cadmium between phosphoric acid solution and solution of p-(1,1,3,3-tetramethylbutyl) phenyl phosphoric acid in kerosene diluent was investigated under various conditions. The aqueous and the organic phases were analyzed by inductively coupled emission spectrometry. It was found that the extraction order of p-(1,1,3,3-tetramethyl butyl) phenyl phosphoric acid for metals was Ti > Cr >Cd for concentration of H_3PO_4 greater than 7M and Cr > Cd > Ti for concentration of H_3PO_4 less than equivalent to 5M.**(38)**

Di-(2-ethylhexyl) phosphoric acid (HDEHP) is used for the separation and purification of uranium, rare earths, copper, cobalt and nickel. Iron is a common impurity in raw industrial acid in either the divalent or trivalent state. It is associated with uranium in wet process phosphoric acid and is co-extracted during uranium recovery by (HDEHP-TOPO). Therefore, it is of importance to know the extraction properties of iron in the system. The purpose of the investigation was to define the influence of U(IV) and Fe(III) extraction from phosphoric acid solution with HDEHP-TOPO in kerosene.**(39)**

1.2.2 Purification of wet process phosphoric acid by solvent precipitation method

In the solvent precipitation method, acid is treated with a completely miscible solvent, usually in combination with alkali or ammonia to cause impurities to precipitate, mostly as phosphate salts. The solids are separated, and the solvent distillated from the liquid phase and leaving the purified as residue.**(2)**

It is possible to introduce the borate ions into the phosphoric as boric oxide or boric acid to precipitate the phosphorous (90%) contained in the acid and it generally forms boron phosphate. The temperature and duration of heating depends on the concentration of feed acid, the more dilute the feed acid, requires higher temperature or more heating to precipitate boron phosphate. The precipitated may be recovered from mother liquor by any means such as filtration, decantation or centrifuging. The BPO_4 was repeatedly washed with water until the wash water was no longer colored. The solid boron phosphate was then hydrolyzed by boiling with equal weight of water until dissolved, then cooled to room temperature until boric acid precipitated and separated from purified phosphoric acid.**(40)**

An aqueous crude phosphoric acid, which in certain circumstances contain other acid too, such as sulphuric acid is dissolved in a water-miscible organic solvent in the presence of small quantities of an alkali metal or ammonium compounds. The quantities of alkali metal are so small, that the major of the phosphoric acid remain dissolved in solvent, while the impurities are separated out in the form of heavy slimy deposits. Generally to 100 part of acid contain 44% P_2O_5 added 10 part by weigh of K_2SO_4, twice the volume of 92% alcohol. After thorough stirring, a slowly deposited viscous green colored mass of oily appearance occurs. The alcoholic solution is purified by decantation and filtration. After the alcohol has been removed by distillation and left the pure phosphoric acid. After treatment with activated carbon this acid is perfectly colorless and no contains calcium. The yield contains 60% P_2O_5, 0.008% Fe and 0.04% Al**(41)**

The separation of lanthanides from kola apatite in phosphoric acid production by two stages, hemihydrate and dihydrate wet process phosphoric acid was studied. The second stage of the process provide the best condition for recovery of lanthanide during hydration of hemihydration, and precipitation-stripping for the removal of lanthanides from the solvent.**(42)**

The phosphoric acid treated with methanol and a small amount of ammonia to precipitate most of the impurities as metal ammonium phosphate, the slurry is centrifuged and the filtrate distilled to remove methanol and water, leaving purified super phosphoric acid. Purification increases with the use of more methanol and /or ammonia, but filtration rates drops off. This method removed about 90% or more of Fe and Al, and up to 70% of the Mg.**(2)**

Phosphoric acid was treated with acetone and small amounts of ammonia. This method form two liquid phases. The light acetone – rich phase contains purified acid, while the heavy, acetone poor phases contains more impurities and about 25% of acid. All of the acetone and part of water are distilled from the acetone-rich phases to yield concentrated purified acid. The acetone-poor phases is ammoniated and dried to form impure diammonium phosphate.**(2)**

1.2.3 Purification of wet process phosphoric acid by ion exchange method

The term ion exchange is generally understood to mean the exchange of ion of like sign between a solution and a solid highly insoluble body contact with it. The solid (ion exchanger) must, of course, contain ions of its own, and for the exchange to proceed sufficiently, rapidly and extensively to be of practical value, the solid must have an open permeable molecular structure so that ions of the solvent molecule can move freely in and out. Many substances, both natural and artificial, have ion exchanging properties, but for analytical work, synthetic organic ion exchanger are chiefly of great interest, although some inorganic materials also possess useful ion exchange capabilities.**(43)** All ion exchanger of value in analysis have several properties in common, they are almost insoluble in water and inorganic solvents, and contains active or counter ions that will exchange reversibly with other ions in the surrounding solution without any physical change occurring in the material. The ion exchanger is complex in nature and is, in fact, polymeric. The polymer carries an electric charge that is exactly neutralized by the charges on the counter ions.**(44)**

The removal of Cd ions by anion exchange from 55-65 wt % H_3PO_4 at 90^0C in the presence of small amount of halides was investigated. Iodide appears to be the most effective additive. The stability constant of Cd complexes in 55-56% H_3PO_4 are much higher than in diluted aqueous solution and the negatively charge of Cd complex have a high affinity for the amine groups of the resin. A description of the complexation and ion exchange equilibrium assuming adsorption of only one negatively charged Cd species is presented.**(45)**

The dependence of Am, Cm, Bk and Cf behavior on anion and cation exchange in solution of (0.1-8)M H_3PO_4 on acid concentration, and oxidant content in solution ($KBrO_3$) have been studied. Significant differences in distribution coefficient of Bk and other transplutonium elements (TPE) have been found that can be explained by BK oxidation to the tetravalent state. A simple and effective method of Bk (IV) separation of trivalent TPE has been developed. The method was applied to the isolation of isotopes Bk^{249} and Bk^{250}. The purification factor of Bk(IV) from other TPE is 10^4 to 10^6 per cycle. The possibility of Bk separation from bromate and phosphate ions by its sorption on a cation exchanger from diluted H_3PO_4 solution with subsequent desorption by mineral acid has been shown.**(46)**

The wet process phosphoric acid, usually contains impurities. The acid has been used not only for the preparation of fertilizers but also for industrial uses and, food additive, after separating the impurities. In the solvent extraction, phosphoric acid is extracted from the wet process acid with organic solvent and the phosphoric acid is recovered from the solvent with an aqueous solution. In these process, the impurities from wet process phosphoric acid are usually found primarily in the raffinate, but sufficient quantities of some of the contaminates are found in the product acid which makes it unsatisfactory for some application. Attempts have been made to remove some contaminates by ion exchange resins. The removal of metals from high strength aqueous phosphoric acid by ion exchange has not been very successful. The large hydrogen ion competes with metal cations for the basic sites on the ion exchange on an organic solvent solution of phosphoric acid from extraction of wet process phosphoric acid. The acid is dissociated in the organic solvent. Therefore, the cation capacity of the ion exchange is greatly increased so that in high strength aqueous solution permitting the cation concentration to be substantially reduced.**(47)** Mg, Ca, Al, Na, K can be reduced by containing an alcoholic solution of phosphoric acid with cation exchange **(47)** .Fe, As may be removed from aqueous phosphoric acid by adding hydrogen chloride and contacting with basic liquid ion exchange.**(47)** Fe, Cr, V, are removed by dissolving phosphoric acid in organic solvent to form non-aqueous solution, then contacting with strongly basic anion exchange resin which usually contains quaternary, preferably ammonium, ion fixed as active sites which appears as hydroxide form. It would rapidly be converted to the phosphate salt form. Then the purified phosphoric acid was recovered by stripping with aqueous solution.**(47)**

A new method has been developed to reduce the concentration of inorganic impurities present in commercial phosphoric acid. This method is based on the modification of activated carbon with sodium dodecyl sulphate to carry out the exchange of ions. The preliminary results with the column used for this purpose was shown to be effective, the concentration of Cd in the acid was reduced to approximately zero, U was reduced to 86% and Zn, B and Cr were reduced to 50%. Another system (activated carbon sodium diethyldithio carbamate) was tested for the purification of H_3PO_4, and it shows an effective result for the elimination of Ni and V specially at lower acid concentration. At high acid concentration, these columns remain effective mainly, for elimination of B by carbon-SDS column and the elimination of Ni by SDDC-carbon-column.**(48)**

1.2.4 Purification of wet process phosphoric acid by electro-electrodialysis method

The electro-electrodialysis (EED) technique is used for the concentration and purification of wet industrial phosphoric acid. The